Reactions of Benzvalene with Tetracyanoethylene, 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone, Chlorosulfonyl Isocyanate, and Sulfur Dioxide. Evidence for Concerted 1,4-Cycloadditions to a Vinylcyclopropane System[1]

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Abstract: The reaction of benzvalene (**4**) with tetracyanoethylene (TCNE) affords a mixture of tetracyclo[3.3.0.0^{2,4}.0^{3,6}]octane derivative **5**, tricyclo[3.3.0.0^{2,6}]oct-7-ene derivative **6**, and tricyclo[3.3.0.0^{2,8}]oct-6-ene derivative **7**. By means of dideuterated benzvalene **4a** and the solvent effect on the ratio of the products the mechanisms have been studied. Accordingly, the formation of the main products **5** and **6** involves zwitterionic intermediates, which arise from electrophilic attack of TCNE at the olefinic portion of **4**. The third compound **7** is thought to be produced in a concerted 1,4-addition of TCNE to the vinylcyclopropane moiety of benzvalene (**4**). Treatment of **4** with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone gives rise to a 1:1 adduct, which is structurally analogous to TCNE adduct **7** and which is most probably formed in a one-step process as evidenced by the positions of the deuterons when **4a** was utilized. In a reinvestigation of the reaction between chlorosulfonyl isocyanate and **4** the new compounds **18a**, a 4-azatricyclo[3.3.0.0^{2,8}]oct-6-en-3-one derivative, and **19**, an 8-azatetracyclo[4.2.0.0^{2,4}.0^{3,5}]octan-7-one derivative, have been discovered in addition to the known products **2a** and **3a**. Even at low temperatures benzvalene (**4**) and sulfur dioxide react to give a mixture of the four-membered ring sulfone **23** and the sultine **24**, with the ratio being dependent on the solvent polarity. That **23** is not the precursor of **24** follows from rate measurements, according to which the rearrangement **23 → 24** is much slower than the formation of **24** from **4** and SO₂. The experiment utilizing dideuterated benzvalene **4a** has revealed a competition between two processes, a concerted 1,4-addition of SO₂ to the vinylcyclopropane system of **4** yielding **23** and an electrophilic attack of SO₂ at C-1 (C-6) of **4** with formation of the zwitterion **25** with a sulfinate function and an allyl cation moiety. The latter species cyclizes with almost the same rates via an oxygen atom or the sulfur atom to give rise to **24** and another portion of **23**, respectively. In the stepwise processes TCNE and SO₂ approach **4** at different sites. This phenomenon is discussed in terms of the HSAB principle.

Due to its high-lying HOMO benzvalene (**4**) reacts with numerous electrophiles.[2] In most cases the attack takes place at the double bond since the HOMO is largely localized there.[3,4] Exceptions are the protonation[5-7] and the mercuration[8] generating products, which indicate addition of the electrophile to the bicyclo[1.1.0]butane skeleton. Also, Ag⁺ and several metals interact with the σ system and catalyze automerizations of **4** and, finally, isomerizations to benzene and fulvene, respectively.[9]

Katz and co-workers have studied the reactions of **4** with 4-phenyl-1,2,4-triazolin-3,5-dione (PTAD)[10] and chlorosulfonyl isocyanate (CSI).[11] By means of 1,6-dideuterated benzvalene (**4a**) it has been shown that both of these electrophiles attack the double bond with formation of zwitterionic intermediates. Subsequently, the latter undergo a Wagner–Meerwein rearrangement. In the PTAD addition only the bicyclo[1.1.0]butane-bridgehead carbon, which is oriented trans relative to the PTAD portion, migrates thus ultimately giving rise to **1** as the single product. In the intermediate formed in the CSI addition migration can also take place on the side of the anionic substituent thus producing a 3:1 mixture of **2a** and **3a** by collapse of the rearranged zwit-

1   2a   R = SO₂Cl   3a
Ph   2b   R = H   3b
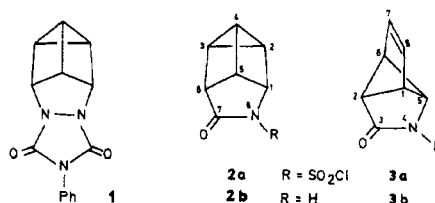
terions. In addition, a third 1:1 adduct of **4** and CSI was observed but defied complete characterization. Herein, we wish to report results, which indicate the simultaneous attack of an electrophile at the π and the σ system of **4**.

Tetracyanoethylene

Results. Tetracyanoethylene (TCNE)[12] resembles PTAD[12a,13] and CSI[14] in that it frequently gives rearranged adducts with

(1) Presented at the Euchem Conference on Pericyclic Reactions, Ferrara, Italy, Sept 1982.
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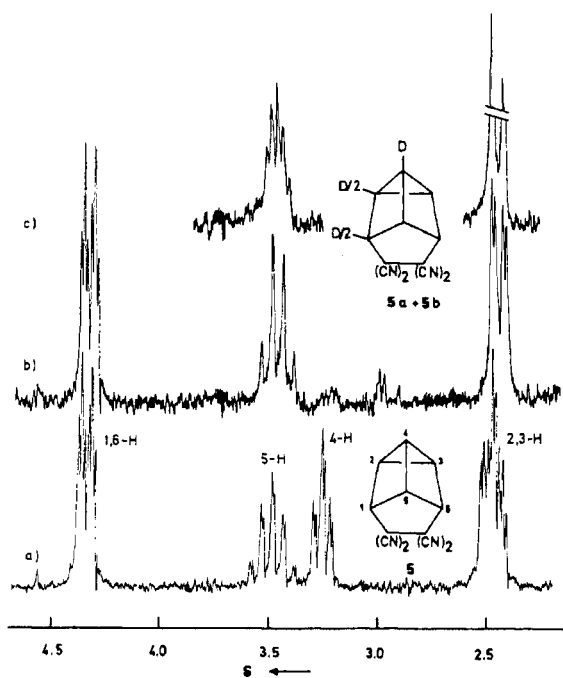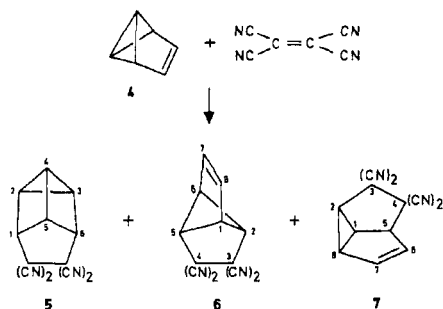
Figure 1. ^{1}H NMR spectrum of **5** (trace a), **5a/5b** (trace b), and **5a/5b** with decoupling at δ 4.33 (trace c) at 90 MHz in acetone-d_6.
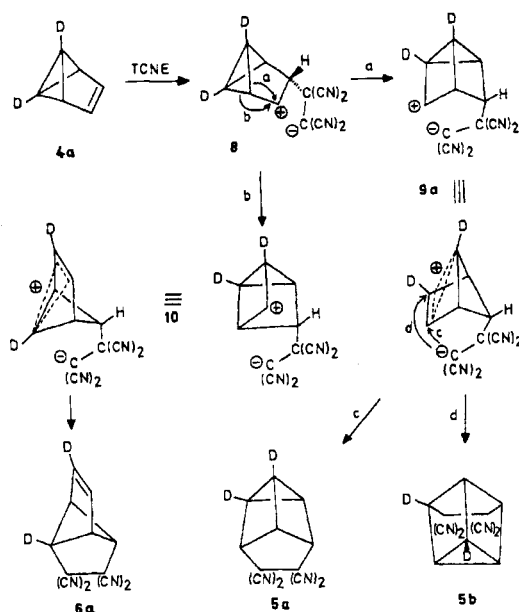
vinylcyclopropane derivatives. From the reaction of **4** with TCNE in ether/ethyl acetate from −78 °C to ambient temperature we obtained a mixture of three 1:1 adducts. Crystallization gave **5** in 16% yield, while chromatography afforded a 7% yield of **6**.
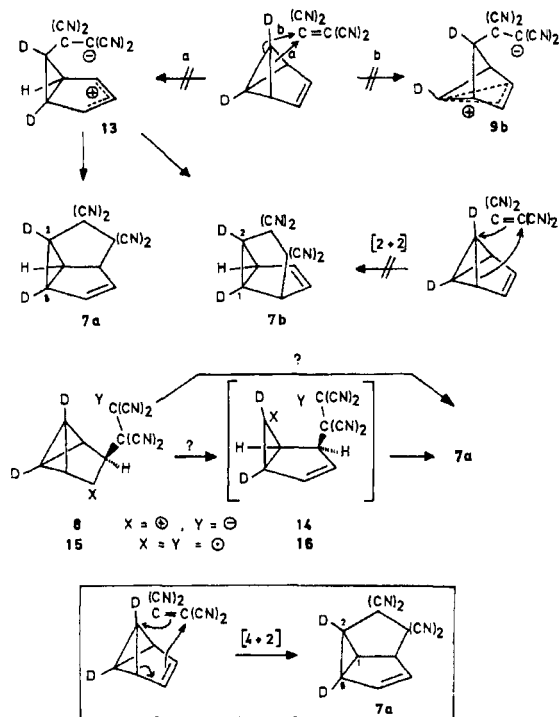

Isomer **7** (6% yield) could not be isolated pure but contained 20% of **5** as an impurity.

The structures of **5** and **6** follow from their characteristic NMR spectra (see Figure 1 for the ^{1}H NMR spectrum of **5**), which are similar to those of **1**, **2**, and **3**. In the ^{13}C NMR spectrum of **6** the signal of C-2,5 appears at extremely low field (δ 86.4) indicating a rigid cyclopentene unit in the envelope conformation.[15] The skeleton of the dihydrosemibullvalene type adduct **7** has precedent in the photoadducts of alkenes to benzene.[16] We were able to assign the ^{1}H NMR spectrum of **7** completely. The data are presented in Chart I. Protons a and e have a cis vicinal relationship, on the basis of which $J_{a,e} = 5.6$ Hz seems reasonable. In accord with the corresponding coupling in a bicyclo[3.1.0]-

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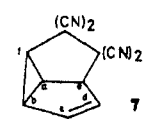
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Scheme I

Scheme II

hex-2-en derivative[17] $J_{b,c}$ is not resolved. Altogether, the consideration of the coupling constants allows a clean distinction between the absorptions of the cyclopropane protons a, b, and f.

The polarity of the solvent in which the reaction is carried out influences the ratio of **5:6:7**. By means of integrals in the 400-MHz ^{1}H NMR spectrum this ratio was determined to be 7.7:2.9:1.0 and 2.7:1.0:1.0 from the reactions in acetonitrile and pentane, respectively. In these runs the concentration of benzene was analyzed quantitatively again by NMR spectroscopy. It
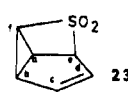
(17) Prinzbach, H.; Hagemann, H.; Hartenstein, J. H.; Kitzing, R. *Chem. Ber.* **1965**, *98*, 2201–2220.

Chart I. ^{1}H NMR Chemical Shifts (δ Values, Diagonal Elements) and Coupling Constants (Absolute Values in Hz, Nondiagonal Elements) of **7** and **17** in Acetone-d_6 and **18a**, **18b**, **23**, **24**, and **19** in CDCl$_3$
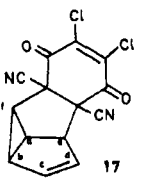
	a	b	c	d	e	f
a	3.55	6.3	<0.4	0.7	5.6	7.1
b		2.67	2.4	0.7	<0.4	7.1
c			6.30	5.5	0.5	<0.4
d				5.93	2.5	0.6
e					4.52	<0.4
f						3.18

(structure **7**, with (CN)$_2$ (CN)$_2$)
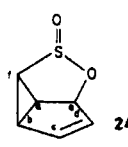
	a	b	c	d	e	f
a	3.40	5.7	0.5	0.5	4.2	5.7
b		2.80	2.3	0.9	≈0.2	5.7
c			6.23	5.3	0.9	0.5
d				6.01	3.2	0.5
e					4.76	2.7
f						3.74

(structure **23**, with SO$_2$)
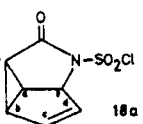
	a	b	c	d	e	f
a	3.47	6.5	<0.4	0.9	5.6	6.8
b		2.52	2.6	0.8	<0.4	7.4
c			5.90	5.5	<0.4	<0.4
d				5.45	2.5	0.5
e					4.12	<0.4
f						3.15

(structure **17**, with Cl, Cl, NC, CN, O, O)
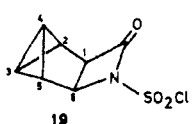
	a	b	c	d	e	f
a	3.27	5.9	0.6	0.6	4.7	7.2
b		2.66	2.2	0.6	0.4	6.9
c			5.84	5.3	0.6	<0.4
d				5.76	1.8	0.6
e					5.98	<0.4
f						3.50

(structure **24**, with O, S, O)
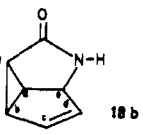
	a	b	c	d	e	f
a	3.18	5.7	<0.5	<0.5	6.1	6.2
b		2.59	2.2	<0.5	<0.5	7.8
c			6.20	5.4	1.0	<0.5
d				6.15	1.7	0.8
e					5.15	<0.5
f						2.62

(structure **18a**, with O, N–SO$_2$Cl)

	1-H	2-H	3-H	4-H	5-H	6-H
1-H	3.58	1.8	<0.5	1.2	<0.5	5.1
2-H		2.49	1.8	1.8	4.4	<0.5
3-H			2.70	8.6	1.6	<0.5
4-H				2.44	1.6	1.2
5-H					2.76	1.6
6-H						4.50

(structure **19**, with O, N–SO$_2$Cl)

	a	b	c	d	e	f
a	3.00	6.0	<0.8	<0.8	6.0	6.0
b		2.50	2.4	1.0	<0.8	7.5
c			5.85	5.5	1.0	<0.8
d				5.82	1.7	<0.8
e					4.20	<0.8
f						2.32

(structure **18b**, with O, N–H)

NH: δ 4.85

turned out that the quantity of benzene, which was present from the benzvalene synthesis, did not increase. Thus, TCNE does not catalyze the isomerization of benzvalene (**4**) to benzene to a measurable extent.

To obtain more informations on the reaction mechanisms we added TCNE to **4a** and identified the products **5a**, **5b**, **6a** (Scheme I), and **7a** (Scheme II). Control experiments demonstrated that the products do not interconvert under both the reaction conditions and workup.

Discussion. With respect to the formation of **5a**/**5b** and **6a** these results suggest a pathway, which begins with an electrophilic attack of TCNE at the double bond of **4a** to produce zwitterion **8** (Scheme I). A [1,2] carbon shift either on the side of the anionic substituent (denoted by b) or on the opposite side (denoted by a) gives rise to the rearranged stereoisomeric zwitterions **10** and **9**, respectively. These are best described in the nonclassical way with the cationic portions being of the 6-bicyclo[2.1.1]hexenyl type.[18]

Due to steric factors in **9**, the anionic center can interact only with the two-carbon bridge of the bishomocyclopropenyl cation system. Since there are two possibilities, namely at the protonated carbon (pathway c) and at the deuterated carbon (pathway d), a 1:1 mixture of the isotopomers **5a** and **5b** is expected if the secondary deuterium isotope effect is neglected. This is supported by the ^{1}H NMR spectrum of the isolated product (Figure 1), in which no signal of 4-H is found whereas the intensities of the 1,6-H and 2,3-H absorptions indicate 1.5 protons each. Interestingly, on decoupling at δ 4.33 the quartet at 3.46 becomes a five-line absorption. It is composed of a 4.5-Hz doublet and a 4.5-Hz triplet with the same chemical shift and equal intensities. These splittings are expected for the 5-H signals of **5a** and **5b**, respectively, if 1,6-H are decoupled. Simultaneously, the 2,3-H resonance simplifies to a 4.5-Hz doublet.

In **10** the ring closure can be achieved only with the one-carbon bridge. The positions of the deuterium labels in the resulting **6a** are established by means of the ^{1}H NMR spectrum. Compared with the spectrum of **6** the intensities of the 2,5-H and 7,8-H resonances are reduced by 50%.

These findings show that the TCNE adducts **5** and **6** are formed via intermediates analogous to those postulated for the CSI adducts **2a** and **3a**. On the other hand the PTAD adduct **1** should emerge from a different pathway, since it is not accompanied by a product of type **3** or **6**. A mechanism allowing a Wagner–Meerwein rearrangement only on the side opposite to the PTAD portion involves the aziridinium betain **11**, which should afford **12**, the


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  4
  +    →
 PTAD
```

11   **12**
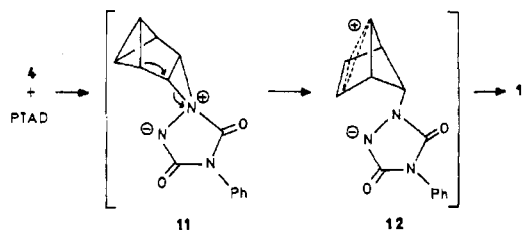
precursor of **1**, as the sole zwitterion. Aziridinium betaines have been proposed as intermediates in the PTAD additions to olefins.[19]

How can the formation of **7** be rationalized? The 400-MHz ^{1}H NMR spectrum leaves no doubt that the labels of **4a** end up in the positions 2 and 8 of the dihydrosemibullvalene skeleton, i.e., **7a** is the only isotopomer produced. The residual four-spin system causes the expected fine structure permitting the unambiguous assignment of the 6-H and 7-H resonances as shown in Chart I. The mechanistic possibilities are presented in Scheme II.

We first considered an electrophilic addition of TCNE to C-1 (C-6) of **4a** with cleavage of a lateral bicyclo[1.1.0]butane bond and formation of zwitterion **13** (pathway a). This corresponds to the first step in the reaction of acids with **1** generating the bicyclo[3.1.0]hexenyl cation.[2,5-7] Because of only one deuteron at the otherwise equivalent bridgehead carbons **13** should collapse to give a 1:1 mixture of the isotopomers **7a** and **7b**, which is at variance with the experiment. Addition of an acid to **4a** indeed generates the expected mixture of isotopomers.[2] Next we examined the possibility of the attack of TCNE at C-1 (C-6) with cleavage of the central bicyclo[1.1.0]butane bond (pathway b). The resulting zwitterion **9b** could rearrange to **7a** by ring closure and simultaneous [1,2] migration of the carbon bearing the TCNE portion. However, such a pathway would also lead to the formation of the two isotopomers **7a** and **7b** from **9a**. Thus, this mechanism must be discarded as well. A concerted [2 + 2] cycloaddition of TCNE to a lateral bicyclo[1.1.0]butane bond is ruled out, since it would afford the wrong isotopomer **7b** exclu-

sively. Starting from **8**, the common precursor of **5a**/**5b** and **6a**, two pathways to **7a** are conceivable: (i) Cyclopropyl-carbinyl-homoallyl-cation rearrangement to the new zwitterion **14**, which could collapse to **7a**, is one pathway. However, the high energy of the cyclopropyl cation portion of **14** should prohibit its formation. (ii) The direct conversion of **8** to **7a** by nucleophilic attack of the anionic moiety at the nearby bicyclo[1.1.0]butane-bridgehead carbon and synchronous development of the double bond is an alternative. Stereochemical considerations suggest that this process would have to be a nucleophilic one-step frontside displacement, which is without analogy.[20a] Furthermore, the diradicals **15** and **16** could be seen as precursors to **7a**, since this type of rearrangement, i.e., **15** → **16**, is known.[2,20b] In this case TCNE would have to attack the double bond of **4a** in essentially the same geometry as in the generation of **8**, which is the precursor of **5a**/**5b** and **6**. Thus, it seems unlikely that both the zwitterion **8** and the diradical **16** are produced by the same mode of approach.

Ultimately, only a concerted [4 + 2] cycloaddition rationalizes the positions of the deuterium labels in **7a** in a straightforward way. Thus, TCNE would interact simultaneously with an olefinic carbon and a bicyclo[1.1.0]butane-bridgehead carbon with rupture of a lateral bicyclo[1.1.0]butane bond and development of the new double bond. The mechanism is a concerted 1,4-addition to a vinylcyclopropane system affording a seven-membered ring. This process is related to the Diels–Alder addition and is classified as a $[(_\sigma 2_s + _\pi 2_s) + _\pi 2_s]$ type,[21a] which is a thermally allowed reaction according to the Woodward–Hoffmann rules and the Dewar–Evans principle.[21b]

The latter interpretation considers the addition of TCNE to **4** as a competition between a polar attack, which via zwitterionic intermediates affords products **5** and **6**, and a concerted reaction leading to **7**, where a rather unpolar transition state should be involved. Since only the former process should be subject to a large solvent effect,[22] we expected a dependence of the isomer ratio on the polarity of the solvent used. Thus, the proportion of **7** should be especially large in an unpolar solvent. This is indeed observed. In pentane the proportion of **7** increases nearly threefold as compared to the reaction in acetonitrile. That the ratio **5**:**6** is approximately the same in both the solvents suggests a common precursor such as **8**.

Certainly, this variation of the isomer ratio is not large in view of the changes in reaction rate, which take place in cycloadditions involving zwitterions. An increase of 4500 in the rate of reaction of ethyl isobutenyl ether with TCNE in acetonitrile as solvent vs. cyclohexane has been observed.[22] In contrast, for the Diels–Alder reaction between TCNE and anthracene in acetonitrile and benzene the ratio of the rate constants has been determined to be only 5.6.[22] Without doubt, a high solvent polarity greatly favors the formation of a zwitterion like **8**. However, the transition state of the one-step process, **4** + TCNE → **7**, need not necessarily be as unpolar as that of the reaction between the symmetric components anthracene and TCNE. It is conceivable that the transition state shows some polarization with a partial negative charge

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(19) Seymour, C. A.; Greene, F. D. *J. Am. Chem. Soc.* **1980**, *102*, 6384–6385.

(20) (a) A referee has commented that the peculiar electronic nature of cyclopropylcarbinyl cations may allow the direct collapse of zwitterion **8** to **7a**. However, such a frontside attack is unlikely, since in nearly all carbocationic species, where σ-bridging has been invoked, nucleophiles approach the two-electron three-center bond from the rear. Furthermore the variation of the ratio (**5** + **6**):**7** with solvent polarity (vide infra) provides evidence against a common precursor, i.e., against **8** as precursor of **7**. We do not agree with the referee's opinion that a stepwise formation of **7** would explain the otherwise curious failure of PTAD to give any of the concerted [4 + 2] adduct. The formation of the aziridinium betain **11**, probably a concerted [2 + 1] addition, seems to be energetically the most favorable reaction of PTAD. A similar pathway, however, is not available for TCNE, which therefore undergoes alternative processes. (b) Christl, M.; Lang, R.; Herbert, R.; Freitag, G. *Angew. Chem.* **1980**, *92*, 465–466; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 457–458.

(21) (a) This process has been labeled a "Homo-Diels-Alder-Reaction".[21] It should not be confused with cycloadditions involving 1,4-dienes. (b) Woodward, R. B.; Hoffmann, R. *Angew. Chem.* **1969**, *81*, 797–869; *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 746. Dewar, M. J. S. *Angew. Chem.* **1971**, *83*, 859–875; *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 761.

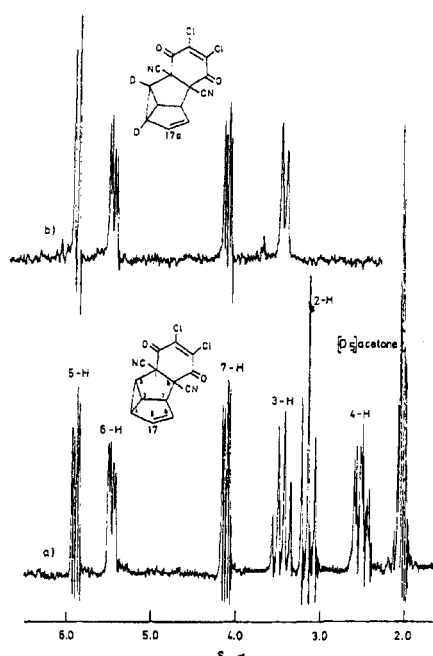(22) Huisgen, R. *Pure Appl. Chem.* **1980**, *52*, 2283–2302 and references cited.

Figure 2. ^{1}H NMR spectrum of **17** (trace a) and **17a** (trace b) at 90 MHz in acetone-d_6.

at the TCNE portion and the positive equivalent being localized in the benzvalene skeleton. Hence, for such a reaction a moderate rate increase can be predicted on going from less polar to more polar solvents. This type of argument has been applied to rationalize the ratio $k_{\text{acetonitrile}}/k_{\text{cyclohexane}} = 160$ for the addition of diphenylketene to butyl vinyl ether.[22]

In principle cycloadditions of TCNE to vinylcyclopropane derivatives are known,[12] but in most cases the step-wise mode has been established or can be suspected. A concerted pericyclic reaction seems probable only in a few examples, e.g., the addition of TCNE to a homofulvene[12e] and tricyclo[5.3.1.0]undeca-2,4,9-triene,[12j] although in the latter case the authors favor a stepwise mechanism initiated by electron transfer. In contrast, the formation of the homogeneous isotopomer **7a** from 1,6-di-deuterated benzvalene (**4a**) provides convincing support for the one-step process.

On treatment with TCNE a highly methylated 2-vinyl-bicyclo[1.1.0]butane derivative was transformed to a compound with a structure related to that of **6**.[12i] In this case as well as in the reaction of hexamethyl dewar benzene with TCNE, which gives rise to the hexamethyl derivatives of **5** and **6**,[23] the rearranged products indicate zwitterionic intermediates.

2,3-Dichloro-5,6-dicyano-p-benzoquinone

Results and Discussion. In addition to its properties as a dehydrogenation agent 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) has dienophilic properties.[24] Scott et al.[12j] treated tricyclo[5.3.1.0]undeca-2,4,9-triene with DDQ and did not arrive at the desired homoazulene but obtained the 1,6-cycloadduct to the butadienyl–cyclopropane moiety. When we stirred DDQ in an ether solution of **4** a 1:1 adduct was isolated in 31% yield. The structure, **17**, was assigned on the basis of its NMR spectra, which are similar to those of **7**. The ^{1}H chemical shifts and coupling constants and shown in Chart I (see also Figure 2). With respect to the question of whether the chlorine-substituted CC double bond of DDQ or the one with the cyano groups undergoes the cyclo-

addition the comparison of the ^{13}C NMR spectrum of the adduct with that of DDQ[25] clearly decides in favor of **17**. The chemical
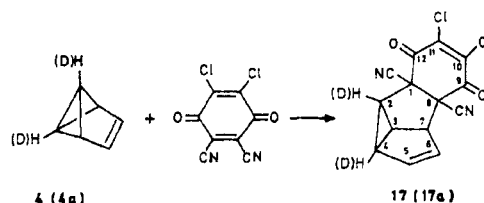

shifts of the substituted olefinic carbons (C-10, C-11, δ 147.0, 147.1) are much more similar to that of the chlorine substituted carbons (δ 141.0) in DDQ than to that of the ones binding the cyano groups (δ 125.1). However, we have no evidence that bears on the stereochemistry at positions 1 and 8 of **17**.

From the reaction of doubly deuterated benzvalene **4a** with DDQ we isolated isotopomer **17a** exclusively. The ^{1}H NMR spectrum (Figure 2) is conclusive in that the labels appear in positions 2 and 4, which correspond to positions 2 and 8 in **7a**. Thus, by analogy with the most probable pathway to **7** we propose a concerted $[(_\sigma 2_s + _\pi 2_s) + _\pi 2_s]$ cycloaddition for the formation of **17**.

Chlorosulfonyl Isocyanate

Results. In view of the formation of compounds **7** and **17** we reinvestigated the reaction of benzvalene (**4**) with CSI with the idea in mind that the third adduct mentioned by Katz and Nicolaou[11] might turn out to have a semibullvalene type structure. The treatment of **4** in ether with CSI gave in addition to the three previously observed products a fourth one. Fortunately the signals of these compounds appear almost completely separated from each other in the 400-MHz ^{1}H NMR spectrum. The characteristic data identified the adducts to be **2a**, **3a**, **18a**, and **19**; on the basis

R = SO$_2$Cl　**18a**
R = H　　**18b**

19
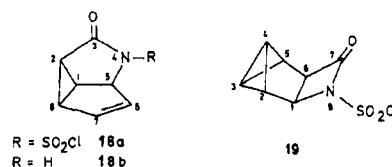
of the integrals the ratio was 4.9:2.0:1.0:1.5. Pentane as solvent instead of ether caused only a slight change of the ratio to 5.3:2.7:1.0:0.7. Since only the parameters of the unsubstituted lactams **2b** and **3b** have been reported,[11] the complete NMR data are given in the Experimental Section for **2a** and **3a**.

Prolonged standing in a CDCl$_3$ solution at room temperature resulted in extensive decomposition of **2a**, **3a**, and **19**. This facilitated the analysis of the spectrum of the remaining component **18a**. Chart I contains the data, which resemble those of **7** rather closely. In a formal sense **19** is a [2 + 2] cycloadduct to the double bond of **4**. Consequently, its NMR parameters should be similar to those of other cis adducts to **4**.[26,27] Chart I corroborates this expectation. Especially the resonances of 2-H and 5-H at δ 2.49 and 2.76, respectively, with their mutual long-range coupling, $J_{2,5} = 4.4$ Hz, are typical. The 4-H signal shows a very characteristic fine structure, which can be interpreted as a doublet of triple triplets. Although the 3-H absorption is superimposed by a band of **2a**, there is no doubt with respect to this assignment, since the four bonds transmitting the coupling to 1-H and 6-H approximate a favorable zig–zag configuration[28] much better starting from 4-H than from 3-H.

(23) Iwamura, H.; Tanabe, Y.; Kobayashi, H. *Tetrahedron Lett.* **1976**, 1987–1990. Schäfer, W.; Hellmann, H. *Angew. Chem.* **1967**, *79*, 566–573; *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 518.

(24) Pointer, D. J.; Wilford, J. B.; Hodder, O. J. R. *J. Chem. Soc. B* **1971**, 2009–2014. Braude, E. A.; Jackman, L. M.; Linstead, R. P.; Lowe, G. J. *Chem. Soc.* **1960**, 3123–3132.

(25) Neidlein, R.; Kramer, W.; Leidholdt, R. *Helv. Chim. Acta* **1983**, *66*, 652–660.

(26) Christl, M. *Angew. Chem.* **1973**, *85*, 666–668; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 660–661.

(27) Gream, G. E.; Smith, L. R.; Meinwald, J. *J. Org. Chem.* **1974**, *39*, 3461–3462. Smith, L. R.; Gream, G. E.; Meinwald, J. *Ibid.* **1977**, *42*, 927–936.

(28) Sternhell, S. *Quart. Rev.* **1969**, *23*, 236–270. Günther, H. "NMR-Spektroskopie", 2nd ed.; Tieme: Stuttgart, 1983; p 112.

378 *J. Am. Chem. Soc., Vol. 106, No. 2, 1984*

Christl, Brunn, and Lanzendörfer

The crude chlorosulfonyl lactams were hydrolyzed to afford a 10:1:2 mixture of **2b**, **3b**, and **18b** in 61% yield referred to the CSI employed. No evidence for a product that originates from **19** could be detected. Our attempts to separate **18b** from the mixture failed, but the ¹H NMR data (Chart I) support its constitution strongly.

Discussion. The formation of β-lactam **19** has ample precedent in other additions of CSI to alkenes.[12j,29] Two pathways have to be considered: (i) the one-step [2 + 2] cycloaddition of the heterocumulene CSI to the double bond of **4** in analogy to the reaction of dichloroketene, which affords the corresponding cyclobutanone in high yield;[27] (ii) the two-step process via zwitterion **20**, which has been proposed to be the precursor of **2a** and **3a**. In contrast to the related zwitterion **8** in the TCNE reaction, the closure of a four-membered ring would compete with the Wagner–Meerwein rearrangements.

The stepwise mechanism is generally accepted on the basis of the fact that the β-lactam formation proceeds faster in more polar solvents.[29] Although acetonitrile is not compatible with CSI, the variation of the proportion of **19** in the product mixtures obtained from reactions in ether and pentane provides some support for the intermediacy of **20**.

20   **21**   **22**
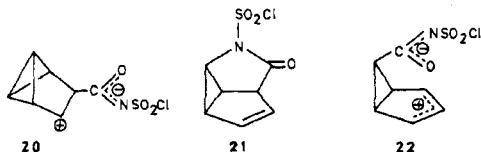
The formation of **18a** reveals a regiochemical preference for the addition of CSI to **4**. The alternative structure **21** is ruled out by the ¹H NMR spectrum. In particular, the signal at δ 2.62, which has to be assigned to 2-H of **18a** on the basis of the coupling constants $J_{1,2}$ ($J_{a,f}$ in Chart I) = 6.2 Hz, $J_{2,8}$ ($J_{b,f}$) = 7.8 Hz, and $J_{2,6}$ ($J_{d,f}$) = 0.8 Hz, would not fit the corresponding proton in **21** because of its position geminal to the nitrogen. By analogy to the reactions of TCNE and DDQ it might be assumed that a concerted mechanism gives rise to **18a**. Unfortunately our experiments employing the doubly deuterated benzvalene **4a** were not conclusive in this respect. They corroborated the findings of Katz and Nicolaou[11] concerning the pathways to **2a** and **3a**, but several impurities, which did not appear in the reaction of unlabeled **4** with CSI, probably because there the olefin concentration was much higher, precluded a reliable determination of the position of the labels in the minor product **18a**. Even a 61.4-MHz ²H NMR spectrum was not helpful. In concerted cycloadditions regiochemistry is controlled mainly by the size of coefficients in the frontier orbitals.[30] The reaction under consideration should be dominated by the HOMO_benzvalene–LUMO_CSI interaction. Since the HOMO of benzvalene is essentially localized at the olefinic carbons[3,4] and CSI has its larger LUMO coefficient at the carbon structure **21** is predicted on the basis of the frontier orbital theory. Therefore, the fact that regioisomer **18a** is found can be seen as an indication for a two-step mechanism with zwitterion **22** as intermediate. Here CSI would attack **4** in the same mode as protons,[2,5–7] mercuric acetate,[8] and sulfur dioxide (vide infra) at C-1 (C-6) from the endo side of the bicyclo[1.1.0]butane moiety, where according to the direction of the dipole moment[31,32] some negative charge resides.

The 1,4-cycloadditions of CSI to vinylcyclopropane derivatives heretofore reported also involve zwitterionic intermediates.[14c,f] A concerted 1,6-addition has been proposed in the case of a homofulvene derivative.[14b] Hexamethyl derivatives of **18a**[33a] and **3a**[33b] have been obtained from CSI and hexamethyl dewar benzene

(29) Bestian, H. *Pure Appl. Chem.* **1971**, *27*, 611–634.

(30) Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361–369.

(31) Suenram, R. D.; Harmony, M. D. *J. Am. Chem. Soc.* **1972**, *94*, 5915–5916.

(32) Newton, M. D.; Schulman, J. M.; Manus, M. M. *J. Am. Chem. Soc.* **1974**, *96*, 17–23.

(33) (a) Paquette, L. A.; Krow, G. R. *Tetrahedron Lett.* **1968**, 2139–2142; *J. Am. Chem. Soc.* **1969**, *91*, 6107–6111. (b) Hogeveen, H.; Kwant, P. W.; Schudde, E. P.; Wade, P. A. *Ibid.* **1974**, *96*, 7518–7524.

**Table I.** Rate Constants for the Rearrangement of **23a** and **23b** to **24a** and **24b** (See Scheme III)

| solvent	temp, °C	k_1, s⁻¹	k_{-1}, s⁻¹	k_2, s⁻¹	k_{-1}/k_2
CDCl₃	21	4.8 × 10⁻⁶	3.4 × 10⁻⁴	3.8 × 10⁻⁴	≈0.9
CDCl₃	41	5.3 × 10⁻⁵	3.4 × 10⁻³	3.8 × 10⁻³	≈0.9
Me₂SO-d₆	21	4.3 × 10⁻⁵	3.0 × 10⁻³	3.4 × 10⁻³	≈0.9

at –15 and –70 °C, respectively.

Sulfur Dioxide

Results. The reaction of benzvalene (**4**) and sulfur dioxide in ether at –35 °C gave in 57% yield a colorless precipitate, consisting of sulfone **23** (ca. 9.5 parts) and sultine **24** (ca. 0.5 part). In addition to polymeric material, the mother liquor contained **24** as the major constituent with a small amount of **23**. Equimolar quantities of **4** and SO₂ gave rise to **23** and **24** in a ratio close

4   **23**   **24**
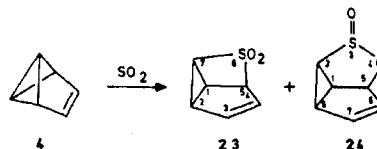
to 2:1. When **4** in CDCl₃ was treated with an excess of SO₂ at –78 °C in an NMR tube the ¹H NMR spectrum, taken at –67 °C after 30 min, showed the completion of the reaction with **23** and **24** having been formed approximately in the ratio 1:1.5. In a third type of experiment we added a solution of **4** in ether slowly to liquid SO₂ at –35 °C and obtained in 69% yield a 1:2.1 mixture of **23** and **24** with the sultine also being formed in excess.

Sulfone **23** rearranges to sultine **24** at room temperature. At 41 °C in CDCl₃ we determined the yield to be 56% by means of the ¹H NMR spectrum; the isolated yield was 42%. In Me₂SO-d₆ this reorganization takes place nine times as fast as in CDCl₃ (see Table I). We consider this solvent effect as good evidence for the rate-determining formation of zwitterion **25**, which undergoes

25
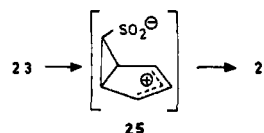
ring closure via an oxygen of the sulfinate function to form **24**. In liquid SO₂ with 10% CDCl₃ no indication for this rearrangement was observed at –10 °C after 30 min, thus proving that the sultine **24** produced from **4** and SO₂ does not originate from preformed sulfone **23**.

The spectral data support the structures of **23** and **24**. Intense absorptions at 1133 and 1283 cm⁻¹ in the IR spectrum of **23** are typical for the sulfone moiety.[34] In contrast, **24** gives rise to only one significant band in this region (1151 cm⁻¹), which is assigned to the sulfinate function.[34] The NMR spectra of **23** and **24** resemble each other closely but are easily distinguished on the basis of the chemical shifts of the allylic CH groups, being connected to the sulfur atom in **23** or an oxygen in **24**. Decoupling experiments support the assignments in the ¹H NMR spectrum of **23**. The coupling interactions, given in Chart I, show the same pattern as in **7**, **17**, **18a**, **18b**, and **24** with the exception of $J_{e,f}$. This coupling could be resolved only in the case of **23** (2.7 Hz), which probably is a consequence of an additional four-bond zig-zag configuration[28] including the sulfur atom. With respect to the stereochemistry at the sulfur atom of **24** the spectral data provide no information. We assume the exo arrangement of the oxygen in analogy to the highly substituted derivative **33** of **24**, the configuration of which has been determined by X-ray analysis.[35] The formation of **33** has been postulated to proceed via

(34) Bellamy, L. J. "The Infra-red Spectra of Complex Molecules"; Champman and Hall: London, 1975; pp 403–405.
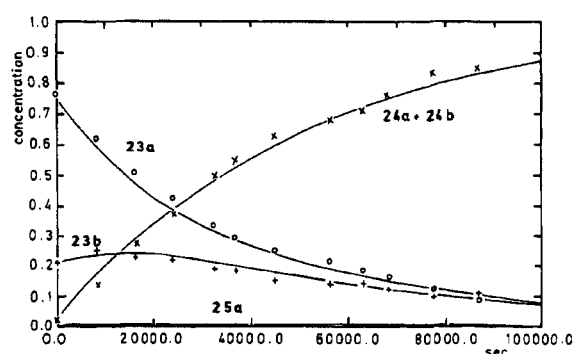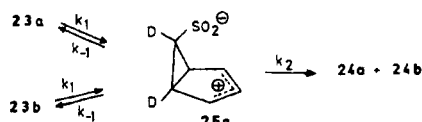
Reactions of Benzvalene

J. Am. Chem. Soc., Vol. 106, No. 2, 1984 379

Figure 3. Simulation of conversion **23a/23b → 24a/24b** at 41 °C in CDCl₃. The symbols O, +, and X are experimental concentrations; the solid lines represent the computed ones.

Scheme III

derivative **29** of zwitterion **25**.[35]

In order to gain more insight in the reaction mechanism we combined labeled benzvalene **4a** with SO₂ in ether. As shown by the ¹H NMR spectrum the precipitate consisted of the sulfone isotopomers **23a** and **23b** (ca. 9.5 parts) in a ratio of about 3.5:1
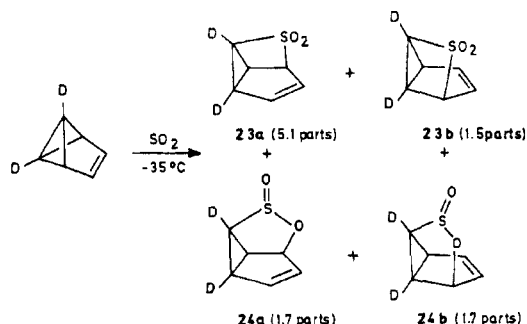

and of the sultine isotopomers **24a** and **24b** (ca. 0.5 part) in the ratio 1:1. Broad bands, probably caused by polymeric material, prevented the analysis of the distributions of the labels in the main quantity of the sultine, which remained in the mother liquor. If we assume that there the ratio of **24a** and **24b** is also unity, that virtually no sulfone product was left in the mother liquor, and that the ratio of sulfones:sultines = 2:1, as in the case of the unlabeled benzvalene, we can calculate the approximate ratio of the products to be 5.1 parts **23a**, 1.5 parts **23b**, 1.7 parts **24a**, and 1.7 parts **24b**.

The crystalline mixture of **23a** and **23b** (3.5:1, ca. 9.5 parts) and **24a** and **24b** (1:1, ca. 0.5 part) was thermolyzed in solution. The progress of the reaction was monitored by ¹H NMR spectroscopy. As the rearrangement proceeded the ratio of the sulfones **23a** and **23b** approached unity while the sultines **24a** and **24b** were formed in the ratio of 1:1 from the beginning. Furthermore, in Me₂SO-d_6 the sulfones disappeared nine times as fast as in CDCl₃. These findings are best rationalized by the assumption that zwitterion **25a** develops from **23a** and **23b**. The intermediate **25a** may regenerate **23a** and **23b** or produce **24a** and **24b** by nucleophilic attack of the sulfur or an oxygen, respectively, at the allyl cation moiety. Because of only one deuteron at the otherwise equivalent bridgehead carbons, zwitterion **25a** must convert to a 1:1 mixture of **23a** and **23b** and also to a 1:1 mixture of **24a**
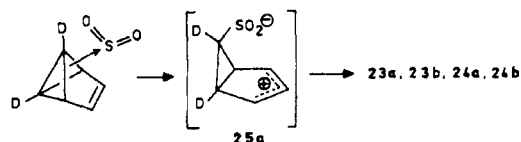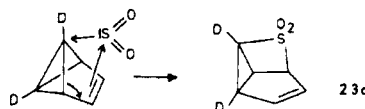
and **24b**, if the secondary deuterium isotope effect is neglected.

This mechanism is presented in Scheme III. By simulation of the conversion diagrams[36] (Figure 3) the rate constants at 21 and 41 °C in CDCl₃ and at 21 °C in Me₂SO-d_6 have been determined. They are summarized in Table I. These data can only be considered as approximate since the yield of this rearrangement is not more than 56% with 44% of the starting material having an unknown fate. In the conversion diagrams the sum of the mole fractions of all components were normalized to be 100% at all times. Significantly these measurements show that the zwitterion **25a** produces sulfones **23a/23b** and sultines **24a/24b** almost with the same rate ($k_{-1}/k_2 \approx 0.9$) and that the rate constants show the same temperature dependence.

Discussion. The experiments described above suggest two statements with respect to the reaction of benzvalene with SO₂: (i) There must be *two* pathways which lead to sulfone **23**, since one mechanism cannot explain the formation of **23a** and **23b** in the ratio 3.5:1. The partial isomerization of **23a** to **23b** via zwitterion **25a** in ether with about 3% SO₂ within 20 min at −35 °C is ruled out, since **23** was found to be completely stable in liquid SO₂ with 10% CDCl₃ at −10 °C for 30 min. If under the latter conditions the equilibrium between **23** and **25** was mobile, substantial quantities of sultine **24** would have to be produced because of $k_{-1}/k_2 \approx 0.9$, which is at variance with experiment. (ii) The pathway leading from benzvalene (**4**) and SO₂ to sultine **24** must involve a symmetric intermediate, since a one-step process cannot rationalize the formation of a 1:1 mixture of **24a** and **24b** from **4a**.

On the basis of these demands we propose that a two-step process (Scheme IV) competes with a concerted cycloaddition (Scheme V). The first step in the former reaction is an electrophilic attack of SO₂ at C-1 (C-6) of **4a** with cleavage of a lateral bond of the bicyclo[1.1.0]butane system to generate zwitterion **25a**, which should collapse to **23a**, **23b**, **24a**, and **24b** in the ratio 0.9:0.9:1.0:1.0. If we count a portion of **23a** corresponding to the quantity of **23b** (1.5 parts) as originating from **25a** the experimental ratio 1.5:1.5:1.7:1.7 harmonizes with the prediction.

With respect to the formation of the remaining 3.6 parts of **23a** we have to discuss in principle all the possibilities mentioned in connection with the origin of TCNE adduct **7a** (Scheme II), since the deuterium distribution of these two molecules corresponds to each other. Here the nonpolar three-step pathway via the diradicals **26** and **27** can be ruled out by a consideration of the
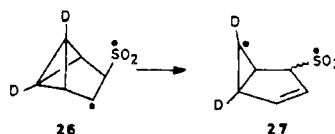
material balance. In the thiophenol addition to benzvalene, which has been shown to be a radical chain reaction,[2,20b] the cyclopropyl-carbinyl-homoallyl-radical rearrangement leads to an exo:endo ratio of 6:1. A similar ratio for the conversion **26 → 27** could

Scheme IV

Scheme V

(35) Hogeveen, H.; Zwart, L. *J. Am. Chem. Soc.* **1982**, *104*, 4889–4895.

(36) We used a revised version of the program by McLaughlin, E.; Rozett, R. W. *Chem. Technol.* **1971**, 120–121. We thank Dipl. Chems. W. von der Saal and R. Jakob for their help.

only account for a tiny quantity of **23a**, since only *endo*-**27** is capable of cyclization.

We consider the most reasonable mechanism, which accounts for the formation of the greater portion of **23a** in ether as the solvent, to be a concerted [4 + 1] cycloaddition of SO_2 to the vinylcyclopropane system of **4a** (Scheme V). The competition between the highly polar two-step process and the one-step cycloaddition, which should proceed through a relatively unpolar transition state, accounts for the variation of the sulfone/sultine ratio observed in solvents of different polarity. In the highly polar solvent SO_2 virtually all of the benzvalene (**4**) reacts via the zwitterionic intermediate **25** as shown by the sulfone/sultine ratio of 0.48. This ratio, which is equal to the ratio of the rate constants k_{-1}/k_2 for the two modes of ring closure of **25**, deviates considerably from the value determined in $CDCl_3$ and $Me_2SO\text{-}d_6$ (0.9). The difference may reflect either the approximate nature of the above kinetic measurements or specific influences of the different solvents on the competing formation of **23** and **24** from **25**. In the less polar solvent, ether, about one third of **4** undergoes the concerted cycloaddition.

The latter process is, as far as we know, the first example in which SO_2 reacts as a cheletrop with a vinylcyclopropane system in a $[(_\pi 2_s + _\sigma 2_s) + _\omega 2]$ cycloaddition. This type of reaction requires an orbital situation similar to that for the addition of SO_2 to 1,3-butadiene[37] with one π bond of the four-electron component being replaced by a σ bond. Thus, it is an allowed linear cheletropic reaction.[21b]

The two-step addition in Scheme IV, however, has precedent. Hogeveen and Zwart[35] treated the highly substituted benzvalene derivative **31** with SO_2 at –95 °C and observed the symmetric zwitterion **28**, which above –70 °C rearranged to the sulfones **32**

28   **29**   **30**

| SO_2 |
| < –70°C |

–70°C   –20°C

31   **32**   **33**
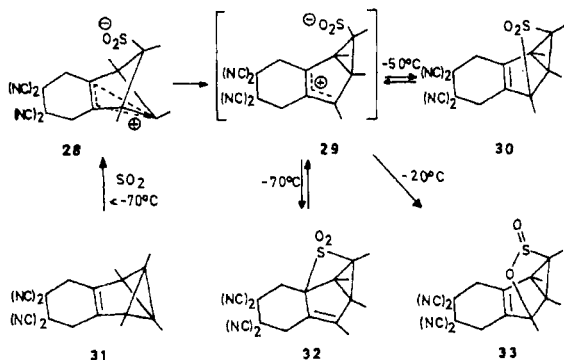
and **30**, presumably via the unsymmetric zwitterion **29**. The sulfones isomerized to the sultine derivative **33** at –20 °C.

Whether unsubstituted benzvalene (**4**) reacts with SO_2 to produce a zwitterion of type **28** with a nonclassical cationic portion, which subsequently rearranges via a [1,2] carbon migration to **25**, the parent compound of **29**, cannot be decided at present. While the intermediate **25** affords sulfone **23** and sultine **24** at almost the same rate, the zwitterion **29** strongly favors sulfones **30** and **32**. This may be explained by means of the HSAB principle.[38] Since three alkyl substituents stabilize the positive charge by hyperconjugation, the allyl cation portion of **29** is a softer acid than that of **25**. Thus in **29** the softer base sulfur reacts more quickly than the harder base oxygen. In **25**, however, the harder base oxygen can compete successfully. The alkyl substitution also accounts for the facile interconversion of the sulfones **30** and **32** and their transformation to the sultine **33** as compared with the much slower isomerizations **23a** → **23a**, **23b** and **23** → **24**. That the sultines **24** and **33** are more stable than the sulfone derivatives **23**, **30**, and **32** is a manifestation of the strain energy

of the four-membered ring sulfones.

The rearrangement of a cyclic sulfone to a sultine is a rare process previously encountered only at elevated temperatures, for example, the transformation of thiete 1,1-dioxide to 5*H*-1,2-oxathiole 2-oxide at 400 °C.[39] The hexamethyl derivative of **23** has been prepared from hexamethyl dewar benzene and SO_2 under catalysis of antimony pentafluoride.[40a] Without a catalyst only rearrangement to hexamethyl benzene occurs.[40b]

Concluding Remarks

The finding that benzvalene (**4**) forms the cycloadducts **7**, **17**, and **23** with TCNE, DDQ, and SO_2, respectively, uncovers a new reaction mode in which **4** acts as four-electron component in concerted six-electron cycloadditions. These are the first well-documented examples of one-step 1,4-additions at a vinylcyclopropane system, a reaction type which has long eluded researchers.[12] In the cases of TCNE and SO_2 there are competing zwitterionic processes. Interestingly, TCNE attacks the double bond of **4** with formation of **8**, while SO_2 attacks the strained system to generate **25**. The electrophile CSI may well be the intermediate case in that it interacts either with the π or the σ system to give rise to the zwitterions **20** and **22**, respectively. Obviously, orbital control directs the soft acid TCNE[38] to the olefinic moiety, where the HOMO of **4** is located.[3,4] In CSI the heteroatoms at the carbon turn this electrophile somewhat harder, thus it is attracted not only by the π bond but also by the σ system, which concentrates some negative charge[31,32] at its endo side. The still harder acid,[38] SO_2, then completely obeys charge control.

With these reactions the plentiful chemistry[2] of the fascinating molecule benzvalene, which is easily accessible by the elegant and efficient synthesis of Katz and co-workers,[6,41] gains a completely new facet.

Experimental Section

Infrared spectra were recorded on a Beckman AccuLab 4 spectrometer. The ^1H NMR spectra were determined with Varian EM-390 and Bruker WM-400 instruments. The ^{13}C NMR spectra were recorded with a Bruker WH-90 or WM-400 spectrometer. Mass spectra were obtained from a Varian MAT CH 7 spectrometer. Microanalytical determinations were performed with a Heraeus equipment. The melting points were determined on a Reichert apparatus by the Kofler method and are uncorrected.

Reaction of Benzvalene (4) with Tetracyanoethylene. A solution of **4**[6,41,42] (835 mg, 10.7 mmol) in 30 mL of ether was cooled to –78 °C and mixed with a solution of TCNE (1.37 g, 10.7 mmol) in 20 mL of ethyl acetate. After removal of the dry ice bath the mixture came to ambient temperature within 2.5 h and changed its color from originally red to brown to deep green. The green solution (prolonged reaction time gave brown products, which were hard to purify) was concentrated in vacuo to about 8 mL and then cooled to –78 °C. A light green solid separated, was collected by filtration, and was washed with pentane. A second crop was obtained from the mother liquor after addition of pentane and cooling to –30 °C overnight. Recrystallization of the combined crops from CH_2Cl_2/pentane afforded a total of 350 mg (16% yield) of tetracyclo[3.3.0.0^{2,4}.0^{3,6}]octane-7,7,8,8-tetracarbonitrile (**5**) as nearly pure colorless crystals. An analytically pure sample was obtained by several recrystallizations from acetone causing substantial losses of the substance: mp 230 °C; IR (KBr) 3120, 3100, 3050, 3030, 2265 (C≡N), 1330, 1310, 1292, 1255, 1230, 1130, 1065, 1038, 965, 812, 803, 749, 715 cm^{-1}; MS (70 eV), m/e 206 (M$^+$, 7%), 152 (11), 78 (100), 51 (13), 39 (16); ^1H NMR (acetone-d_6, see Figure 1) δ 2.46 (2,3-H, m), 3.25 (4-H, td, $J_{2,4}$ = 3.5 Hz, $J_{4,5}$ = 1.1 Hz), 3.46 (5-H, quint d, $J_{1,5}$ = $J_{2,5}$ = 4.5 Hz), 4.33 (1,6-H, m); ^{13}C NMR (acetone-d_6) δ 16.0 (C-2,3, d, J = 192 Hz), 22.0 (C-4, d, J = 206 Hz), 47.8 (C-5, d, J = 167 Hz), 48.9 (C-7,8, s), 54.8 (C-1,6, d, J = 164 Hz), 112.1 (CN, s). Anal. Calcd for $C_{12}H_6N_4$: C, 69.90; H, 2.93; N, 27.17. Found: C, 70.10; H, 3.28; N, 27.33. The molecular weight was determined to be 207 (calcd 206.2) with a Me-

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(42) We used methyllithium free of bromide from CHEMETALL, Frankfurt/Main.

chrolab vapor-pressure osmometer in acetone.

After separation of **5** the solvent of the mother liquor was removed in vacuo. The residue was treated with 5 mL of CCl_4, and the extract was decanted. After two repetitions, the black gum-like residue was triturated five times with 10 mL of ether. The combined brownish red ether extracts were concentrated in vacuo and dissolved in the minimum amount of ethyl acetate. Column chromatography on silica gel (elution as quick as possible with 25% ethyl acetate in petroleum ether) gave two fractions.

Fraction 1. Concentration and recrystallization from $CHCl_3$ afforded 155 mg (7%) of tricyclo[3.3.0.0^{2,6}]oct-7-ene-3,3,4,4-tetracarbonitrile (**6**) as colorless crystals: mp 126–128 °C; IR (KBr) 3010, 2260 (C≡N), 1565, 1292, 1229, 1221, 1175, 971, 931, 700, 637 cm^{-1}; MS (70 eV), m/e 206 (M$^+$, 27%), 205 (33), 180 (38), 179 (51), 152 (78), 141 (34), 128 (35), 78 (100), 65 (31), 51 (33), 39 (46); ^{1}H NMR (acetone-d_6) δ 2.97 (1,6-H, t, line distance 2.1 Hz), 4.52 (2,5-H, s), 6.72 (7,8-H, t); ^{13}C NMR (acetone-d_6) δ 45.8 (C-3,4), 53.3 (C-1,6), 86.4 (C-2,5), 112.3 (CN), 135.8 (C-7,8). Anal. Calcd for $C_{12}H_6N_4$: C, 69.90; H, 2.93; N, 27.17. Found: C, 69.37; H, 3.17; N, 27.24.

Fraction 2. Concentration and recrystallization from CH_2Cl_2 gave 195 mg of a 2:1 mixture of tricyclo[3.3.0.0^{2,8}]oct-6-ene-3,3,4,4-tetracarbonitrile (**7**) (6%) and **5**: mp 150–155 °C. Spectral data of **7**: MS (70 eV) fragments have the same m/e as those of **5** and **6**; the intensities are similar to those of **6** with m/e 152 being the 100% peak; ^{1}H NMR, see Chart I; ^{13}C NMR (acetone-d_6) δ 34.8 (d, J = 177 Hz) and 38.1 (d, J = 183 Hz) (C-2, C-8), 39.2 (C-1, d, J = 187 Hz), 45.1 (s) and 58.7 (s) (C-3, C-4), 60.8 (C-5, d, J = 155 Hz), 110.44 (s), 112.71 (s), 112.77 (s), 112.83 (s), (4 CN), 129.6 (d, J = 171 Hz) and 137.8 (d, J = 173 Hz) (C-6, C-7). Anal. Calcd for $C_{12}H_6N_4$: C, 69.90; H, 2.93; N, 27.17. Found for the 2:1 mixture of **7** and **5**: C, 70.31; H, 3.39; N, 26.90.

In another attempt to isolate **6** and **7**, the ethyl acetate solution of the ether extract was filtered through aluminum oxide of activity grade I on a short column (elution with 400 mL of 25% ethyl acetate in petroleum ether). After concentration of the colorless solution and treatment of the residue with $CHCl_3$, 155 mg (7%) of **6** were obtained. On preparative TLC (silica gel, 25% ethyl acetate in petroleum ether) the mother liquor afforded some more **6** (larger R_f value) and a mixture of **7** and **5** (smaller R_f value), the recrystallization of which gave 30 mg of a 4:1 mixture of **7** (1.1%) and **5**.

Reaction of 4a with TCNE. According to the procedure described above from **4a**[43] (603 mg, 7.54 mmol) in 22 mL of ether and TCNE (967 mg, 7.48 mmol) in 20 mL of ethyl acetate the dideuterated products **5a/5b, 6a,** and **7a** were obtained. The ^{1}H NMR of **5a, 5b** is shown in Figure 1.

The ^{1}H NMR spectrum of **6a** shows a doublet (2.1 Hz) at δ 2.98, a singlet at 4.55, and a triplet (2.1 Hz) at 6.72 with the relative intensities of 2:1:1.

In the ^{1}H NMR spectrum of **7a**, no signals are found at δ 2.67 and 3.18, where 2-H and 8-H of **7** absorb. Accordingly, the resonance at δ 3.53, which is assigned to 1-H, is a broad 5.6-Hz doublet. The signal of 5-H at δ 4.55 is unchanged relative to that of **5**, but the absorptions of the olefinic protons at δ 6.32 and 5.95 are simplified by a 2.4-Hz coupling and two long-range couplings, respectively. Since the coupling constant of 2.4 Hz is assigned most properly to $J_{7,8}$, the low-field olefinic signal must originate from 7-H. In the ^{13}C NMR spectrum no intense absorptions are found at δ 35.7 and 38.1, which indicates that the signals of **7** with these chemical shifts belong to C-2 and C-8.

Solvent Dependence of the Product Ratio 5:6:7. Solutions of benzvalene (**4**) in acetonitrile and pentane were obtained by a modification of the published procedure,[6,41] which furnishes **4** in ether. The second portion of methyllithium in ether was replaced by butyllithium in decalin. During the final distillation at the aspirator vacuum, only **4**, accompanied by some benzene, methylene chloride, and residual ether (from the first portion of methyllithium in ether), evaporated and this was condensed in a flask containing acetonitrile. After 30 min the distillation was interrupted and the flask with **4** in acetonitrile was replaced by an empty one. To collect the benzvalene, retained by the decalin, pentane was added to the distillation flask and the distillation continued. The condensate (–78 °C) in the receiver flask consisted of **4** in pentane and contained no ether.

A solution of **4** (250 mg, 3.20 mmol) in 50 mL of acetonitrile, kept at –30 °C, was treated with TCNE (320 mg, 2.50 mmol). The stirred mixture was allowed to come to room temperature. After 6 h the removal of the solvent gave 590 mg (515 mg = 100%) of a brown solid, which consisted of **5, 6,** and **7** in the ratio 7.7:2.9:1.0 with only minor impurities as determined by means of a 400-MHz ^{1}H NMR spectrum.

The addition of TCNE to **4** in pentane, carried out analogously, took place in suspension, since TCNE as well as the products are only slightly soluble in pentane. The product, a yellow powder, contained **5, 6,** and

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7 in the ratio 2.7:1.0:1.0 in addition to more impurities than in the acetonitrile case.

The benzene concentrations in the acetonitrile and pentane solutions were analyzed before and after the reactions with mesitylene as internal standard (^{1}H NMR determination). No increase was observed, therefore TCNE did not catalyze the isomerization of **4**.

10,11-Dichlorotetracyclo[6.4.0.0^{2,4}.0^{3,7}]dodeca-5,10-diene-9,12-dione-1,8-dicarbonitrile (17). A suspension of DDQ (2.95 g, 13.0 mmol) in 80 mL of ether containing **4** (1.17 g, 15.0 mmol) was stirred for 5 days at room temperature. During this time the color of the solution changed from brown to orange, while the undissolved material decolorized to a slight yellow. The precipitate was collected by filtration and washed with pentane to yield 2.50 g of a yellow powder containing about 1.25 g (31%) of **17**. Column chromatography (SiO$_2$, elution with 15% pentane in methylene chloride) gave a yellow fraction, from which 250 mg of pure **13** was obtained after several recrystallizations from acetone as nearly colorless crystals: mp 213–215 °C; IR (KBr) 2260 (C≡N), 1710 (C=O), 1563 (C=C), 1360, 1353, 1272, 1248, 1235, 1199, 1153, 1117, 1060, 990, 972, 955, 930, 889, 822, 780, 761, 730, 653 cm^{-1}; MS (70 eV), m/e 308, 306, 304 (M$^+$, 3%, 14%, 22%), 271, 269 (M$^+$ – Cl, 17, 53), 241 (70), 225 (47), 213 (51), 178 (33), 177 (26), 154 (28), 128 (29), 127 (54), 94 (30), 89 (36), 87 (100), 78 (77), 77 (33), 76 (32), 52 (47), 51 (50), 50 (35), 39 (60); ^{1}H NMR, see Chart I and Figure 2; ^{13}C NMR (acetone-d_6) δ 34.8 (d, J = 176 Hz), 41.5 (d, J = 182 Hz) (C-2, C-4), 39.5 (C-3, d, J = 182 Hz), 62.1 (C-7, d, J = 148 Hz), 55.6 (s), 72.0 (s) (C-1, C-8), 115.4 (s), 116.4 (s) (2 CN), 130.7 (d, J = 172 Hz), 138.8 (d, J = 160 Hz) (C-5, C-6), 147.0 (s), 147.1 (s) (C-10, C-11), 177.9 (s), 180.9 (s) (C-9, C-12). Anal. Calcd for $C_{14}H_6Cl_2N_2O_2$: C, 55.11; H, 1.98; N, 9.18. Found: C, 55.04; H, 1.73; N, 9.00.

The doubly labeled adduct **17a** was obtained according to the above procedure from **4a** (320 mg, 4.00 mmol) and DDQ (830 mg, 3.66 mmol): 770 mg of precipitate and after purification 100 mg of **17a** as yellowish crystals; ^{1}H NMR (acetone-d_6, see Figure 2) δ 3.47 (3-H, br d, J = 5.6 Hz), 4.13 (7-H, dd, J = 5.6 Hz, J = 2.5 Hz), 5.48 (6-H, ddd, J = 5.4 Hz, J = 2.5 Hz, J = 0.8 Hz), 5.92 (5-H, d, J = 5.4 Hz). When the ^{13}C NMR (acetone-d_6) spectrum is compared to the broadband decoupled spectrum of **17**, instead of the high-intensity signals at δ 34.8 and 41.5 low intensity 1:1:1 triplets with $J_{C,D}$ = 26.2 and 27.7 Hz, respectively, are observed at 34.8 and 41.5.

Addition of CSI to Benzvalene (4). Benzvalene (**4**) (4.5 g, 57.6 mmol) in 300 mL of ether was treated with LiAlH$_4$ (2.5 g), evaporated in the aspirator vacuum, and condensed onto CSI (5.66 g, 40.0 mmol) kept at –78 °C. With stirring the mixture was allowed to warm up and left at room temperature for 5 h. From 30 mL of the mixture the solvent was removed in vacuo to give a brownish oil, which was shown to be a 4.9:2.0:1.0:1.5 mixture of 8-chlorosulfonyl-8-azatetracyclo-[3.3.0.0^{2,4}.0^{3,6}]octan-7-one (**2a**), 4-chlorosulfonyl-4-azatricyclo-[3.3.0.0^{2,6}]oct-7-en-3-one (**3a**), 4-chlorosulfonyl-4-azatricyclo-[3.3.0.0^{2,8}]oct-6-en-3-one (**18a**), and 8-chlorosulfonyl-8-azatetracyclo-[4.2.0.0^{2,4}.0^{3,5}]octan-7-one (**19**) on the basis of the ^{1}H NMR spectrum. The main quantity of the reaction mixture was hydrolyzed (see below).

According to the same procedure a pentane solution of **4**, obtained as described above, afforded a 5.3:2.7:1.0:0.7 mixture of **2a, 3a, 18a,** and **19,** respectively.

On standing at room temperature for 60 days a 50-mg sample of the mixture in 0.5 mL of CDCl$_3$ turned black. A precipitate was removed by filtration and the NMR spectrum of the solution showed that **19** had entirely decomposed as well as **2a** and **3a** to a large extent. Small quantities of new compounds were present. The ratio of **2a:3a:18a** was determined to be 6:1:12. The six ^{1}H NMR absorptions of **18a** could be identified unambiguously.

2a: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 2.38 (3-H, m, $J_{3,6}$ = 2.8 Hz, $J_{2,3}$ = 4.0 Hz, $J_{3,4}$ = 3.4 Hz, $J_{3,5}$ = 4.6 Hz), 2.72 (2-H, m, $J_{2,4}$ = 3.4 Hz, $J_{2,5}$ = 4.6 Hz, $J_{1,2}$ = 2.2 Hz), 2.81 (5-H, ≈ quint d, $J_{4,5}$ = 0.9 Hz), 3.13 (4-H, td), 3.76 (6-H, dd, $J_{5,6}$ = 4.4 Hz), 5.14 (1-H, dd, $J_{1,5}$ = 5.2 Hz). The assignment of the signals belonging to 2-H and 3-H were established by decoupling at δ 5.14 and 3.76.

3a: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.48 (1,6-H, t, line distance 2 Hz), 4.04 (2-H, d, $J_{2,5}$ = 7.8 Hz), 5.41 (5-H, d), 6.47 (7,8-H, t).

18a and **19:** See Chart I.

Hydrolysis of the Chlorosulfonyl Lactams. The main quantity of the solution obtained from the reaction of CSI and **4** (ca. 270 mL) was diluted with 180 mL of acetone and added at 20 °C within 30 min to a stirred mixture of 54.0 g of sodium sulfite, 180 mL of water, and 90 mL of ether, the pH of which had been brought to 9–10 by means of concentrated KOH. After the mixture was stirred for 1 h at 20 °C, the two phases were separated, and the water layer was extracted with 180 mL of CH$_2$Cl$_2$. The combined organic layers were dried over anhydrous MgSO$_4$ and concentrated under reduced pressure (20 °C, 15 torr). The residue was flash distilled (bath temperature 30–150 °C, 10^{-3} torr) to

382 *J. Am. Chem. Soc., Vol. 106, No. 2, 1984*

Christl, Brunn, and Lanzendörfer

afford 2.67 g (61%) of a yellow oil, which solidified in the refrigerator and was shown to be a 10:1:2 mixture of **2b**, **3b**, and **18b** with only minor impurities by NMR spectroscopy. The ^{1}H NMR data of **2b** and **3b** have been published,[11] and those of **18b** are shown in Chart I. We could not separate **18b** from the mixture.

Addition of Sulfur Dioxide to Benzvalene (4). By means of a cooled pipette sulfur dioxide[44] (1.36 g, 21.2 mmol) was added to a flask containing benzvalene (4) (829 mg, 10.6 mmol) in 30 mL of ether at −35 °C. The flask was stoppered and left for 19 h at −30 °C. The colorless precipitate formed was collected by filtration to give 860 mg (57%, mp 76–82 °C) of 6-thiatricyclo[3.2.0.0^{2,7}]hept-3-ene 6,6-dioxide (**23**) contaminated with a few percent of **24**: IR (KBr) 3097, 1341, 1322, 1283 (sulfone functionality), 1248, 1221, 1211, 1133 (sulfone functionality), 1075, 936, 920, 898, 832, 811, 794, 777, 738, 722 cm^{-1}; MS (70 eV), *m/e* 142 (1%, M$^+$), 78 (100, M$^+$ − SO$_2$), 77 (19), 66 (29), 65 (13), 52 (31), 51 (20), 50 (16), 39 (33); ^{1}H NMR, see Chart I; ^{13}C NMR (Me$_2$SO-d_6) δ 31.5, 36.5 (C-1, C-2), 51.9 (C-7), 82.8 (C-5), 127.8, 132.4 (C-3, C-4). Anal. Calcd for C$_6$H$_6$O$_2$S: C, 50.69; H, 4.25; S, 22.55. Found: C, 50.68; H, 4.22; S, 21.90.

On concentration in vacuo the mother liquor provided 560 mg (37%) of a brown oil, the ^{1}H NMR spectrum of which showed clearly the signals of sultine **24** and of some residual **23** besides broad bands probably caused by polymeric material.

To determine the ratio of **23:24** equimolar quantities of **4** and SO$_2$ were mixed in ether and left for 15 min at −35 °C. The volatile components were removed in vacuo. On the basis of the peak intensities the residue, which indicated about 20% conversion, contained **23** and **24** in a ratio close to 2:1 in addition to polymeric material.

A sample of benzvalene (4) (24 mg) in 0.7 mL of CDCl$_3$[15] in an NMR tube was treated with several drops of liquid SO$_2$ at −78 °C. While the tube was cooled with liquid nitrogen it was sealed under vacuum. After having been kept at −78 °C for 30 min the sample was placed into the precooled probe of the NMR spectrometer. The spectrum taken at −67 °C showed that **4** had already disappeared completely and that **23** and **24** were present in a ratio of approximately 1:1.5 in addition to substantial quantities of polymeric material.

Inverse Addition. Benzvalene (4) (120 mg, 1.54 mmol) in 12 mL of ether was added dropwise to 80 mL of liquid SO$_2$ at −35 °C within 10 min. The mixture was stirred for 1.5 h at −35 °C. Then, at −30 °C the solvents were evaporated in vacuo. The residue, 220 mg of a brown oil, was dissolved completely in Me$_2$SO-d_6 (2.40 g). Using benzoic acid as internal standard we determined the yield to be 66% by ^{1}H NMR spectroscopy. The ratio **23:24** was 1:1.8. A second experiment gave a yield of 72% and a ratio of 1:2.4.

Addition of Sulfur Dioxide to 1,6-Dideuteriobenzvalene (4a). As described above for unlabeled **4** 2 equiv of SO$_2$ were syringed to **4a** in ether at −35 °C. After 20 min of stirring at that temperature the precipitate was isolated by filtration in the cold and dried in a stream of air. The ^{1}H NMR spectrum revealed the presence of **23a**, **23b**, **24a**, and **24b** in the ratio of 71.4:21.4:3.6:3.6. A second experiment provided a 76.0:21.0:1.5:1.5 ratio.

Compared to the spectrum of **23** (CDCl$_3$) the signal at δ 3.74 (7-H) is completely missing, while the absorption at δ 3.40 (1-H) and 2.80

(44) Sulfur dioxide was dried by passing it through a tube with phosphorous pentoxide on glass wool. The use of commercial high-purity SO$_2$ had no effect on the results.

(2-H) indicate 0.77 (0.78) and 0.23 (0.22) protons, respectively. Therefore an approximate ratio of **23a:23b** = 3.5:1 is calculated. Compared to the spectrum of **24** (CDCl$_3$) the signal at δ 3.50 (2-H) is completely absent and the absorptions at δ 3.27 (1-H) and 2.66 (8-H) show 0.5 proton each; thus the ratio of **24a:24b** is 1:1.

Rearrangement of 23 to 24. Dissolved in 25 mL of CHCl$_3$ **23** (1.00 g, 7.04 mmol, already containing a few percent of **24**) was warmed to 50–55 °C for 8 h. The resulting black mixture was filtered through a short column of silica gel to remove some insoluble material and dissolved polymers. Concentration of the resulting solution in vacuo afforded a brown highly viscous oil, which on sublimation at 80 °C (bath) (0.0004 torr) (under higher pressure extensive decomposition was observed) gave 420 mg (42%) of brownish crystals of 4-oxa-3-thiatricyclo[3.3.0.0^{2,8}]-oct-6-ene 3-oxide (**24**): mp 53–54 °C; IR (KBr) 2960, 2928, 2858, 1470, 1460, 1151 (sultine functionality), 961, 929, 897, 666 cm^{-1}; MS (70 eV), *m/e* 142 (1%, M$^+$), 78 (100, M$^+$ − SO$_2$), 77 (15), 66 (36), 65 (13), 52 (26), 51 (16), 50 (12), 40 (11), 39 (41); ^{1}H NMR, see Chart I; ^{13}C NMR (Me$_2$SO-d_6) δ 33.8, 34.4 (C-1, C-8), 66.9 (C-2), 92.0 (C-5), 130.9, 131.9 (C-6, C-7). Anal. Calcd for C$_6$H$_6$O$_2$S: C, 50.69; H, 4.25; S, 22.55. Found: C, 50.91; H, 4.28; S, 22.20.

A 30-mg sample of **23**, containing a few per cent **24** and sealed in an NMR tube with 1 mL of liquid SO$_2$ and 0.1 mL of CDCl$_3$, was completely stable for 30 min at −10 °C. No evidence for the rearrangement to **24** was found at this or lower temperatures.

Rate Measurements of the Rearrangement of 23a, 23b → 24a, 24b. A sample of the precipitate obtained from the reaction of SO$_2$ with **4a** was placed in an NMR tube, dissolved in CDCl$_3$, and kept at 41 °C. From time to time the concentration of the components were measured by means of the integrals in the 400-MHz ^{1}H NMR spectrum. With mesitylene as internal standard the yield of **24a, 24b** was determined to be 56%. The progress of this reaction is shown in Figure 3, where the sum of the mole fractions of all components have been set to be 100% over all time values. Computer simulation[36] of this conversion diagram provided the rate constants. Further experiments were carried out at 21 °C in CDCl$_3$ and at 21 °C in Me$_2$SO-d_6. The rate constants are summarized in Table I.

As the rearrangement proceeded the signals of **23a**, **23b** at δ 3.40 (1-H) and 2.80 (2-H) changed their ratio of intensities from ca. 3.5:1 at the beginning to 1:1 after about three half lives. The sultines **24a** and **24b** were formed in the ratio of 1:1 from the beginning, since the signals at δ 3.27 (1-H) and 2.66 (8-H) had equal intensities all the time.