Tetrahedron Vol. 45, No. 10, pp. 2905 to 2915, 1989
Printed in Great Britain.

0040-4020/89 $3.00+.00

7-METHYL- AND 7-PHENYLCYCLOHEPTA-1,3,5-TRIENES FROM BENZVALENE VIA 3,3a,4,5,6,6a-HEXAHYDRO-4,5,6-METHENOCYCLOPENTAPYRAZOLES AND TETRACYCLO[4.1.0.$0^{2,4}$.$0^{3,5}$]HEPTANES

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(*Received in Belgium* 8 *August* 1988)

Abstract: The addition of benzvalene (1) to diazomethane, diazoethane, 2-diazopropane, phenyldiazomethane, and diphenyldiazomethane afforded the 1-pyrazolines **2a-g** in good yields. By means of competition experiments, the relative reactivities of benzvalene (1) and norbornene with regard to diazomethane and 2-diazopropane have been determined. The fact that benzvalene reacts about twice as fast as norbornene with both diazoalkanes cannot be rationalized on the basis of frontier orbital energies. On direct photolysis, the pyrazolines **2a-g** were converted into the tetracyclo[4.1.0.$0^{2,4}$.$0^{3,5}$]heptanes **4a-g** exclusively. These compounds gave the 1,3,5-cycloheptatrienes **5a,b,d,e,g** in high yields on treatment with silver ions, thus providing better access to 7,7-dimethyl-(**5d**) and 7,7-diphenylcycloheptatriene (**5g**) than before. Surprisingly, the latter compound is in equilibrium with a substantial quantity of the norcaradiene form. - The heat of reaction for the rearrangement of **4a** to **5a** has been determined, which allows to derive the heat of formation of tetracyclo-[4.1.0.$0^{2,4}$.$0^{3,5}$]heptane (**4a**).

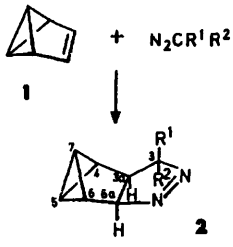
The most generally applicable methods for the synthesis of 1,3,5-cycloheptatriene derivatives are reactions of the tropylium cation with nucleophiles and the addition of carbenes to benzene.[1] While the former can give unequivocally only 7-monosubstituted cycloheptatrienes, the latter is also suitable for the preparation of certain derivatives disubstituted in the 7-position. However, many carbenes do not react with benzene or give products only in low yields. Obviously, 7,7-dimethylcycloheptatriene (**5d**) cannot be obtained via this route, since it has exclusively been prepared by using other approaches.[2,3] Formed in low yield on thermolysis or photolysis of diphenyldiazomethane in benzene, 7,7-diphenylcycloheptatriene (**5g**) appears in the literature for the first time in 1988.[4] We wish to report here a three-step reaction sequence rendering cycloheptatrienes with one or two methyl or phenyl substituents in the 7-position accessible in good yields. This method demonstrates a utilization of benzvalene as benzene equivalent.

1,3-Dipolar cycloadditions of diazoalkanes with benzvalene[5]

As early as 1973, we described the addition of diazomethane to benzvalene.[6] The yield of 1-pyrazoline **2a** has now been increased considerably, and in addition diazoethane, 2-diazopropane, phenyldiazomethane, and diphenyldiazomethane have been found to give the corresponding pyrazolines **2b-g** in good yields. In the cases of diazoethane and phenyldiazomethane, the ratios of the diastereomers **2b** : **2c** = 1.7 : 1.0 and **2e** : **2f** = 1.5 : 1.0, respectively, indicate only a minor stereoselectivity.

The structure of the 1-pyrazolines **2** is established unambiguously by analytical and spectral data. The stereochemical assignment within the isomeric pairs **2b,c** and **2e,f** is based on the magnitude of the coupling constants $^3J_{3,3a}$ in the ^{1}H-NMR

spectra (see Table 1) and on the γ-gauche effect of the endo-3-substituent (R^1) on the chemical shift of C-4 in the ^{13}C-NMR spectra (see Table 2). Although C-5 and C-7 match each other rather closely, their signals can be distinguished by means of long-range ^{13}C-H coupling constants as noted earlier for related tricyclo-[3.1.0.$0^{2,6}$]hexane derivatives.[7] Similarly, the absorptions of C-4 and C-6 differ markedly in their fine structure with that of C-4 being much better resolved.



diazoalkane	R^1	R^2	product	yield (%)
N_2CH_2	H	H	2a	83
N_2CHCH_3	H	CH_3	2b	31 (58)
	CH_3	H	2c	
$N_2C(CH_3)_2$	CH_3	CH_3	2d	93
$N_2CHC_6H_5$	H	C_6H_5	2e	44 (73)
	C_6H_5	H	2f	
$N_2C(C_6H_5)_2$	C_6H_5	C_6H_5	2g	72

Table 1. ^1H-NMR chemical shifts (δ values) and coupling constants (absolute values, Hz) of cis-3, 3a, 4, 5, 6, 6a-hexahydro-4, 5, 6-methenocyclopentapyrazoles (2) in $CDCl_3$. The multiplicities are given only for the parent compound (2a); they are observed only in a high-field spectrum, since at low field second order effects interfere. The following coupling constants are those of 2a with the deviations in the spectra of the derivatives being at most ±0.5 Hz: $J_{3,3} = 18.0$, $J_{3_{exo},3a} = 8.5$, $J_{3_{exo},6a} = 1.8$, $J_{3_{endo},3a} = 3.5$, $J_{3_{endo},6a} = 2.5$, $J_{3a,4} = 1.5$, $J_{3a,6a} = 7.0$, $J_{3a,7} = J_{6a,7} = 1.3$, $J_{4,5} = J_{4,7} = J_{5,6} = J_{6,7} = 1.7$, $J_{4,6} = 5.0$, $J_{5,7} = 9.2$, $J_{6,6a} = 1.7$.

compd	exo-3-H	endo-3-H	3a-H	4-H	5-H	7-H	6-H	6a-H
2a	4.06 ddd	4.15 ddd	2.23 dddt	2.05 dq	2.12 dt	1.83 dqui	2.79 dq	5.15 ddq
2b[a]	-	4.23		1.70-2.40			2.78	5.20
2c[b]	4.06	-		1.70-2.40			2.78	5.12
2d[c]	-	-		1.70-2.30			2.73	5.12
2e[d]	-	5.18		2.00-2.30		1.93	2.85	5.33
2f[e]	[f]	-	2.46	1.30	1.93	1.71	2.85	[f]
2g[g]	-	-	2.93	1.38	2.00	1.70	2.87	5.35

[a] 1.23 (d, J = 7.3, CH_3). [b] 1.52 (d, J = 7.5, CH_3). [c] 1.10 (s, exo-CH_3), 1.43 (s, endo-CH_3). [d] 7.00-7.30 (m, C_6H_5). [e] 6.9-7.5 (m, C_6H_5). [f] 4.9-5.4. [g] 7.30 (m, 2 C_6H_5).

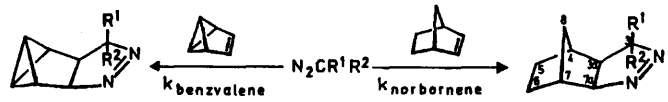
Table 2. ^{13}C-NMR chemical shifts (δ values) and ^{13}C-H coupling constants (Hz) of cis-3, 3a, 4, 5, 6, 6a-hexahydro-4, 5, 6-methenocyclopentapyrazoles (2). The $^1J_{C,H}$ values are given only for the parent compound (2a) (second line) with the deviations in the spectra of the derivatives being at most ±3 Hz. Among the coupling constants across two or more bonds, the following are considered to be unambiguous: $^3J_{C-4,4-H} = {}^3J_{C-6,6-H} = 13$, $^2J_{C-5,7-H} = {}^2J_{C-7,5-H} = 3$, $^3J_{C-7,3a-H} = {}^3J_{C-7,6a-H} = 8$. The specific assignments are based on $^1J_{C,H}$, substituent effects, and fine-structure patterns in the proton-coupled spectra.

compd	C-3	C-3a	C-4	C-5	C-6	C-6a	C-7
2a[a]	77.5 [b]	37.1 141	38.4 170	7.7 216	39.2 170	98.7 150	0.4 218
2b[c,d]	83.0	44.4	36.7	6.6	37.9	97.0	-0.4
2c[c,e]	80.2	39.0	32.8	5.8	37.9	97.8	0.7
2d[c,f]	84.8	46.8	34.1	6.7	38.0	97.3	1.1
2e[a,g]	93.3	47.0	38.2	8.0	39.0	100.0	1.0
2f[a,h]	89.0	41.5	35.0	6.3	38.8	98.9	2.1
2g[c,i]	97.8	46.4	36.0	6.3	38.2	99.3	2.1

[a] Solvent D_6D_6. [b] 141 (endo-H), 139 (exo-H). [c] Solvent $CDCl_3$. [d] 18.1 (CH_3). [e] 12.9 (CH_3). [f] 20.9 (endo-CH_3), 27.6 (exo-CH_3). [g] 127.5-128.9 (o-C, m-C, p-C), 140.0 (ipso-C) (C_6H_5). [h] 127.1-128.8 (o-C, m-C, p-C), 138.6 (ipso-C) (C_6H_5). [i] 126.4-128.4 (o-C, m-C, p-C), 142.6, 142.9 (ipso-C) (2 C_6H_5).

Ethyl diazoacetate did not react with benzvalene (1). However, methyl 2-diazopropionate and 1 afford both the stereoisomeric 1-pyrazolines.[8] The results of the reactions of 1 with tetrachlorodiazocyclopentadiene, diazofluorene, and 5-diazo-10,11-dihydro-5H-dibenzo[a,d]cycloheptene will be described elsewhere.[9]

With regard to the mechanism, the reaction of diazoalkanes with alkenes is one of the most thoroughly studied 1,3-dipolar cycloadditions. This is true for experimental as well as theoretical investigations.[10a] Therefore, it was of interest to determine the rate of the reaction between diazomethane and benzvalene (1) and to integrate 1 into the scale of dipolarophiles.[10] Because of the simple experimental set-up, we have carried out competition experiments, in which 1 and norbornene, both in excess relative to the 1,3-dipole, competed for diazomethane and, in a second series, also for 2-diazopropane. The norbornene adduct 3a of diazomethane[10b] and the rate constant for its formation are known.[10] The norbornene adduct 3d of 2-diazopropane has now been obtained in 79% yield. In the experimental part, the data of the individual competition experiments are collected, from which the following ratios of the rate constants have been calculated according to ref. 11.



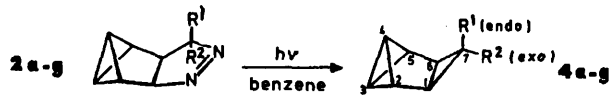
2a $R^1 = R^2 = H$ **3a**
2d $R^1 = R^2 = CH_3$ **3d**

diazomethane: $\frac{k_{benzvalene}}{k_{norbornene}} = 1.6 \pm 0.2$; 2-diazopropane: $\frac{k_{benzvalene}}{k_{norbornene}} = 2.3 \pm 0.4$

Thus, benzvalene (1) reacts somewhat faster than norbornene with both the diazoalkanes. However, the rate ratios are closely related to the competition constant with regard to benzonitrile oxide, which takes up these olefins equally fast.[12] The FMO-theory describes the cycloadditions of nitrile oxides with electron-rich olefins, in which category 1 and norbornene have to be included on the basis of the ionization potentials,[13] as controlled by the LUMO of the 1,3-dipole.[10a] On the contrary, the control by the HOMO of diazomethane rationalizes the relative rates of the cycloadditions of this 1,3-dipole best.[10a] This should be valid to an even greater extent for 2-diazopropane. Since 1 has a lower ionization potential (corresponding to the π-orbital) and, most probably, a less accessible π*-orbital than norbornene, we had expected that 1 would react slower than norbornene with these 1,3-dipoles. This is not the case, however. Obviously, the rates of these cycloadditions are not dominated by frontier orbital interactions, but by the relief of olefin strain.[14]

Preparation of tetracyclo[4.1.0.$0^{2,4}$.$0^{3,5}$]heptanes 4 from the 1-pyrazolines 2[5]

Heretofore, the exclusive route for the synthesis of the tetracyclo[4.1.0.-$0^{2,4}$.$0^{3,5}$]heptane system was the addition of halocarbenes to benzvalene.[15,16] The parent hydrocarbon 5a has been obtained by reduction of the 7,7-dibromo and 7,7-dichloro derivatives.[15] Another access to cyclopropane derivatives is provided by the nitrogen extrusion from 1-pyrazolines.[17,18] Thus, the 1-pyrazolines 2 offered the possibility to prepare 5a as well as derivatives thereof with methyl and phenyl groups in position 7. And indeed, the irradiation of 2a-g in benzene through Pyrex glass afforded the tetracycloheptanes 4a-g in 27 - 81% yield.



The new route to **4a** is less efficient than the one published earlier,[15] but the derivatives **4b-g** are not available by any previous pathway. In the cases of the methyl pyrazolines **2b,c** and the phenyl pyrazoline **2f**, the nitrogen extrusion appears to proceed largely with retention, but the isomer ratios of the starting materials and of the products were not analyzed with sufficient accuracy to allow a more precise statement. Irradiation of pure **2e** afforded pure **4e**, however.

The NMR spectra of the hydrocarbons **4** (for ^{1}H-NMR, see Table 3; for ^{13}C-NMR, see ref. 19) are characterized by large differences between the chemical shifts of the structurally related 3- and 4-CH groups (^{1}H-NMR, 0.53-1.52 ppm; ^{13}C-NMR, 18.5-26.1 ppm). These differences originate from the orientation of the respective CH group relative to the anellated cyclopropane ring. The ^{1}H-NMR spectrum of **4a**[15] and the ^{13}C-NMR spectra of **4a-g**[19] have been discussed in detail. Within the isomeric pairs **4b,c** and **4e,f**, the stereochemical assignments are based on the ^{13}C chemical shifts[19] as well as on ^{1}H-^{1}H coupling constants, in particular on $J_{1,7\,endo}$ = 2.6 and $J_{1,7\,exo}$ = 6.7 Hz. Because of the endo phenyl group in **4f,g**, 4-H experiences the anisotropy effect resulting in a remarkable upfield shift (δ 0.93 and 1.06, respectively) of the signal relative to that of **4e** (δ 1.55).

Table 3. ^{1}H-NMR chemical shifts (δ values) and coupling constants (absolute values, Hz) of tetracyclo[4.1.0.$0^{2,4}$.$0^{3,5}$]heptanes (**4**) in $CDCl_3$. Average values of coupling constants excluding those of **4a**[15]: $J_{1,4}$ = 0.5, $J_{1,7\,endo}$ = 2.6, $J_{1,7\,exo}$ = 6.7, $J_{2,3}$ = 1.0 ± 0.2, $J_{2,4}$ = 2.5 ± 0.2, $J_{3,4}$ = 9.1 ± 0.5, $J_{3,7\,exo}$ = 1.1 (**5c**), 1.6 (**5f**), $J_{4,7\,endo}$ = 0.6.

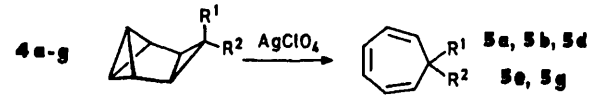
compd	1,6-H	2,5-H	3-H	4-H	R¹(endo)	R²(exo)
4a	1.07	2.15	2.29	1.51	0.57	0.50
4b[a]	0.86	2.16	2.26	1.56	0.71	0.86
4c[b]	1.19	1.92	2.47	1.80	1.27	0.83
4d	0.93	1.92	2.41	1.88	1.26	0.78
4e	1.34	2.16	2.26	1.55	1.93	6.8-7.3
4f	1.52	1.85	2.40	0.93	6.8-7.4	2.17
4g	1.92	2.06	2.58	1.06	6.9-7.5	

[a] J_{7,CH_3} = 6.2. [b] J_{7,CH_3} = 5.8.

As reported for the parent hydrocarbon **4a**[20], the derivatives **4b-g** rearrange on heating at temperatures above 160°C to bicyclo[3.2.0]hepta-2,6-dienes and cycloheptatrienes.[21] Characteristically for bicyclo[1.1.0]butane derivatives,[22] **4a-g** are sensitive to acids, which undergo addition across a lateral bicyclobutane bond and/or cause the conversion into the corresponding cycloheptatriene.[21] Such processes occur more easily the greater the strain in the respective compound. Thus, the endo-methyl (**4c**) and endo-phenyl derivatives (**4f**) are transformed to 7-methyl- and 7-phenylcycloheptatriene, respectively, at 20°C in deuteriochloroform within several days, whereas the stereoisomers **4b** and **4e** survive under these conditions.

Conversion of tetracyclo[4.1.0.$0^{2,4}$.$0^{3,5}$]heptanes 4 into cycloheptatrienes 5

Many polycyclic hydrocarbons are subject to isomerization on treatment with catalytic quantities of silver ions.[23] This reagent transforms the majority of bicyclo[1.1.0]butane derivatives to 1,3-butadienes.[22,23] We have shown that silver salt catalysis gives rise to the formation of 1,3-cyclohexadiene from tricyclo[3.1.0.$0^{2,6}$]hexane[24] and of cycloheptatriene **5a** from tetracycloheptane **4a** with the latter process being highly exothermic.[15] This reaction has been utilized to prepare 3,4-dideuteriocycloheptatriene free of isotopomers.[15] We describe now the application of this method to the tetracycloheptanes **4b-g**.



On treatment with silver perchlorate in benzene, with a catalytic quantity being sufficient in three out of four cases, **4b-g** rearranged in high yield to 7-methyl- (**5b**), 7,7-dimethyl- (**5d**), 7-phenyl- (**5e**), and 7,7-diphenylcycloheptatriene (**5g**), respectively. As to the mechanism of these processes, we refer to the speculations advanced in connection with the conversion of **4a** into **5a**.[15]

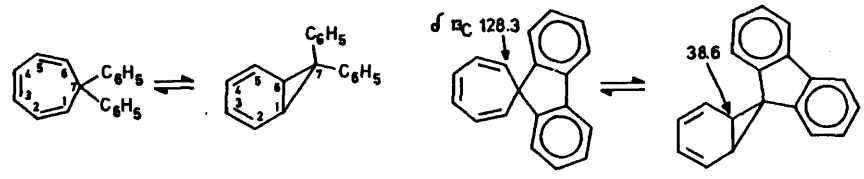
For the synthesis of 7-methyl-(**5b**) and 7-phenylcycloheptatriene (**5e**), the above method provides no progress since these compounds can be expeditiously prepared from the tropylium ion and the corresponding Grignard reagent.[1] However, 7,7-dimethyl- (**5d**) and 7,7-diphenylcycloheptatriene (**5g**) are made more readily accessible than before by the reaction sequence described herein. In both cases, the overall yield for the three steps from benzvalene (1) is 40 - 45% and for the four steps from cyclopentadiene 17 - 20%. Of course, the diazoalkanes have to be provided requiring two or three steps, but very simple ones. Hoffmann and Frickel[2] obtained **5d** in 17% yield in three steps starting from 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene and 3,3-dimethylcyclopropene with three additional steps necessary for the synthesis of the latter educt. Because of the simultaneous formation of α-methylstyrene, the route to **5d** from methyl 7-methylcycloheptatriene-7-carboxylate is even less efficient.[3] The direct pathway from benzene and diphenyldiazomethane to **5g** affords a yield of only 8% after elaborate chromatographic separation.[4] For the preparation of synthetically useful quantities of **5g**, our procedure utilizing benzvalene (1) as benzene equivalent certainly has its merits. Doubtless many other cycloheptatrienes with alkyl and aryl substituents in the 7-position should be conveniently accessible by means of this methodology.

The cycloheptatrienes **5b,d,e,g** have been characterized by their NMR spectra (see Table 4 for the ^{13}C-NMR chemical shifts of **5d,e,g**). Here we noticed that 1,6-H of the diphenyl derivative **5g** resonate substantially more upfield (δ 4.65) than 1,6-H of the monophenyl compound **5e** (δ 5.42). Additionally, the signal of C-1,6 of **5g** appears at much higher field (δ 95.6) than the corresponding line of **5e** (δ 126.2). These phenomena indicate that **5g** is not a single substance but an equilibrium mixture of the cycloheptatriene (**5gC**) and the norcaradiene form (**5gN**). On the basis of these chemical shifts, Hannemann[4] has estimated the ratio **5gC** : **5gN** to be about 65 : 35 at ambient temperature. We recorded the ^{13}C-NMR spectrum of **5g** at lower temperatures too and observed that the signal of C-1,6 moved from δ 95.6 at 314 K to 82.6 at 183 K. Due to extensive broadening, this absorption disappeared in the noise at 163 K. With our instrument we were unable to reach a temperature sufficiently low to freeze the equilibrium **5gC** ⇌ **5gN** and so provide the individual resonances of both forms.

Table 4. ^{13}C-NMR chemical shifts (δ values) of some cycloheptatrienes **5**

compd	solvt	temp. (K)	C-1,6	C-2,5	C-3,4	C-7	substituent			
							26.1			
							ipso-C	o-C	m-C	p-C
5d	$CDCl_3$	314	134.3	124.1	129.8	35.4	143.9	127.6	128.7	126.6
5e	$CDCl_3$	314	126.2	124.5	130.9	45.3	143.9	127.6	128.9	126.6
5g	$CDCl_3$	314	95.6	125.5[a]	127.5[a]	43.5	145.6	127.6	128.9	125.9[a]
	$CD_2Cl_2/CHClF_2$	233	89.7	126.5[a]	127.9[a]	[b]	146.6	128.7	130.0	127.0[a]
	$CD_2Cl_2/CHClF_2$	212	86.6	126.3[a]	127.5[a]	[b]	146.2	128.6	129.9	126.9[a]
	$CD_2Cl_2/CHClF_2$	183	82.6	126.2[a]	127.0[a]	[b]	145.7	128.5	129.6	126.8[a]
	$CD_2Cl_2/CHClF_2$	163	[b]	126.0[a]	126.6[a]	[b]	145.3	128.3	129.4	126.6[a]

[a] The assignment of C-2,5, C-3,4, and p-C is only tentative. [b] Not observed due to low intensity because of broadening.



5gC **5gN** **6C** **6N**

To calculate the exact ratio **5gC** : **5gN**, the individual chemical shifts are necessary, however. Accordingly, we have estimated these with the aid of the corresponding values for the spiro compounds **6C** and **6N**, the individual chemical shifts of which have been determined by Dürr and Kober.[25] The compounds **6** as well as **5g** carry two phenyl groups in position 7 though these are directly connected to each other via the ortho-positions in **6**. To a first approximation, we assume that the 7-substituents of **5g** and **6** exert equal effects on the ^{13}C-NMR chemical shifts of the ring carbon atoms. By transfer of the C-1,6 values of **6C** (δ 128.3) and **6N** (δ 36.8) to **5gC** and **5gN**, respectively, we have calculated the ratio **5gC** : **5gN** for those temperatures at which the C-1,6 signal was observed: 314 K, 63 : 37; 233 K, 56 : 44; 212 K, 53 : 47; 183 K, 49 : 51. From the temperature dependence of these ratios we have obtained the enthalpy and the entropy for the conversion **5gC** → **5gN**: ΔH_R = -530 cal/mol, ΔS_R = -3 eu. Because of the above-mentioned assumption, these values are only rough estimates. The greater temperature dependence of the ratio **6C** : **6N** (290 K, 78 : 22; 160 K, 49 : 51) indicates a larger negative enthalpy as well as a larger negative entropy of reaction for the process **6C** → **6N**. In spite of that, the ratios **5gC** : **5gN** and **6C** : **6N** appear astoundingly similar in view of the different orientation of the phenyl groups in these systems. Being arranged in a bisected manner, the π orbitals of the fluorene moiety in **6N** interact optimally with the cyclopropane Walsh orbitals thus exerting the maximum acceptor ability of the aromatic unit. Good π acceptors in the 7-position are one of the requisites for a high norcaradiene share in a cycloheptatriene/norcaradiene equilibrium.[24] However, in **5gN** both the phenyl groups should be twisted relative to the bisected conformation by about 90° due to mutual steric hindrance. Thus, an interaction of the π orbitals and the cyclopropane Walsh orbitals cannot be operative. Nevertheless, the proportion of **5gN** in the **5gC**/**5gN** mixture is rather high. The fact that the introduction of a methyl group in one ortho-position of one phenyl group of **5g** causes the equilibrium to shift virtually completely to the side of the norcaradiene[4] indicates the relative unimportance of electronic effects and the dominance of steric effects[27] in these systems.

Heat of formation of tetracyclo[4.1.0.$0^{2,4}$.$0^{3,5}$]heptane (4a)

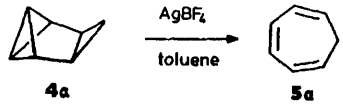
The strong exothermicity and the high yield of the silver ion catalized rearrangement **4a** → **5a** offered the possibility to determine the enthalpy of reaction, from which the heat of formation of **4a** can be derived. The measurements have been conducted in toluene as solvent by isothermal titration-calorimetry. The calorimeter, experimental method, accuracy of measurements have already been reported.[26]

Cycloheptatriene (**5a**) forms a complex with $AgBF_4$ used to effect the rearrangement of **4a**. To calculate ΔH_R of **4a** → **5a** the corresponding heat of complexation has to be accounted for. It was determined in analogy to ΔH_R of **4a** → **5a** by titration of a toluene solution of **5a** to the stock of $AgBF_4$.

For an accurate calculation of the heat of reaction a correction for the difference in enthalpies of solution and evaporation of educts and products has to be made. As has been shown previously, these differences generally are small for isomers.[29] The heat of solution difference in isooctane can be estimated by a

"double-bond increment" of 0.1 kcal/mol per double bond.[29] To test whether this relation is valid also in toluene, the solvent used in this study, first heats of solution of **5a** and cycloheptane in toluene were measured by using the method described earlier.[28] The values of ΔH_{sol}^{∞} = 0.06 and 0.58 kcal/mol indicate that within the accuracy of the method (±0.1 kcal/mol[28]) the increment approach can also be applied to toluene solutions.

With the data given in Table 7 (see experimental part) and the known heat of formation of 5a[30] the heat of formation of 4a is obtained by:



4a **5a**

heat of rearrangement	+46.3 kcal/mol
corr. for complex formation of 5a	-2.2 kcal/mol
corr. $\Delta\Delta H_L$	-0.3 kcal/mol
ΔH_f° of 5a	+44.6 kcal/mol
ΔH_f° of 4a	88.4 kcal/mol

Derived from this value and ΔH_f° of strain free 4a, which is obtained by using group increments,[31] the strain energy of 4a can be calculated. In Table 5, this value (ΔH_s) is compared to the strain energy of bicyclo[1.1.0]butane, benzvalene (1), and tricyclo[4.1.0.$0^{2,7}$]heptane.

Table 5. Strain energies (kcal/mol) of several bicyclo[1.1.0]butane derivatives

				
ΔH_f°	51.9[32]	87.3[33]	88.4	44.6[34]
ΔH_s	65.5	77.7	104.7	67.0

EXPERIMENTAL

General and instrumentation. See ref. 35.

Addition of diazoalkanes to benzvalene (1) - preparation of cis-3,3a,4,5,6,6a-hexahydro-4,5,6-methenocyclopentapyrazoles (2)

Parent compound (2a): A mixture of 40% aqueous KOH (25 ml) and ether (20 ml) containing benzvalene (1)[36] (780 mg, 10.0 mmol) was cooled to -5 °C, treated with 1-methyl-1-nitrosourea[37] (10.0 g, 97.1 mmol) in a manner that the temperature did not rise above 0 °C and, thereafter, stirred at -5 °C for 30 min. The layers were separated, and the yellow ether layer was set aside in a dark place at 20 °C until the color had disappeared (several days). Concentration in vacuo and distillation of the residue at 55-60 °C (bath)/0.1 Torr afforded 1.00 g (83%) of **2a** as a colorless liquid. IR (film) 1548 (N=N) cm^{-1}. UV (cyclohexane) λ_{max} (ϵ) 330 (280) nm. ^{1}H-NMR, see Table 1. ^{13}C-NMR, see Table 2. (Found: C, 69.75; H, 6.72; N, 23.47. Calc for $C_7H_8N_2$ (120.2): C, 69.97; H, 6.71; N, 23.32%.)

exo- (2b) and endo-3-Methyl (2c) derivatives: The reaction of 1 and diazoethane (from 1-ethyl-1-nitrosourea[38]) was carried out as above. The orange-yellow color of the ether layer had disappeared after 15 h at 20 °C in the dark. Distillation at 40-50 °C (bath)/0.001 Torr afforded a colorless oil (58%), which contained mainly **2b** and **2c** in the ratio 1.7 : 1.0. An analytically pure sample (31% yield) consisting of **2b** and **2c** in the ratio 3.0 : 1.0 was obtained by chromatography (SiO_2, 3 : 2 ether/hexane). IR (film) 1548 (N=N) cm^{-1}. UV ($CHCl_3$) λ_{max} (ϵ) 330 (290) nm. MS (70 eV) m/z (%) 134 (1, M^+), 91 (100). ^{1}H-NMR, see Table 1. ^{13}C-NMR, see Table 2. (Found: C, 71.68; H, 7.45; N, 20.66. Calc for $C_8H_{10}N_2$ (134.2): C, 71.61; H, 7.51; N, 20.88%.)

3,3-Dimethyl derivative (2d): According to ref. 39, 2-diazopropane was prepared from acetone hydrazone. Thus, mercuric oxide (60.0 g, 270 mmol), 3 M KOH in ethanol (4.5 ml), and ether (60 ml) were placed under nitrogen in a three-necked flask equipped with a dropping funnel and a magnetic stirrer, externally cooled by -

water bath (20 °C). The flask was connected to a trap containing 1 (1.00 g, 12.8 mmol) in ether (25 ml), which was cooled to -80 °C. This trap was connected to an empty trap cooled with liquid nitrogen. Via the two traps, the pressure in the apparatus was reduced to about 200 Torr, and acetone hydrazone (15.0 g, 210 mmol) was added dropwise to the vigorously stirred mixture within 20 min. With continued stirring, the pressure was then reduced to 15 Torr for 10 min. Thereafter, the traps were allowed to warm to 20 °C under normal pressure. Their contents (red solutions) were combined and set aside in a dark place at 20 °C for 15 h. Concentration in vacuo and distillation of the residue at 60 °C (bath)/0.001 Torr gave 1.90 g of rather pure **2d** as a colorless oil, which rapidly solidified. Chromatography (SiO_2, ether/hexane) and a second distillation furnished 1.76 g (93%) of analytically pure **2d**, m.p. 35 °C. IR (film) 1550 (N=N) cm^{-1}. UV ($CHCl_3$) λ_{max} (ε) 330 (220) nm. MS (70 eV) m/z (%) 148 (0.2, M^+), 105 (100). ^{1}H-NMR, see Table 1. ^{13}C-NMR, see Table 2. (Found: C, 73.15; H, 7.98; N, 18.85. Calc for $C_9H_{12}N_2$ (148.2): C, 72.94; H, 8.16; N, 18.90%.)

exo- (**2e**) and endo-3-Phenyl (**2f**) derivatives: Phenyldiazomethane[40] (3.00 g, 25.4 mmol) was dissolved in ether (75 ml) containing 1 (1.98 g, 25.4 mmol). After 5 d at 20 °C in the dark, the mixture was concentrated in vacuo and the residue distilled at 110-120 °C (bath)/0.001 Torr to give a brownish oil, which solidified on standing and consisted of **2e** and **2f** in the ratio of about 1.5 : 1.0 (73%) and some benzaldehyde azine. Chromatography (SiO_2, 12 : 1 cyclohexane/ethyl acetate) afforded a brownish solid. Distillation as above and recrystallization from n-hexane provided 2.18 g (44%) of **2e** as a colorless solid, m.p. 94-95 °C. The endo-isomer **2f** could not be recovered from chromatography. Analytical data for **2e**: IR (KBr) 1534 (N=N) cm^{-1}. UV ($CHCl_3$) λ_{max} (ε) 260 (sh 630), 267 (sh 400), 283 (240), 296 (230), 332 (300) nm. MS (70 eV) m/z (%) 196 (2, M^+), 167 (100). (Found: C, 79.64; H, 6.32; N, 14.19. Calc for $C_{13}H_{12}N_2$ (196.3): C, 79.56; H, 6.16; N, 14.28%.) NMR-spectra of **2e** and **2f**, see Tables 1 and 2.

3,3-Diphenyl derivative (**2g**): Diphenyldiazomethane[41] (1.00 g, 5.15 mmol) was stirred in ether (15 ml) containing 1 (400 mg, 5.12 mmol) at 20 °C in the dark for 8 d. Brownish crystals precipitated from the red solution. The mother liquor was concentrated in vacuo to give a solid residue. The combined products were washed with cold hexane and proved to be rather pure **2g** (1.00 g, 72%). Recrystallization from dichloromethane/n-hexane gave colorless crystals, m.p. 152 °C. IR (KBr) 1582 (C=C), 1544 (N=N) cm^{-1}. UV (ethanol) λ_{max} (ε) 220 (sh 510), 241 (2430), 260 (910), 266 (780), 273 (sh 470), 336 (310) nm. MS (70 eV) m/z (%) 245 (14), 244 (23), 165 (100). ^{1}H-NMR, see Table 1. ^{13}C-NMR, see Table 2. (Found: C, 83.81; H, 5.64; N, 10.57. Calc for $C_{15}H_{14}N_2$ (272.4): C, 83.79; H, 5.92; N, 10.29%.)

Competition of benzvalene (1) and norbornene for diazomethane and 2-diazopropane: Solutions of the diazoalkanes in ether were prepared according to refs. 37, 39 and their concentrations determined by reaction with an excess of benzoic acid and titration of the remaining benzoic acid with 0.1 N NaOH. The diazoalkane solutions were mixed with solutions of 1 and norbornene of known concentrations and set aside in a dark place at 20 °C over night. The ether was evaporated in vacuo and the residues were distilled as described for the isolation of **2a** and **2d** to give pure mixtures of **2a**, **3a** and **2d**, **3d**, respectively. The ratios of the products were determined by integration of the ^{1}H-NMR signals of **2a** at δ 4.70, of **3a** at 3.90-4.30, of **2d** at 5.12, and of **3d** at 4.62. Pyrazoline **3a** is a known compound[10b] and its 3,3-dimethyl derivative **3d** is described below. The ratios of the rate constants $k_{benzvalene}$: $k_{norbornene}$ (k_b : k_n) were calculated according to ref. 11. In Table 6 the data of the individual experiments are collected.

Table 6. Competition reactions of benzvalene (1) and norbornene with diazomethane and 2-diazopropane

experiment	mmol diazoethane	mmol benzvalene (1)	mmol norbornene	mmol **2a**	mmol **3a**	ratio k_b : k_n	combined yield (%) of adducts
1	8.40	15.2	16.0	4.06	2.66	1.71	80
2	2.84	10.1	13.1	1.06	0.95	1.46	71
3	2.92	10.1	14.0	1.34	1.32	1.45	90
4	5.68	6.9	32.4	1.20	3.34	1.75	80
5	7.05	6.9	35.3	1.37	4.27	1.72	80
	2-diazopropane			**2d**	**3d**		
6	4.20	7.7	4.9	2.55	0.91	1.95	83
7	7.16	8.0	5.1	4.25	1.49	2.21	80
8	5.97	5.4	18.2	1.96	2.81	2.66	80

(3aα,4β,7β,7aα)-3a,4,5,6,7,7a-Hexahydro-3,3-dimethyl-4,7-methano-3H-benzo[c]pyrazole (**3d**): The preparation from 2-diazopropane and norbornene was carried out according to the procedure for dimethylpyrazoline **2d**: 79% yield of **3d** as colorless

liquid, b.p. 50-70 °C (bath)/0.001 Torr. IR (film) 1547 (N=N) cm^{-1}. MS (70 eV) m/z (%) 164 (0.1, M^+), 108 (40), 93 (100), 82 (80), 67 (50), 41 (46), 39 (36). ^{1}H-NMR ($CDCl_3$) δ 0.53 (dqui, $J_{8,8}$ = 10.5, $J_{4,8_{syn}} = J_{5\alpha,8_{syn}} = J_{6\alpha,8_{syn}} = J_{7,8_{syn}}$ = 1.8 Hz, syn-8-H), 0.90 (dqui, $J_{3a,8_{anti}} = J_{4,8_{anti}} = J_{7,8_{anti}} = J_{7a,8_{anti}}$ = 1.4 Hz, anti-8-H), 0.95-1.80 (m, 6 H), 1.07 (s, α-CH_3), 1.35 (s, β-CH_3), 2.00 (m, 7-H), 2.77 (m, 3a-H), 4.62 (dt, $J_{3a,7a}$ = 6.6, $J_{7,7a}$ = 1.4 Hz, 7a-H).

Preparation of tetracyclo[4.1.0.$0^{2,4}$.$0^{3,5}$]heptanes (4)

General procedure: A 1-pyrazoline **2** (5.03-22.9 mmol) was dissolved in anhydrous benzene (50 ml). The solution was deoxygenated by a gentle stream of nitrogen for 15 min, and then irradiated (mercury vapor lamp, Hanau TQ 718) at 15 °C through Pyrex glass until the generation of nitrogen ceased (2-4 h). Thereafter, the solvent was removed at 15 Torr (**4e-g**) or at 200 Torr through a 2 m spinning band column (**4a-d**). Further work-up was effected as described in the individual procedures.

Parent compound (**4a**): Distillation through a 2 m spinning band column at 30-40 °C (bath)/100 Torr afforded a fraction containing 21% **4a** (27% yield) and 79% benzene. Compound **4a** was identified by it ^{1}H-NMR spectrum.[15]

exo- (**4b**) and endo-7-Methyl (**4c**) derivatives: A 2.7 : 1.0 mixture of **2b** and **2c** was photolyzed. Distillation of the crude product through an effective column (Fischer Spaltrohr ®, 20 cm) provided a 47% yield of **4b** and **4c** in the ratio 3.2 : 1.0 as colorless liquid, b.p. 63-65 °C/95 Torr. MS (70 eV) m/z (%) 106 (19, M^+), 91 (100). ^{1}H-NMR, see Table 3. ^{13}C-NMR, see ref. 19. (Found: C, 90.07; H, 9.56. Calc for C_8H_{10} (106.2): C, 90.51; H, 9.49%.)

7,7-Dimethyl derivative (**4d**): Distillation of the crude product through an effective column (Fischer Spaltrohr ®, 20 cm) provided a 46% yield of **4d** as colorless liquid, b.p. 75-80 °C/90 Torr. MS (70 eV) m/z (%) 120 (15, M^+), 105 (100). ^{1}H-NMR, see Table 3. ^{13}C-NMR, see ref. 19. (Found: C, 89.33; H, 10.34. Calc for C_9H_{12} (120.2): C, 89.94; H, 10.06%.)

exo- (**4e**) and endo-7-Phenyl (**4f**) derivatives: A 1.5 : 1.0 mixture of **2e** and **2f** containing some benzaldehyde azine was photolyzed. Distillation of the crude product at 40-70 °C (bath)/0.01 Torr afforded an 81% yield of **4e** and **4f** in the ratio 2.4 : 1.0 as colorless oil. IR (film) 1601 (C=C) cm^{-1}. MS (70 eV) m/z (%) 168 (83, M^+), 167 (100), 165 (47), 153 (26), 152 (37), 91 (20). ^{1}H-NMR, see Table 3. ^{13}C-NMR, see ref. 19. (Found: C, 92.24; H, 7.17. Calc for $C_{13}H_{12}$ (168.2): C, 92.81; H, 7.19%.) Pure **4e** (colorless oil) was obtained analogously from pure **2e** in 73% yield.

7,7-Diphenyl derivative(**4g**): Sublimation of crude product at 80 °C (bath)/0.001 Torr furnished a 78% yield of **4g** as slightly yellow crystals, m.p. 73-75 °C. IR (KBr): 1594 (C=C) cm^{-1}. MS (70 eV) m/z (%) 244 (53, M^+), 243 (25), 167 (47), 166 (38), 165 (100). ^{1}H-NMR, see Table 1. ^{13}C-NMR, see ref. 19. (Found: C, 93.66; H, 6.82. Calc for $C_{19}H_{16}$ (244.3): C, 93.40; H, 6.60%.)

Preparation of cycloheptatrienes (5)

7-Methyl-1,3,5-cycloheptatriene (**5b**): A mixture of **4b,c** (50 mg) dissolved in $CDCl_3$ (1 ml) was cooled to 0 °C and treated with 0.2 M anhydrous $AgClO_4$ in benzene (1 drop). A strong exothermicity was observed, and the ^{1}H-NMR spectrum showed that **5b** had been formed exclusively. The NMR spectra of **5b** have been described: ^{1}H-NMR, see ref. 42; ^{13}C-NMR, see ref. 43.

7,7-Dimethyl-1,3,5-cycloheptatriene (**5d**): The same procedure as described above for **5b** was used to prepare **5d** from **4d**. Larger quantities of **5d** required for reaction with singlet oxygen,[3] were isolated by distillation. The solvent was removed through a column at about 100 Torr and **5d** was obtained by distillation of the residue through an effective column (Fischer Spaltrohr ®, 20 cm) at about 15 Torr. ^{1}H-NMR ($CDCl_3$) δ 1.00 (s, CH_3), 5.15 (d, $J_{1,2}$ = 9.6 Hz, 1-H), 6.05 (m, 2-H), 6.43 (m, 3-H), see also refs. 2, 3. ^{13}C-NMR, see Table 4.

7-Phenyl-1,3,5-cycloheptatriene (**5e**): A mixture of **4e,f** (50 mg) dissolved in $CDCl_3$ (1 ml) was cooled to 0 °C and treated with 0.2 M anhydrous $AgClO_4$ in benzene (1 drop). A strong exothermicity was observed. After 10 min, the solution was concentrated in vacuo, and 40 mg (80%) of pure **5e** distilled from the residue at 25 °C (bath)/0.001 Torr as a colorless liquid, which crystallized, m.p. 28-30 °C (30-31.5 °C[44]). ^{1}H-NMR, see ref. 42. ^{13}C-NMR, see Table 4.

7,7-Diphenyl-1,3,5-cycloheptatriene (**5g**): A solution of **4g** (250 mg, 1.02 mmol) in benzene (3 ml) was mixed with 0.2 M anhydrous $AgClO_4$ in benzene (3 ml) and stirred at 20 °C in the dark for 20 h. After addition of dichloromethane (20 ml), the mixture was extracted three times with 15% aqueous ammonia (15 ml each) and three times with water (15 ml each). The organic phase was dried with Na_2SO_4 and

concentrated in vacuo to give 230 mg of yellow crystals. Dissolution in the minimum possible volume of ether and cooling to -30 °C gave 200 mg (80%) of **5g** as colorless crystals, m.p. 105-106 °C. M.p., NMR-spectra and MS are in accord with the data reported earlier.[4] IR (KBr) 3060, 3040, 3018, 1600, 1493, 1446, 1039, 762, 752, 745, 727, 600, 687 cm^{-1}. UV ($CHCl_3$) λ_{max} (ε) 254 (sh 6600), 262 (sh 6000), 270 (sh 5300), 282 (sh 4200), 302 (sh 2600). ^{1}H-NMR ($CDCl_3$) δ 4.65 (m, 1,6-H), 6.06 and 6.29 (each m, 2,5-H and 3,4-H), 7.0-7.3 (m, 2 C_6H_5). ^{13}C-NMR, see Table 4. (Found: C, 93.32; H, 6.64. Calc for $C_{19}H_{16}$ (244.3): C, 93.40; H, 6.60.)

Heat of reaction of the rearrangement 4a → 5a

By using the experimental set-up described previously[28], the toluene solution of **4a** was titrated to a 0.046 M solution of $AgBF_4$ in toluene. Experimental data are given in Table 7.

Table 7. Heat of reaction of the rearrangement **4a** → **5a** and heat of complexation of **5a** with $AgBF_4$

substrate	titration [10^7 mol/s]	energy [mcal/s]	$-\Delta H^a$ [kcal/mol]	
4a	1.042	4.7839	46.47[b]	
4a	1.063	4.8319	46.18[c]	
4a	1.063	4.8291	46.16[c]	
4a	0.946	4.2899	46.10[d]	
4a	0.946	4.3110	46.34[d]	46.3 ± 0.1
5a	1.080	0.2386	2.21	
5a	1.080	0.2350	2.17	2.2 ± 0.1

[a]Corrected for cycloheptatriene impurity in **4a** by: [b]1.3%; [c]1.6%; [d]1.7%.

Acknowledgements - The support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Intudstrie is gratefully acknowledged. In addition, we thank Dr. D. Wendisch, Bayer AG, Leverkusen, for recording the ^{1}H-NMR spectrum of **2a** and carrying out decoupling experiments, and the Union Rheinische Braunkohlen Kraftstoff AG, Wesseling, for gifts of dimethyl ether required for the preparation of benzvalene.

REFERENCES AND FOOTNOTES

[1]H. Kessler in Methoden der organischen Chemie (Houben-Weyl-Müller) (4th Edn.), Vol. V/1d, p. 301. Thieme, Stuttgart (1972).
[2]R. W. Hoffmann, F. Frickel, Synthesis **1975**, 444.
[3]W. Adam, F. Adamsky, F.-G. Klärner, E.-M. Peters, K. Peters, H. Rebollo, W. Rüngeler, H. G. von Schnering, Chem. Ber. **116** (1983) 1848.
[4]K. Hannemann, Angew. Chem. **100** (1988) 273; Angew. Chem. Int. Ed. Engl. **27** (1988) 284.
[5]Communication: M. Christl, E. Brunn, Angew. Chem. **93** (1981) 474; Angew. Chem. Int. Ed. Engl. **20** (1981) 468.
[6]M. Christl, Angew. Chem. **85** (1973) 666; Angew. Chem. Int. Ed. Engl. **12** (1973) 660.
[7]M. Christl, H. Leininger, P. Kemmer, Chem. Ber. **117** (1984) 2963.
[8]Cf. footnote 2 of ref. 5.
[9]M. Christl, E. Brunn, A. Kraft, H. Irngartinger, U. Huber-Patz, H. Rodewald, to be submitted for publication.
[10]R. Huisgen in 1,3-Dipolar Cycloaddition Chemistry (A. Padwa, Ed.), Vol. 1, p. 1, Wiley, New York (1984). [b]J. Geittner, Dissertation, Universität München (1973).
[11]R. Huisgen in Methoden der organischen Chemie (Houben-Weyl-Müller) (4th Edn.), Vol. III/1, p. 99, Thieme, Stuttgart (1955).
[12]M. Christl, B. Mattauch, H. Irngartinger, A. Goldmann, Chem. Ber. **119** (1986) 950.
[13]Cf. footnotes 18 and 19 of ref. 12.
[14]R. Huisgen, P. H. J. Ooms, M. Mingin, N. L. Allinger, J. Am. Chem. Soc. **102** (1980) 3951.
[15]M. Christl, G. Freitag, G. Brüntrup, Chem. Ber. **111** (1978) 2307.
[16]M. Christl, Angew. Chem. **93** (1981) 515; Angew. Chem. Int. Ed. Engl. **20** (1981) 529.
[17]D. Wendisch in Methoden der organischen Chemie (Houben-Weyl-Müller) (4th Edn.), Vol. IV/3, Thieme, Stuttgart (1971).
[18]K. Mackenzie in The Chemistry of the Hydrazo, Azo, and Azoxy Groups (S. Patai, Ed.), Part 1, p. 329, Wiley, London (1975).
[19]M. Christl, H. Leininger, E. Brunn, J. Org. Chem. **47** (1982) 661.
[20]M. Christl, U. Heinemann, W. Kristof, J. Am. Chem. Soc. **97** (1975) 2299.
[21]E. Brunn, Dissertation, Universität Würzburg (1983).
[22]S. Hoz in The Chemistry of the Cyclopropyl Group (S. Patai, Z. Rappoport, Eds.), Part 2, p. 1121, Wiley, Chichester (1987).
[23]L. A. Paquette, Synthesis **1975**, 347 and refs. cited therein.
[24]M. Christl, G. Brüntrup, Chem. Ber. **107** (1974) 3908.