7-METHYL- AND 7-PHENYL CYCLOHEPTA-1,3,5-TRIENES FROM BENZVALENE VIA 3,3a,4,5,6,6a-
HEXAHYDRO-4,5,6-METHYNYL CYCLOPENTAPTRAIOLES AND TETRACTYL[4.1.0.02;4.03;7]HEPTANES

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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 benz-
valene reacts about twice as fast as norbornene with both diazokanes
cannot be rationalized on the basis of frontier orbital energies. On
direct photolysis, the pyrazolines 2a-g were converted into the tetracy-
clol[4.1.0.02;4.03;7]heptanes 4a-g exclusively. These compounds gave the
1,3,5-cycloheptatrienes 5a,b,d,e,g in high yields on treatment with sil-
ver ions, thus providing better access to 7,7-dimethyl(5d) and 7,7-
diphenylcycloheptatriene (5g) than before. Surprisingly, the latter com-
pound 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-
[4.1.0.02;4.03;7]heptane (4a).

The most generally applicable methods for the synthesis of 1,3,5-cyclohepta-
triene derivatives are reactions of the tropylium cation with nucleophiles and the
addition of carbenes to benzene. 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-di-
methylcycloheptatriene (5d) cannot be obtained via this route, since it has exclu-
sively been prepared by using other approaches. Formed in low yield on ther-
molysis or photolysis of diphenyldiazomethane in benzene, 7,7-diphenylcyclohepta-
triene (5g) appears in the literature for the first time in 1988. 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

As early as 1973, we described the addition of diazomethane to benzvalene. The
yield of 1-pyrazolines 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 : 2e = 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 stereocchemical assignment within the isomeric pairs 2b,c and
2e,f is based on the magnitude of the coupling constants in the 1H-NMR
spectra (see Table 1) and on the y-gauche effect of the endo-3-substituent (R') 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[13.1.0.0\(^{1,4}\)]hexane derivatives. Similarly, the absorptions of C-4 and C-6 differ markedly in their fine structure with that of C-4 being much better resolved.

Table 1. \(^{1}H\)-NMR chemical shifts (\(\delta\) values) and coupling constants (absolute values, Hz) of cis-3,4a,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 \(20.5\) Hz: \(2a\) = 18.0, \(2a\) = 8.5, \(2a\) = 7.0, \(2a\) = 9.0, \(2a\) = 7.0.

### Table 1

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<th>(7-H)</th>
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<td>ddd</td>
<td>dddd</td>
<td>dq</td>
<td>dq</td>
<td>dq</td>
<td>dq</td>
<td>dq</td>
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<tr>
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<td>1.70-2.40</td>
<td>2.78</td>
<td>5.12</td>
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<tr>
<td>2e</td>
<td>-</td>
<td>1.70-2.30</td>
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<tr>
<td>2g*</td>
<td>-</td>
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<td>2.85</td>
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<td></td>
<td></td>
<td>2.93, 1.38</td>
<td>2.00</td>
<td>1.70</td>
<td>2.87</td>
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</table>

\(2a\) = 4.06, 4.15, 2.23, 2.05, 2.12, 1.83, 2.79, 5.15; \(2b\) = 4.23, 1.70-2.40, 2.78, 5.20; \(2c\) = 4.06, 4.15, 1.70-2.40, 2.78, 5.12; \(2d\) = 1.70-2.30, 2.73, 5.12; \(2e\) = 2.00-2.30, 1.93, 2.85, 5.33; \(2f\) = 2.46, 1.30, 1.93, 2.85; \(2g\) = 2.93, 1.38, 2.00, 1.70, 2.87.

Table 2. \(^{13}\)C-NMR chemical shifts (\(\delta\) values) and \(^{13}\)C-H coupling constants (Hz) of cis-3,4a,5,6,6a-hexahydro-4,5,6-methenocyclopentapyrazoles (2). The \(\delta_{2a}\) 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: \(2a\) = 13, \(2a\) = 3, \(2a\) = 8. The specific assignments are based on \(\delta_{2a}\), substituent effects, and fine-structure patterns in the proton-coupled spectra.

### Table 2

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<tr>
<th>Compd</th>
<th>(C-3)</th>
<th>(C-3a)</th>
<th>(C-4)</th>
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<th>(C-6)</th>
<th>(C-6a)</th>
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<td>98.7</td>
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<tr>
<td>2b**</td>
<td>83.0</td>
<td>44.4</td>
<td>36.7</td>
<td>6.6</td>
<td>37.9</td>
<td>97.0</td>
<td>-0.4</td>
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<tr>
<td>2c***</td>
<td>80.2</td>
<td>39.0</td>
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<td>5.8</td>
<td>37.9</td>
<td>97.8</td>
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<td>46.8</td>
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<td>6.7</td>
<td>38.0</td>
<td>97.3</td>
<td>1.1</td>
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<td>38.2</td>
<td>8.0</td>
<td>39.0</td>
<td>100.0</td>
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<tr>
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<td>89.0</td>
<td>41.5</td>
<td>35.0</td>
<td>6.3</td>
<td>38.8</td>
<td>98.9</td>
<td>2.1</td>
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<tr>
<td>2g*******</td>
<td>97.8</td>
<td>46.4</td>
<td>36.0</td>
<td>6.3</td>
<td>38.2</td>
<td>99.3</td>
<td>2.1</td>
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*Solvent \(\text{DCl}_2\). **141 (\(\text{endo-CH}_3\)). 139 (\(\text{exo-CH}_3\)). **Solvent \(\text{CDCl}_3\). 18.1 (\(\text{CH}_3\)). 112.9 (\(\text{CH}_2\)). 20.9 (\(\text{exo-CH}_2\)). 27.6 (\(\text{exo-CH}_3\)). 137.5-128.9 (g-C, m-C, g-O). 140.0 (\(\text{iPr}_{2}C\) (C-H)). 138.1-128.8 (g-C, m-C, g-O). 138.6 (\(\text{iPr}_{2}C\) (C-H)). 126.4-128.4 (g-C, m-C, g-O). 142.6. 142.9 (\(\text{ipso-C}\) (2 C-H)).
Ethyl diazoacetate did not react with benzvalene (1). However, methyl 2-diazopropionate and 1 afford both the stereoisomeric 1-pyrazolines. The results of the reactions of 1 with tetrachlorodiazocyclopentadiene, diazofluorene, and 5-diazotoluene will be described elsewhere.

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. Therefore, it was of interest to determine the rate of the reaction between diazomethane and benzvalene (1) and to integrate it into the scale of dipolarophiles. 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 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.

\[
\frac{k_{\text{benzvalene}}}{k_{\text{norbornene}}} = 1.6 \pm 0.2; \quad \frac{k_{\text{diazomethane}}}{k_{\text{2-diazopropane}}} = 2.3 \pm 0.4
\]

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. 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, as controlled by the LUMO of the 1,3-dipole. On the contrary, the control by the HOMO of diazomethane rationalizes the relative rates of the cycloadditions of this 1,3-dipole best. This should be valid to an even greater extent for 2-diazopropane. Since 1 has a lower ionization potential (corresponding to the n-orbital) and, most probably, a less accessible n-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.

Preparation of tetracyclo(4.1.0.0².⁴,0³.⁷)heptanes 4 from the 1-pyrazolines 2

Heretofore, the exclusive route for the synthesis of the tetracyclo(4.1.0.0².⁴,0³.⁷)heptane system was the addition of halocarbenes to benzvalene. Another access to cyclopropane derivatives is provided by the nitrogen extrusion from 1-pyrazolines. 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, 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 ratio 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 'H-NMR, see Table 3; for 13C-NMR, see ref. 19) are characterized by large differences between the chemical shifts of the structurally related 3- and 4-CH groups ('H-NMR, 0.53-1.52 ppm; 13C-NMR, 18.5-26.1 ppm). These differences originate from the orientation of the respective CH group relative to the anellated cyclopropane ring. The 'H-NMR spectrum of 4a-19 and the 13C-NMR spectra of 4a-g19 have been discussed in detail. Within the isomeric pairs 4b,c and 4e,f, the stereochemical assignments are based on the 13C chemical shifts19 as well as on 'H-1H coupling constants, in particular on $\delta_1$, $\delta_{11}$, $\delta_{11}$, $\delta_{21}$ = 2.6 and $\delta_{11}$, $\delta_{11}$, $\delta_{21}$ = 6.7 Hz. Because of the endo phenyl group in 4f,g, 4-H experiences the anisotropy effect resulting in a remarkable upfield shift (\delta 0.93 and 1.06, respectively) of the signal relative to that of 4e ($\delta$ 1.55).

<table>
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<tr>
<th>compd</th>
<th>1.6-H</th>
<th>2.5-H</th>
<th>3-H</th>
<th>4-H</th>
<th>$\delta$(endo)</th>
<th>$\delta$(exo)</th>
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<tr>
<td>4a</td>
<td>1.07</td>
<td>2.15</td>
<td>2.29</td>
<td>1.51</td>
<td>0.57</td>
<td>0.50</td>
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<tr>
<td>4b°</td>
<td>0.86</td>
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<td>2.25</td>
<td>1.56</td>
<td>0.71</td>
<td>0.86</td>
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<tr>
<td>4c°</td>
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<td>1.92</td>
<td>2.41</td>
<td>1.88</td>
<td>1.26</td>
<td>0.78</td>
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<tr>
<td>4e°</td>
<td>1.34</td>
<td>2.16</td>
<td>2.26</td>
<td>1.55</td>
<td>1.93</td>
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<tr>
<td>4f°</td>
<td>1.52</td>
<td>1.85</td>
<td>2.40</td>
<td>0.93</td>
<td>6.8-7.4</td>
<td>2.17</td>
</tr>
<tr>
<td>4g°</td>
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<td>2.06</td>
<td>2.58</td>
<td>1.06</td>
<td>6.9-7.5</td>
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</table>

* $\delta_{1,4}$ = 6.2, $\delta_{1,4}$ = 5.8.

As reported for the parent hydrocarbon 4a20, 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,19 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[4.1.0.02',6']heptanes 4 into cycloheptatrienes 5

Many polycyclic hydrocarbons are subject to isomerization on treatment with catalytic quantities of silver ions.22 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(3.1.0.02',6')hexane20 and of cycloheptatriene 5a from tetracycloheptane 4a with the latter process being highly exothermic.19 This reaction has been utilized to prepare 3,4-dideuteriocycloheptatriene free of isotopomers.19 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.  

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. However, 7,7-dimethyl- (5d) and 7,7-diphenylcycloheptatriene (5g) are 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 dioxalkanes have to be provided requiring two or three steps, but very simple ones. Hoffmann and Frickel 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. The direct pathway from benzene and diphenyl-diazomethane to 5g affords a yield of only 8% after elaborate chromatographic separation. 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 13C-NMR chemical shifts of 5d,e,g). Here we noticed that 1,6-H of the diphenyl derivative 5g resonate substantially more upfield (§ 4.65) than 1,6-H of the monophenyl compound 5e (§ 5.42). Additionally, the signal of C-1,6 of 5g appears at much higher field (§ 95.6) than the corresponding line of 5e (§ 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 has estimated the ratio 5gC : 5gN to be about 65 : 35 at ambient temperature. We recorded the 13C-NMR spectrum of 5g at lower temperatures too and observed that the signal of C-1,6 moved from § 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. 13C-NMR chemical shifts (§ values) of some cycloheptatrienes 5

<table>
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<tr>
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<td>130.9</td>
<td>45.3</td>
<td>143.9 127.6 128.7 126.6</td>
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<tr>
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<td>CDCl3</td>
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<td>125.5*</td>
<td>127.5*</td>
<td>43.5</td>
<td>145.6 127.6 128.9 125.9</td>
</tr>
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<td>127.9*</td>
<td>*</td>
<td>146.6 128.7 130.0 127.0</td>
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<td>127.5*</td>
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<td>146.2 128.6 129.9 126.9</td>
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<tr>
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</table>

*The assignment of C-2,5, C-3,4, and p-C is only tentative. *Not observed due to low intensity because of broadening.
To calculate the exact ratio $6\text{C} : 6\text{N}$, the individual chemical shifts are necessary, however. Accordingly, we have estimated these with the aid of the corresponding values for the spiro compounds $6\text{C}$ and $6\text{N}$, the individual chemical shifts of which have been determined by Dürr and Kober. The compounds $6\text{C}$ as well as $6\text{N}$ 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 $6\text{C}$ and $6\text{N}$ exert equal effects on the $^{13}$C-NMR chemical shifts or the ring carbon atoms. By transfer of the C-1, 6 values of $6\text{C}$ ($\delta 128.3$) and $6\text{N}$ ($\delta 36.8$) to $5\text{C}$ and $5\text{N}$, respectively, we have calculated the ratio $5\text{C} : 5\text{N}$ 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 $5\text{C} \rightarrow 5\text{N}$: $\Delta H = -530 \text{ cal/mol}$, $\Delta S = -3 \text{ eu}$. Because of the above-mentioned assumption, these values are only rough estimates. The greater temperature dependence of the ratio $6\text{C} : 6\text{N}$ (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 $6\text{C} \rightarrow 6\text{N}$. In spite of that, the ratios $5\text{C} : 5\text{N}$ and $6\text{C} : 6\text{N}$ appear astoundingly similar in view of the different orientation of the phenyl groups in these systems. Being arranged in a bisected manner, the $\pi$ orbitals of the fluorene moiety in $6\text{N}$ interact optimally with the cyclopropane Walsh orbitals thus exerting the maximum acceptor ability of the aromatic unit. Good $\pi$ acceptors in the 7-position are one of the requisites for a high norcaradiene share in a cycloheptatriene/norcaradiene equilibrium. However, in $5\text{N}$ 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 $\pi$ orbitals and the cyclopropane Walsh orbitals cannot be operative. Nevertheless, the proportion of $5\text{N}$ in the $5\text{C}/5\text{N}$ mixture is rather high. The fact that the introduction of a methyl group in one ortho-position of one phenyl group of $5\text{g}$ causes the equilibrium to shift virtually completely to the side of the norcaradiene indicates the relative unimportance of electronic effects and the dominance of steric effects in these systems.

Heat of formation of tetracyclo[4.1.0.0\(^2\).0\(^3\).0\(^4\)]heptane ($4\text{a}$)

The strong exothermicity and the high yield of the silver ion catalyzed rearrangement $4\text{a} \rightarrow 5\text{a}$ offered the possibility to determine the enthalpy of reaction, from which the heat of formation of $4\text{a}$ 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. $\Delta H$ forms a complex with AgBF$_4$ used to effect the rearrangement of $4\text{a}$. To calculate $\Delta H$ of $4\text{a} \rightarrow 5\text{a}$ the corresponding heat of complexation has to be accounted for. It was determined in analogy to $\Delta H$ of $4\text{a} \rightarrow 5\text{a}$ by titration of a toluene solution of $5\text{a}$ 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. The heat of solution difference in isooctane can be estimated by a
Benzvalene additions

"double-bond increment" of 0.1 kcal/mol per double bond. 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. The values of $\Delta H^\circ = 0.06$ and 0.58 kcal/mol indicate that within the accuracy of the method (20.1 kcal/mol) 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 the heat of formation of 4a is obtained by:

$$
\Delta H^\circ = 46.3 \text{ kcal/mol}
$$

$$
\text{corr. for complex formation of 5a} = -2.2 \text{ kcal/mol}
$$

$$
\text{corr. } \Delta H^\circ = -0.3 \text{ kcal/mol}
$$

$$
\Delta H^\circ = 44.6 \text{ kcal/mol}
$$

Derived from this value and $\Delta H^\circ$ of strain free 4a, which is obtained by using group increments, the strain energy of 4a can be calculated. In Table 5, this value ($\Delta H^\circ$) is compared to the strain energy of bicyclo[1.1.0]butane, benzvalene (1), and tricyclo[4.1.0.0^2]heptane.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$\Delta H^\circ$</th>
<th>$\Delta H^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>51.9^22</td>
<td>87.3^22</td>
</tr>
<tr>
<td>4a</td>
<td>65.5</td>
<td>77.7</td>
</tr>
<tr>
<td>4a</td>
<td>104.7</td>
<td>67.0</td>
</tr>
</tbody>
</table>

EXPERIMENTAL

General and instrumentation. See ref. 35.

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

Parent compound (2a): A mixture of 40% aqueous KOH (25 ml) and ether (20 ml) containing benzvalene (1) (1.7 g) (780 mg, 10.0 mmol) was cooled to -5 °C, treated with 1-methyl-1-nitrosourea (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) $\lambda_{max}$ (4) 330 (280) nm. 1H-NMR, see Table 1. 13C-NMR, see Table 2. (Found: C, 69.75; H, 6.72; N, 23.47. Calc for C83H82N2 (202.2): C, 69.97; H, 6.71; N, 23.32.)

exo- (2b) and endo-3-Methyl (2c) derivatives: The reaction of 1 and diazomethane (from 1-ethyl-1-nitrosourea) 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 (SiO2, 3:2 ether/hexane). IR (film) 1548 (N-N) cm^-1. UV (CHCl3) $\lambda_{max}$ (4) 330 (290) nm. MS (70 eV): m/z (5%) 134 (1, M^+), 91 (100), 1H-NMR, see Table 1. 13C-NMR, see Table 2. (Found: C, 71.68; H, 7.45; N, 20.66. Calc for C93H92N2 (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 hydrazones. 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. A solution of triethyl phosphite (64.0 ml, 0.30 M) in 200 ml of chloroform was added. After 3 h, ethereal extracts were washed with water, dried (MgSO4), and evaporated in vacuo to afford an oil which was distilled at 60-61 °C (bath)/0.05 Torr to yield $\sim$95% pure 2b.

For general and instrumentation, see ref. 35.
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 hydrasone (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 oily liquid, which rapidly solidified.

Chromatography (SiO2, ether/n-hexane) and second distillation furnished 1.932 g of analytically pure 2d, m.p. 35 °C. IR (film) 1550 (N=N) cm⁻¹. UV (CHCl3) λmax (ε) 330 (220) nm. MS (70 eV) m/z (%) 148 (10.2, M⁺), 105 (100). "H-NMR, see Table 1. 13C-NMR, see Table 2. (Found: C, 73.15; H, 7.98; N, 18.85. Calc for C12H14N2 (148.2): C, 72.94; H, 8.16; N, 18.90%)

exo- (2e) and endo-3-Phenyl (2f) derivatives: Phenyldiazomethane 6 (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 2a and 2f in the ratio of about 1.5:1.0 (73%) and some benzaldehyde azine. Chromatography (SiO2, 12:1 cyclohexane/ethyl acetate) afforded a brownish solid. Distillation as above and recrystallization from n-hexane provided 2.18 g (44%) of 2a as a colorless solid, m.p. 94-95 °C. The endo-isomer 2f could not be recovered from chromatography. Analytical data for 2a: IR (KBr) 1534 (N=N) cm⁻¹. UV (CHCl3) λmax (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 C11H9N2 (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 6 (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, 725 mg). Crystals from dichloromethane/n-hexane gave colorless crystals, m.p. 152 °C. IR (KBr) 1582 (C=N), 1544 (N=N) cm⁻¹. UV (ethanol) λmax (ε) 220 (sh 510), 241 (2430), 260 (910), 264 (2700), 336 (2400) nm. MS (70 eV) m/z (%) 214 (14), 148 (14), 179 (24), 155 (100). "H-NMR, see Table 1. 13C-NMR, see Table 2. (Found: C, 83.81; H, 5.64; N, 10.57. Calc for C13H14N2 (272.4): C, 83.79; H, 5.92; N, 10.29%)

Compartment of benzvalene (1) and norbornene for diisomethane and 2-diazopropene: Solutions of the daisokanes 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 daisokane 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 residue was distilled as described above to give pure mixtures of 2a,3a and 2d,3d, respectively. The ratios of the products were determined by integration of the "H-NMR signals of 2a at 5.4.70, of 3a at 3.00-3.05, of 2d at 4.60, and of 3d at 4.62. Pyrazoline 3a and 3d, as well as its 3,3-dimethyl derivative 3d is described below. The ratios of the rate constants k1/k2: k3/k4: k5: k6 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 diisomethane and 2-diazopropene

<table>
<thead>
<tr>
<th>experiment</th>
<th>mmol</th>
<th>mmol</th>
<th>mmol</th>
<th>mmol</th>
<th>mmol</th>
<th>ratio</th>
<th>combined yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>diazomethane</td>
<td>benzvalene</td>
<td>norbornene</td>
<td>2a</td>
<td>3a</td>
<td>k₃/k₂</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>8.40</td>
<td>15.2</td>
<td>16.0</td>
<td>4.06</td>
<td>2.66</td>
<td>1.71</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
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<td>10.1</td>
<td>13.1</td>
<td>1.06</td>
<td>0.95</td>
<td>1.40</td>
<td>71</td>
</tr>
<tr>
<td>3</td>
<td>2.92</td>
<td>10.1</td>
<td>14.0</td>
<td>1.34</td>
<td>1.32</td>
<td>1.45</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>5.68</td>
<td>6.9</td>
<td>32.4</td>
<td>1.20</td>
<td>3.34</td>
<td>1.75</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>7.05</td>
<td>6.9</td>
<td>35.3</td>
<td>1.37</td>
<td>4.27</td>
<td>1.72</td>
<td>80</td>
</tr>
<tr>
<td>6</td>
<td>4.20</td>
<td>7.7</td>
<td>4.9</td>
<td>2.55</td>
<td>0.91</td>
<td>1.95</td>
<td>83</td>
</tr>
<tr>
<td>7</td>
<td>7.10</td>
<td>8.49</td>
<td>5.0</td>
<td>4.25</td>
<td>1.49</td>
<td>2.21</td>
<td>80</td>
</tr>
<tr>
<td>8</td>
<td>5.97</td>
<td>5.4</td>
<td>18.2</td>
<td>1.96</td>
<td>2.81</td>
<td>2.66</td>
<td>80</td>
</tr>
</tbody>
</table>

(3ag,4b,7a-Tac=3a,4,5,6,7a-Hexahydro-3,3-dimethyl-4,7-methano-3H-benzo[cd]pyrazole (3d): The preparation from 2-diazopropene 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=H) cm⁻¹. MS (70 eV) m/z (S) 164 (0.1), 159 (1), 82 (100), 67 (150), 61 (46), 39 (36). ¹H-NMR (CDCl₃) δ 0.53 (dq, J₆,₇ = 10.5, J₇,₈ = 3.5 Hz), δ₆ = 2.77 (d, J₆,₇ = 10.5 Hz), δ₈ = 1.8 Hz, ν₂ = 8-H), δ₉ = 0.90 (dq, J₆,₇ = 5.5 Hz). See ref. 42; for 5b liquid, b.p. 95-160 °C (6 H). ¹H-NMR, see ref. 43.

Preparation of tetracyclo[4.1.0.0⁷,⁹]heptanes (4)

General procedure: A 1-pyrazoline (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, Hansa 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 its ¹H-NMR spectrum.¹⁹

exo-(4b) and endo-7-Methyl (4o) 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 4o in the ratio 3.2:1.0 as a colorless liquid. b.p. 63-65 °C/95 Torr. MS (70 eV) m/z (S) 106 (19, M⁺), 91 (100). ¹H-NMR, see Table 3. ¹³C-NMR, see ref. 19. (Found: C, 90.07; H, 9.56. Calc for C₇H₁₈: 92.79, 8.21.)

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 a colorless liquid. b.p. 78-80 °C/90 Torr. MS (70 eV) m/z (S) 120 (15, M⁺), 105 (100). ¹H-NMR, see Table 3. ¹³C-NMR, see ref. 19. (Found: C, 92.24; H, 7.76. Calc for C₇H₁₈: 92.81, 7.19.)

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 4f and 4f in the ratio 2.4:1.0 as a colorless oil. IR (film) 1601 (C=O) cm⁻¹. MS (70 eV) m/z (S) 168 (83, M⁺), 165 (100), 165 (47), 153 (26), 152 (37), 91 (20). ¹H-NMR, see Table 3. ¹³C-NMR, see ref. 19. (Found: C, 92.24; H, 7.76. Calc for C₁₅H₁₈: 92.81, 7.19.)

Preparation of cycloheptatrienes (5)

7-Methyl-1,3,5-cycloheptatriene (5b): A mixture of 4b,c (50 mg) dissolved in CDCl₃ (1 ml) was cooled to 0 °C and treated with 0.2 M anhydrous AgClO₄ in benzene (1 drop). A strong exothermicity was observed, and the ¹H-NMR spectrum showed that 5b had been formed exclusively. The NMR spectra of 5b have been described: ¹H-NMR, see ref. 42; ¹³C-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 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. ¹H-NMR (CDCl₃) δ 1.00 (s, CH₃), 5.15 (d, J₃,₅ = 2.6 Hz). ¹³C-NMR, see Table 4. ²H-NMR, see ref. 42. ¹³C-NMR, see Table 4.

7-Phenyl-1,3,5-cycloheptatriene (5a): A mixture of 4e,f (50 mg) dissolved in CDCl₃ (1 ml) was cooled to 0 °C and treated with 0.2 M anhydrous AgClO₄ in benzene (1 drop). A strong exothermicity was observed. After 10 min, the solution was concentrated in vacuo, and 40 mg (80%) of pure 5a 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). ¹H-NMR, see ref. 42. ¹³C-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 AgClO₄ 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 Na₂SO₄ and
concentrated in vacuo to give 230 mg of yellow crystals. Dissolution in the minimum possible volume of ether and cooling to 0-30 °C gave 200 mg (80%) of 5a as colorless crystals, m.p. 105-106 °C. NMR-spectra and MS are in accord with the data reported earlier. *IR (KBr) 3060, 3040, 3018, 1600, 1493, 1446, 1035, 762, 752, 745, 727, 600, cm 3H), UV (CHCl3) λmax (sh) 294 (sh 6600), 262 (sh 6400), 270 (sh 5300), 282 (sh 4200), 302 (sh 2600). δH (CDCl3) 6 4.65 (m, 1,6-H), 6.06 and 6.29 (each m, 2.5-9 and 3.4-H), 7.0-7.3 (m, 2 CH3). *H-NMR, see Table 4. (Found: C, 93.52; H, 6.64. Calcd for C19H19, (244.3): C, 93.40; H, 6.60.)

Heat of reaction of the rearrangement 4a → 5a

By using the experimental set-up described previously, the toluene solution of 4a was titrated to a 0.046 M solution of AgBF4 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 AgBF4

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Titration (10 mol/s)</th>
<th>Energy (J/mol)</th>
<th>-AH° (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>1.042</td>
<td>4.7839</td>
<td>46.47°</td>
</tr>
<tr>
<td>4a</td>
<td>1.063</td>
<td>4.8319</td>
<td>46.18°</td>
</tr>
<tr>
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<td>4.8291</td>
<td>46.16°</td>
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<td>0.946</td>
<td>4.2899</td>
<td>46.10°</td>
</tr>
<tr>
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<td>4.3110</td>
<td>46.34° ± 0.1</td>
</tr>
<tr>
<td>5a</td>
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<td>2.21</td>
</tr>
<tr>
<td>5a</td>
<td>1.080</td>
<td>0.2350</td>
<td>2.22 ± 0.1</td>
</tr>
</tbody>
</table>

*Corrected for cycloheptatriene impurity in 4a by: 1.3%, 1.6%, 1.7%.

Acknowledgements - The support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. In addition, we thank Dr. D. Wendisch, Bayer AG, Leverkusen, for recording the 1H-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

8. Cf. footnotes 2 of ref. 5.
14. Cf. footnotes 18 and 19 of ref. 12.