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SYNTHESES, PROPERTIES AND SOME REACTIONS OF 8-PHENYL- AND 8,8-DIPHENYL-HEPTAFULVENES

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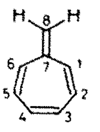
Abstract—8-Phenyl- (**2**) and 8,8-diphenyl-heptafulvenes (**3**) have been synthesized and fully characterized. The 220 MHz NMR data on **2** and **3**, as well as the ^{13}C NMR data on **3**, indicates only a small contribution of the dipolar structure for this system. The electrophilic and nucleophilic reagents react at different sites of this system: while protonation of **2** and **3** occurs at the exocyclic methylene carbon, butylation occurs at the 7-membered ring, i.e. the 1- and 3-positions of **2** and only at the 3-position of **3**, when treated with n-BuLi. Cycloaddition with tetracyanoethylene gives the [8 + 2]-cycloadduct for **2** and the [4 + 2]-adduct for **3**.

Chemistry of the heptafulvenes has attracted much interest from both theoretical and synthetic chemists since the first synthesis of the parent hydrocarbon (**1**) reported by Doering and Wiley.[1] However, only recently the compound **1** was fully characterized by means of various spectroscopic methods,[2] mainly because of the instability of **1** and the intricacy in the synthetic process originally reported. On the other hand, various types of heptafulvenes having electron-withdrawing substituents at the exocyclic methylene carbon have been synthesized and shown to be relatively stable as a result of the polarization inducing the 6-π-electron system in the 7-membered ring.[3] In contrast with this, thermolabile heptafulvenes with a reverse polarization were reported very recently.[4] Complexation with transition metals has also been found to be effective in stabilizing the heptafulvene system.[5]

In order to obtain more information on the intrinsic physical and chemical properties in the heptafulvene system, it seems desirable to prepare the heptafulvene having the substituent which would stabilize the parent system but bring about only little electronic perturbation to it. For such a purpose, 8-vinylheptafulvene has been synthesized and characterized as the species rather polyolefinic than aromatic.[6] However, information on the heptafulvenes having a simpler and more essential hydrocarbon-substituent, i.e. the phenyl group, appears to be still lacking in the literature: 8,8-diphenylheptafulvene has been known,[7] but its chemical reactivity has not been examined. In this paper we wish to report the syntheses, properties, and some chemical reactions of 8-phenylheptafulvene (**2**) and 8,8-diphenylheptafulvene (**3**) in comparison with those of the hitherto known heptafulvenes.



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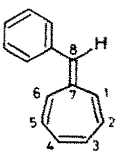

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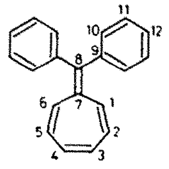

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*Syntheses and properties of 8-phenyl- (**2**) and 8,8-diphenylheptafulvenes (**3**)*

Reactions of the tropylium ion with benzylmagnesium chloride and with benzhydryllithium gave 7-benzyl- and 7-benzhydryl-1,3,5-cycloheptatrienes, respectively, which were then transformed into the corresponding substituted tropylium ions by hydride abstraction with the triphenylmethyl cation.

Treatment of the benzyltropylium ion with the equivalent amount of triethylamine in dichloromethane resulted in an immediate red coloration, indicating the formation of the heptafulvene structure. The solvent was then replaced by carbon tetrachloride, and after purification by passing through a short alumina column, the red solution was shown to contain substantially pure **2** by analysis with the ^{1}H NMR spectroscopy (*vide infra*). Although an attempt to isolate **2** by solvent evaporation resulted in the formation of a polymeric resinous material, **2** is unchanged for several days at room temperature when kept in solution (*ca.* 5% in CCl_4) under nitrogen. This suggests that the stability of **2** is comparable to that of 8-vinylheptafulvene[6] and greater than that of the parent compound **1**.

On the other hand, as has been reported by Dauben and Metz,[7] the reaction of the benzhydryltropylium ion with triethylamine afforded **3** in a 75% yield as a dark red solid, which slowly decomposed by contact with air. The compound **3** was obtained also by the reaction of 7-benzhydryl-1,3,5-cycloheptatriene with chloranil in carbon tetrachloride in a lower yield (17.1%).

Though the 60 MHz NMR spectra of the heptafulvenes **2** and **3** only gave partially resolved multiplets for the 7-membered ring protons, their signals clearly separated into individual peaks by the use of 220 MHz NMR spectroscopy as shown in Fig. 1. The spectrum of **3** consisted of four signals centered at τ 2.91, 3.90, 4.33 and 4.58 ppm in the ratio of 10:2:2:2. The signals were unambiguously assigned based on the coupling pattern as shown in Fig. 1. Then the assignment of the signals for **2** was made by referring to the assignment for **3** and also from the coupling pattern. Between the two doublets at τ 3.77 and 4.18, the one resonating at the higher field may be assigned to the proton attached to the C-6 carbon *cis* to the phenyl substituent, taking the diamagnetic anisotropy effect of the twisted phenyl group into account.

As models for the 7-membered ring compounds with full π-electron delocalization, Bertelli *et al.* chose 8,8-dicyanoheptafulvene, tropone, and heptafulvalene, and reported their 60 MHz NMR spectra.[6] While the ring protons in these compounds all appear as broad singlets with less than 0.2 ppm half-height width, those for the heptafulvenes **2** and **3** are located in the ranges of 0.9 and

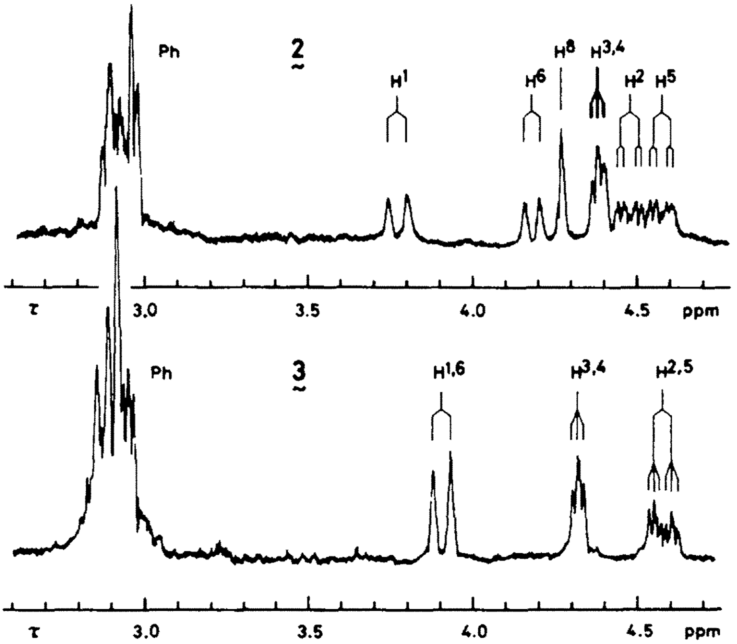


Fig. 1. 220 MHz ^{1}H NMR spectra of the heptafulvenes **2** and **3** in CCl_4 with Me_4Si as an internal standard.

0.75 ppm, respectively, when recorded at 220 MHz. This illustrates that there is much less π-electron delocalization in the 7-membered ring of **2** and **3** compared with the highly conjugated compounds cited above. On the other hand, the values of averaged chemical shifts for the ring protons in **2** and **3** are τ 4.30 and τ 4.27 ppm, respectively. These values are comparable to the corresponding averaged chemical shifts in the parent compound **1** (τ 4.35 ppm[2c]) and in 8-vinylheptafulvene (τ *ca.* 4.4[6]), and are much higher than the proton chemical shifts for the dipolar compounds, such as 8,8-dicyanoheptafulvene (τ 2.9[6]) and tropone (τ 3.0[6]). This result is indicative that there is not much, if any, contribution from the dipolar resonance structure to the ground state of 8-phenylheptafulvenes.

In order to obtain more precise information on the possible charge distribution in the present heptafulvene system, the ^{13}C NMR spectrum of the compound **3** was examined next. The results are shown in Table 1 together with the carbon chemical shifts for 7-benzhydryl-1,3,5-cycloheptatriene and those reported for the parent hydrocarbon **1**.[2b] Assignment of the signals was made based on comparison with the spectra of these reference compounds. The chemical shift values for the 7-membered ring carbons in **3** are similar to those in **1** except for C-7, in accord with the results of ^{1}H NMR described above. The chemical shifts for C-7 and C-8 in **1** differ for 34.7 ppm, indicating some charge separation with respect to the exocyclic double bond. On the contrary, the difference in chemical shifts for the corresponding carbons in **3** is quite small (0.9 ppm), which demonstrates a charge averaging effect of the phenyl substituents. Thus, it is concluded that **3** has even less dipolar character than the parent hydrocarbon **1**.

The IR spectral data are shown in Table 2. Both **2** and **3** exhibit rather strong and broad absorptions at 1580 and 1570 cm^{-1}, respectively. This is ascribed to the stretching vibration of the exocyclic double bond, and the wavenumbers are close to the one (1583 cm^{-1}) reported for **1**.[2c]

In contrast to the electronic spectrum of the parent compound **1**, which shows a fine structure with maximum absorptions in the visible region at 400, 423, 498, 546 and 596 nm,[1,2c] both **2** and **3** exhibit only two main absorptions throughout the UV and visible regions as shown in Table 2. In the visible region are only end absorptions, and no fine structure was observed. These results seem to be indicative of even less π-electron delocalization in **2** and **3** than in **1**. Furthermore, only little shift of the maximum absorption observed for **3** upon changing the solvent polarity (see the footnote *a* in

Table 1. ^{13}C NMR data of **3**, 7-benzhydryl-1,3,5-cycloheptatriene, and **1**

Carbon	^{13}C Chemical shift,[a] ppm from Me_4Si		
	3	Ph_2CH-C_7C_7[b]	**1**[c]
1,6	135.7 (d)	131.0 (d)	138.3
2,5	127.3 (d)	125.4 (d)	126.9
3,4	131.9 (d)	124.7 (d)	130.8
7	136.5 (s)	54.4 (d)	146.6
8	135.6 (s)	43.0 (d)	111.9
9	142.2 (s)	143.9 (s)	—
10	128.5 (d)	128.4 (d)	—
11	129.5 (d)	128.7 (d)	—
12	126.9 (d)	126.5 (d)	—

[a] Solvent: $CDCl_3$. Signal multiplicity obtained by off-resonance experiments is given in the parentheses.

[b] 7-Benzhydryl-1,3,5-cycloheptatriene: Each carbon is numbered according to the numbering in **3**.

[c] Data reported in Ref. 2b.

Table 2. Spectral data of the heptafulvenes 2 and 3

Comp'd	IR ν, cm^{-1}	UV λ_{max}^{MeCN}, nm (log ε)	220 MHz NMR (CCl_4) τ, ppm
2	3030 m, 2980 w, 1595 m, 1580 s	241 (3.94)	2.93 (m, 5H, Ph), 3.77 (d, 1H, H^1)
	1575sh, 1495 m, 1455 w, 1445 w	340.5 (4.06)	4.18 (d, 1H, H^6), 4.27 (s, 1H, H^8)
	1260 w, 1030 w, 920 w, 860 w		4.39 (br t, 2H, $H^{3,4}$)
	695 s (CCl_4)		4.48 (dm, 1H, H^2), 4.59 (dm, 1H, H^5)
3	3025 m, 1595 m, 1570 s, 1560sh	242sh (4.17)	2.91 (m, 10H, Ph)
	1490 s, 1440 s, 1390 w, 1150 w	329[a] (4.13)	3.90 (d, 2H, $H^{1,6}$)
	1075 m, 1030 m, 805 m, 765 s		4.33 (t, 2H, $H^{3,4}$)
	755 s, 730 m, 700 s (KBr)		4.58 (dt, 2H, $H^{2,5}$)

[a] The maximum absorption observed in other solvents is as follows: 334 nm (THF), 334.5 nm (CH_2Cl_2), and 336 nm (cyclohexane).

Table 2), again, indicates the limited contribution by the dipolar structure to the electronic state of 3 in the ground state.

Reactions of heptafulvenes 2 and 3

Hydrogenation. In order to confirm the structures, heptafulvenes 2 and 3 were catalytically hydrogenated. The products were identified as benzylcycloheptane (4) and diphenylmethylenecycloheptane (5), respectively, by comparison of the physical and spectral properties with those of the authentic compounds prepared by the independent synthetic routes shown in Scheme 1.

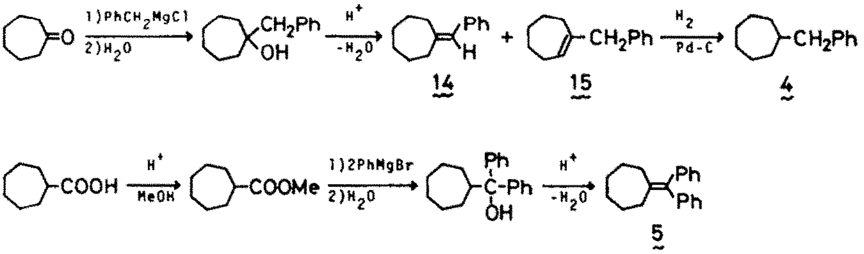
Reactions with electrophilic and nucleophilic reagents. The spectroscopic data on 2 and 3, as described above, indicated that there is only little, if any, dipolar character in these heptafulvenes. In order to chemically substantiate any dipolar contribution, some reactions of 2 and 3 with electrophilic and nucleophilic reagents were attempted.

When trifluoroacetic acid was added to the carbon tetrachloride solutions of 2 and 3, the original red color of the solution disappeared, and the ^1H NMR spectra of the solutions exhibited the quantitative formation of the benzyl- and benzhydryl-tropylium ions, respectively. This clearly demonstrates the highest proton affinity at the exocyclic methylene carbon in both 2 and 3. A dipolar heptafulvene with only one cyano group attached at the 8-position has been reported to react also with the tropylium ion at the 8-position in the presence of a base, yielding 8-cyano-8-(7-cycloheptatrienyl)heptafulvene.[8] However, the reactions of 2 and 3 either with the tropylium ion or with the more electrophilic triethyloxonium ion did not give any 8-alkylated products except that some small amounts (5–33% yields) of the 8-protonated products, i.e. the benzyl- and benzhydryl-tropylium ions, were formed. Although the source of the proton has not been clarified, this result seems to be in accord with the less polarization in 2 and 3 compared with 8-cyanoheptafulvene.

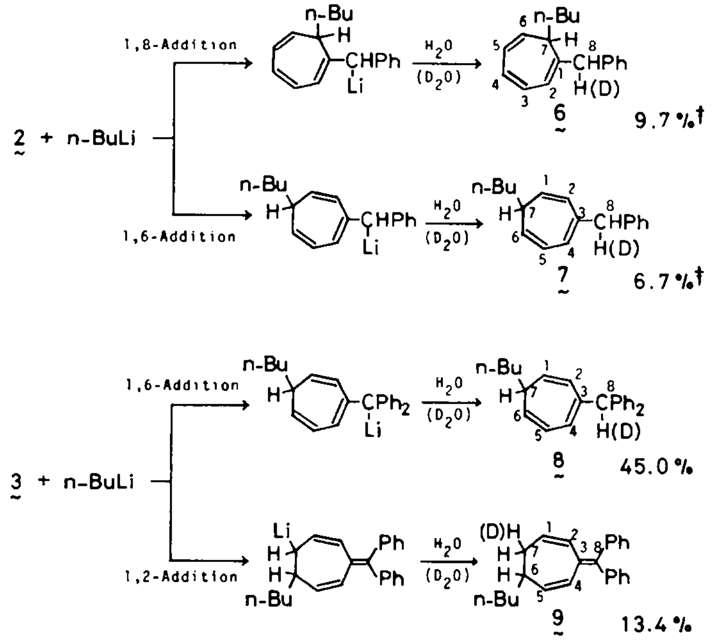
It has been reported that 7,8:9,10-dibenzo- and 7,8,9,10-tetraphenyl-sesquifulvalenes react with the hydride anion from LAH at the 7-membered ring, giving rise to isomeric mixtures of dihydrocompounds after hydrolysis, but the sites of the hydride attack have not been clarified.[9] We have examined the reactions of 2 and 3 with n-butyllithium, and established the sites of both the nucleophilic attack and lithiation by means of 220 MHz NMR analyses on the products which were isolated by repeated preparative TLC. In duplicate runs, the mixtures were hydrolyzed with deuterium oxide to confirm the sites of lithiation (Experimental). The results are summarized in Scheme 2.

Yields of the butylated products are somewhat low, but other products were mainly decomposition products resulting from 2 and 3 themselves. No other butylated product was isolated. The ^1H NMR spectral data on each product isomer are shown in Table 3. It is noteworthy that the butylation occurs only at the 7-membered ring, specifically only at the 1(or 6)- and 3(or 4)-positions in 2 and the 3-position in 3. No butylation occurs at the 2-position in both 2 and 3. These results are in accord with the ^{13}C NMR data on 3, which indicated that the carbons at 1- and 3-positions are slightly more electropositive than that at the 2-position. The steric hindrance exerted by the two phenyl groups might prevent butylation at the 1-position in 3.

Cycloaddition reactions. Electrocyclic reactions of the

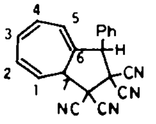


Scheme 1.



Scheme 2.

unsubstituted-,[1] 8-cyano-,[3e] and trimethylene-8,8-dithiaheptafulvenes[3g] with either dimethyl acetylenedicarboxylate or tetracyanoethylene (TCNE) are reported to give [8 + 2] cycloadducts in all cases. The 8-phenyl-substituted heptafulvenes **2** and **3** were also found to react with TCNE in benzene readily at room temperature. Although the ^{1}H NMR spectrum on the crude sample of the adduct from **2** suggests its structure as the [8 + 2] cycloadduct **10**, it was quite unstable, causing considerable decomposition during the isolation process, and did not allow further characterization or purification.



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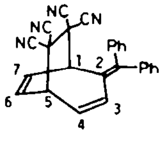

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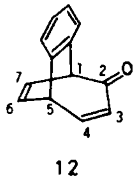

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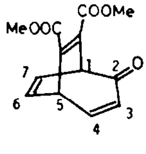

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On the other hand, the adduct from **3** was stable enough for full characterization, and was identified as the [4 + 2] cycloadduct **11** based on the following spectral properties. The IR spectrum indicates an absorption due to the CN stretching at 2250 cm^{-1}, and the UV spectrum is similar to that of 1,1-diphenyl-1,3-butadiene (Experimental). Furthermore, comparison of the values of chemical shifts and coupling constants of the ^{1}H NMR spectrum with those for the [4 + 2] cycloadducts of tropone with benzyne (**12**)[10] and with dimethyl acetylenedicarboxylate (**13**)[11] strongly supports its structure. Thus, the cycloaddition of **3** with TCNE occurred in a thermally allowed [4 + 2] manner. No [8 + 2]-type product was obtained in this case. This may be attributable to the steric hindrance caused by two phenyl groups which are presumably twisted out of the molecular plane.

EXPERIMENTAL

General. M.ps and b.ps are uncorrected. The IR and UV spectra were taken on a Hitachi 215 spectrometer and on a Shimadzu UV-50M spectrometer, respectively. The ^{1}H NMR spectra were recorded on a Hitachi R-24 (60 MHz), JEOL JNM PM-60 (60 MHz), or Varian HR-220 (220 MHz) spectrometer, using TMS as an internal standard. The ^{13}C NMR spectra were obtained on a JEOL JNM PS-100 spectrometer operated in the pulse Fourier transform mode. The mass spectra were taken on a JEOL JMS-01SG spectrometer. The elemental analyses were performed by the Microanalytical Center, Kyoto University, Kyoto.

All the reagents employed were of a reagent-grade quality except when otherwise noted. MeCN, CH_2Cl_2, and CCl_4 were refluxed and distilled over P_2O_5. THF was distilled over LAH. Tropylium fluoroborate and 7-methoxy-1,3,5-cycloheptatriene were prepared according to the methods of Conrow[12] and of Doering and Knox,[13] respectively. Triphenylmethyl (trityl) perchlorate was prepared following the method of Dauben *et al.*[14]

7-Benzyl-1,3,5-cycloheptatriene. This compound was prepared by a method similar to that reported[15] from benzylmagnesium chloride and 7-methoxy-1,3,5-cycloheptatriene in an 84.0% yield; b.p. 97.5–99.5°/0.5 mm Hg; NMR (CCl_4) τ 2.92 (s, 5H, Ph), 3.50 (t, 2H, $H^{3,4}$), 3.98 (m, 2H, $H^{2,5}$), 4.90 (dd, 2H, $H^{1,6}$), 7.10 (d, 2H, $-CH_2-$), 8.05 (tt, 1H, H^7).

7-Benzhydryl-1,3,5-cycloheptatriene. A soln of benzhydryllithium prepared from benzhydryl chloride (30.0 g; 0.148 mol) and Li (2.5 g; 0.36 g atom) in 100 ml of THF was slowly added to a stirred suspension of tropylium fluoroborate (21.0 g; 0.118 mol) in 200 ml THF. After stirring for 3 hr at room temp., the mixture was hydrolyzed with water (200 ml), and extracted with ether. The ethereal soln was washed with 10% NaCl, dried over $MgSO_4$, and evaporated *in vacuo* to give 32.5 g of the product mixture, from which was isolated 7-benzhydryl-1,3,5-cycloheptatriene

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†These values are based on the benzyltropylium ion which was used to generate **2**. The actual yields should be increased when decomposition of **2** during its preparative process is taken into account.

Table 3. 220 MHz ^{1}H NMR spectral data of the butylated compounds **6**, **7**, **8** and **9**

Comp'd	^{1}H Chemical shift (CCl$_4$), τ ppm (Coupling constant, J Hz)										
	Ph	H^1	H^2	H^3	H^4	H^5	H^6	H^7	H^8	α-CH$_2$	β,γ-CH$_2$	CH$_3$
6	3.02(m)	—	4.26(br d)	3.79(br t)		4.12(dt)	5.05(dd)	7.75(q)	6.56(s)	8.74 (br s)	8.83(br s)	9.20(t)
						($J_{5,6}$=9.0^a; | $J_{6,7}$=7.0)					
7	2.99(m)	5.05(dd)	4.23(d)	—	3.73(d)	4.10(dd)	5.07(dd)	∿8.4^b	6.45(s)	8.41 (br s)	8.68 (br s)	9.11(t)
		($J_{1,2}$=9.5)			($J_{4,5}$=6.0, | $J_{5,6}$=8.5)						
8	2.90(m)	∿5.0^b	4.11(d)	—	3.84(d)	4.04(dd)	∿5.0^b	∿8.3^b	4.96(s)	8.34 (br s)	8.64 (br s)	9.08(t)
			($J_{2,1}$=9.5)		($J_{4,5}$=6.0, | $J_{5,6}$=9.4)						
9^c	2.85(s)	4.40(br m)	3.85(br d)	—	3.85(br d)	4.40(br m)	7.63(br m)	7.63(br m)	—	8.62 (br m)		9.06(t)

^{a} Ascertained by the use of spin decoupling technique.

^{b} These signals were obscured by overlapping with other peaks.

^{c} Measured at 60 MHz.

(15.8 g; 51.8% yield) as white crystals by recrystallization from CCl$_4$: m.p. 81.0–82.0°; IR (KBr) ν 3020 m, 2820 w, 1588 m, 1575 w, 1495 s, 1445 s, 1390 m, 1057 w, 1027 m, 745 s, 727 s, 708 s, 695 s cm^{-1}; NMR (CCl$_4$) τ 2.81 (s, 10H, Ph), 3.34 (t, 2H, H^{3,4}), 3.91 (m, 2H, H^{2,5}), 4.91 (dd, 2H, H^{1,6}), 5.86 (d, 1H, -C$\underline{H}$Ph$_2$), 7.66 (dt, 1H, H^7). (Found: C, 92.87; H, 7.00. Calc. for C$_{20}$H$_{18}$: C, 92.98; H, 7.02%).

Benzyltropylium perchlorate. Trityl perchlorate (1.90 g; 5.60 mmol) was added to a stirred soln of 7-benzyl-1,3,5-cycloheptatriene (1.01 g; 5.54 mmol) in MeCN (5 ml). After the mixture was stirred at 60° for 3 hr, dry EtOAc (10 ml) and dry ether (20 ml) were added. The brownish viscous oil which separated was washed with ether and dried under vacuum to give a brown solid (1.48 g; 95.2% yield) identified as benzyltropylium perchlorate. This salt was very hygroscopic, as reported for the fluoroborate salt,[15] and any attempt to obtain the analytically pure sample was not successful; UV λ_{max}^{MeCN} 279 nm (log ε 3.67), 322 (3.51); NMR (CF$_3$COOH) τ 0.87 (s, 6H, -C$_7$H$_6$$^+$), 2.65 (s, 5H, Ph), 5.26 (s, 2H, -CH$_2$-).

Benzhydryltropylium perchlorate. Trityl perchlorate (3.94 g; 11.5 mmol) was added to a stirred soln of 7-benzhydryl-1,3,5-cycloheptatriene (3.01 g; 11.6 mmol) in CH$_3$CN (5 ml). After stirring at 60° for 1.5 hr and at 80° for 20 min, dry EtOAc (30 ml) was added with ice cooling. The yellow plates which precipitated were filtered off, washed with ether, and dried under vacuum to give benzhydryltropylium perchlorate (2.48 g; 60.5% yield); m.p. 218.0–219.5° (dec); IR (KBr) ν 3020 w, 1595 m, 1580 w, 1525 m, 1490 sh, 1485 s, 1440 s, 1080 br vs, 805 w, 760 sh, 755 s, 720 sh, 705 s cm^{-1}; UV λ_{max}^{MeCN} 267 sh nm (log ε 3.81), 273.5 (3.82), 324 (3.69); NMR (CF$_3$COOH) τ 0.86 (s, 6H, -C$_7$H$_6$$^+$), 2.45–2.85 (m, 10H, Ph), 3.64 (s, 1H, -C$\underline{H}$Ph$_2$). (Found: C, 67.30; H, 4.66. Calc. for C$_{20}$H$_{17}$ClO$_4$: C, 67.32; H, 4.80%).

8-Phenylheptafulvene (**2**). A soln of triethylamine (0.20 g; 2.0 mmol) in CH$_2$Cl$_2$ (5 ml) was added to a stirred soln of benzyltropylium perchlorate (0.485 g; 1.73 mmol) in CH$_2$Cl$_2$ (5 ml) under N$_2$ at room temp. After 15 min the resulting red soln was concentrated to *ca.* 4 ml under vacuum, and dry CCl$_4$ (10 ml) was added under N$_2$. This procedure was repeated twice, and then the CCl$_4$ soln was quickly passed through a short alumina column (10 cm). The eluent was concentrated and subjected to NMR measurement to give the result shown in Fig. 1. The addition of a drop of CF$_3$COOH resulted in quantitative formation of the benzyltropylium ion as observed by NMR.

The IR and UV spectra were taken on the samples freshly prepared in a similar manner to give the results shown in Table 2. In order to determine the extinction coefficient (ε) of the UV spectrum, the concentration of the freshly prepared soln was estimated from the weight of a red oil, which was obtained by quickly evaporating a 2-ml aliquot of the soln under high vacuum.

8,8-*Diphenylheptafulvene* (3)

Method A. A soln of triethylamine (0.70 g; 7.0 mmol) in CH$_2$Cl$_2$ (15 ml) was added to a stirred suspension of benzhydryltropylium perchlorate (1.68 g; 4.71 mmol) in CH$_2$Cl$_2$ (15 ml). After stirring for 30 min at room temp., the solvent and the excessive base were removed by evaporation under reduced pressure. The residual material was extracted with ether, washed with water, dried over MgSO$_4$, and evaporated *in vacuo* to give 1.38 g of the crude product. A preparative TLC over SiO$_2$ (Merck PF$_{254}$) using n-hexane-benzene (9:1) afforded **3** (0.907 g; 75.0% yield) as a dark red solid; m.p. 56.0–58.5° (lit. 59–60°[7]); the spectral data are shown in Fig. 1 and Table 2; *m/e* 256 (100%), 179 (79%), 178 (80%). (Found: C, 92.84; H, 6.22. Calc. for C$_{20}$H$_{16}$: C, 93.71; H, 6.29%). The NMR spectrum of **3** changed to that of the benzhydryltropylium ion immediately after addition of a drop of CF$_3$COOH.

Method B. Chloranil (2.39 g; 9.71 mmol) was added to a stirred soln of 7-benzhydryl-1,3,5-cycloheptatriene (0.614 g; 2.38 mmol) in CCl$_4$ (23 ml). After refluxing for 20 hr, the excessive chloranil was filtered off. The red filtrate was evaporated *in vacuo* to give 0.878 g of a dark red oil, from which was isolated **3** (0.104 g; 17.1% yield) by means of preparative TLC over SiO$_2$ developed with n-hexane-benzene (95:5).

Catalytic hydrogenation of **2** *and* **3**. 8-Phenylheptafulvene **2**, which was freshly prepared from benzyltropylium perchlorate (0.945 g; 3.37 mmol), was catalytically hydrogenated over Pd–C in dry benzene for 1 day at room temp. Purification of the crude product (0.154 g) by the use of preparative TLC over SiO_2 with n-hexane as the solvent and subsequent vacuum distillation afforded **4** (0.0805 g; 12.6% yield based on benzyltropylium perchlorate) as a colorless oil, which agreed in all the physical and spectral properties with the authentic sample prepared by an independent synthetic route as described below; b.p. 90–95° (bath temp.)/0.04 mm Hg; IR (neat) ν 3025 m, 2920 s, 2850 s, 1600 m, 1580 w, 1495 m, 1455 sh, 1450 s, 745 s, 720 m, 695 s cm^{-1}; NMR (CCl_4) τ 2.94 (s, 5H, Ph), 7.54 (d, 2H, –$C\underline{H}_2$Ph), 8.46 (br s, 13H, $>$CH– + –$(CH_2)_6$–). (Found: C, 89.39; H, 10.87. Calc. for $C_{14}H_{20}$: C, 89.29; H, 10.71%).

Similarly, hydrogenation of **3** (0.0748 g; 0.292 mmol) over Pd–C in a mixture of dry MeOH (5 ml) and dry benzene (1 ml) afforded, after 2 hr, **5** (0.0721 g; 94.1% yield) as a colorless oil, which was identical with the authentic sample prepared as described below; b.p. 150–155° (bath temp.)/0.4 mm Hg; IR (neat) ν 3055 w, 3020 w, 2925 s, 2860 s, 1595 m, 1575 w, 1490 s, 1440 s, 1075 m, 770 m, 760 m, 740 m, 700 s, 695 s cm^{-1}; UV λ_{max}^{MeCN} 224 sh nm (log ϵ 4.08), 242 (3.90); NMR (CCl_4) τ 2.88 (s, 10H, Ph), 7.67 (br s, 4H, $>$C–CH_2–), 8.40 (br s, 8H, –$(CH_2)_4$–). (Found: C, 91.31; H, 8.20. Calc. for $C_{20}H_{22}$: C, 91.55; H, 8.45%).

Benzylcycloheptane (**4**). 1-Benzylcycloheptanol was prepared by the reaction of cycloheptanone with benzylmagnesium chloride in an 87% yield; NMR (CCl_4) τ 2.83 (s, 5H, Ph), 7.36 (s, 2H, –$C\underline{H}_2$Ph), 8.49 (br s, 12H, –$(CH_2)_6$–), 8.71 (s, 1H, OH). Dehydration was effected by refluxing a mixture of 1-benzylcycloheptanol (1.52 g; 7.44 mmol) in 20% H_2SO_4 (20 ml) for 2 hr yielding a 26:74 mixture (1.29 g; 93.1% yield) of **14** and **15** after the usual work up. The composition of the mixture was determined by NMR analysis; NMR (CCl_4) τ 2.89 (s, 5.0H Ph (**14** + **15**)), 3.77 (s, 0.26H, =CH– (**14**)), 4.40 (t, 0.74H, =CH– (**15**)), 6.75 (s, 1.48H, –$C\underline{H}_2$Ph (**15**)), 7.6–8.0 (m, 4.0H, $>$C–CH_2– (**14** + **15**)), 8.38 (br s, 6.52H, –$(CH_2)_4$– (**14**) + –$(CH_2)_3$– (**15**)). Then, the mixture of the olefinic compounds (0.812 g; 4.36 mmol) was catalytically hydrogenated over Pd–C in a mixture of dry MeOH (15 ml) and ether (5 ml), yielding **4** (0.656 g; 80.0% yield) as a colorless oil after vacuum distillation.

Diphenylmethylenecycloheptane (**5**). Cycloheptanecarboxylic acid was prepared by the reaction of CO_2 upon cycloheptylmagnesium bromide in a 53.2% yield; IR (CCl_4) ν 3200–2500 br, 2940 s, 2870 s, 1710 vs, 1465 m, 1450 m, 1420 m, 1300 m, 1280 m, 1230 s, 880 w cm^{-1}. Refluxing the carboxylic acid in MeOH containing a catalytic amount of H_2SO_4 gave methyl cycloheptanecarboxylate in an 85.0% yield as a colorless oil; IR (CCl_4) ν 2945 s, 2870 m, 1740 br s, 1460 m, 1440 m, 1260 w, 1220 s, 1200 m, 1160 m, 1035 w, 1000 w cm^{-1}; NMR (CCl_4) τ 6.43 (s, 3H, OCH_3), 7.63 (br m, 1H, $>$CH–), 8.50 (br s, 12H, –$(CH_2)_6$–). To a stirred soln of PhMgBr prepared from bromobenzene (1.42 g; 9.02 mmol) and Mg (0.201 g; 8.27 mg atom) in 4 ml of ether, there was added a soln of methyl cycloheptanecarboxylate (0.602 g; 3.85 mmol) in 3 ml of ether. The mixture was refluxed for 1.2 hr and then hydrolyzed with cold 10% HCl (8 ml). The usual work up afforded 1.06 g of the crude product, from which was isolated diphenylcycloheptylcarbinol (0.694 g; 64.4% yield) as a colorless oil by means of preparative TLC over SiO_2 with benzene as the solvent; IR (CCl_4) ν 3640 m, 3070 m, 3040 w, 2940 s, 2870 s, 1600 m, 1495 s, 1450 s, 1160 m, 970 m, 900 w, 705 s cm^{-1}; NMR (CCl_4) τ 2.6–2.9 (m, 10H, Ph), 7.40 (m, 1H, $>$CH–), 8.20 (s, 1H, OH), 8.47 (br s, 12H, –$(CH_2)_6$–). A mixture of the carbinol (0.227 g; 0.811 mmol) and 20% H_2SO_4 (2.6 ml) was refluxed for 3 hr. The usual work up gave 0.203 g of the crude product, from which was isolated **5** (0.176 g; 83.0% yield) as a colorless oil by vacuum distillation.

Reactions of **2** *and* **3** *with the triethyloxonium and tropylium ions*. A soln of triethyloxonium fluoroborate[16] (0.060 g; 0.32 mmol) in 1,2-dichloroethane (1 ml) was added to a stirred soln of **3** (0.0727 g; 0.284 mmol) in 1,2-dichloroethane (1 ml). After stirring for 1 hr at room temp., dry ether (5 ml) was added yielding benzhydryltropylium fluoroborate (0.0317 g; 32.9% yield) as a ppt. Similarly, the reaction of **3** with tropylium fluoroborate afforded benzhydryltropylium fluoroborate in a 13.2% yield, while the reactions of **2** with triethyloxonium and tropylium fluoroborates gave benzyltropylium fluoroborate in 6.8 and 5.0% yield, respectively.

Reaction of **2** *with n-butyllithium*. A soln of **2** in dry benzene (*ca.* 6 ml) was prepared from benzyltropylium perchlorate (1.088 g; 3.88 mmol) and purified as described before. To this soln dry THF (6 ml) was added, and the resulting soln was added dropwise to 5 ml of an ice-cooled soln (1.6 N) of n-BuLi in hexane with stirring under N_2. The deep red soln was stirred at 0° for 30 min and subsequently at room temp. for 1 hr. After hydrolysis the mixture was worked up in the usual way to give 0.632 g of the product mixture. The TLC analysis over SiO_2 with n-hexane–benzene (9:1) as the solvent indicated the existence of two hardly separating spots with R_f 0.67 and 0.60, in addition to some components with R_f 0.2–0.0. The NMR spectrum of the material corresponding to the lower spots (R_f 0.2–0.0) exhibited rather broad signals of the phenyl and olefinic protons but not those of the butyl protons. On the other hand, the fraction with R_f 0.67–0.60 afforded a colorless oil (0.152 g; 0.638 mmol), which was shown to be a 59:41 mixture of **6** and **7** by the NMR analysis. The composition was determined from integrated peak areas of the two different benzylic methylenes; **6**, 9.7% yield; **7**, 6.7% yield; b.p. (mixture) 95–100° (bath temp.)/0.1 mm Hg. (Found (mixture): C, 90.97; H, 9.46. Calc. for $C_{18}H_{22}$: C, 90.69; H, 9.31%). Complete separation of **6** and **7** was effected by repeated preparative TLC over SiO_2 with n-hexane as the solvent. The NMR data on each isomer are shown in Table 3.

In a duplicate run the mixture was hydrolyzed with D_2O and worked up exactly in the same way, yielding a mixture of 1- and 3-(benzyl-1-*d*)-7-n-butyl-1,3,5-cycloheptatrienes. The incorporation of deuterium at the methylene carbon of the benzyl group was ascertained from the integrated peak area (1H) of the benzylic proton in the NMR spectrum. The rest of the spectrum was superimposable with the spectrum of the 59:41 mixture of **6** and **7** described above, indicating that the isomer composition was not changed in duplicate runs.

Reaction of **3** *with n-butyllithium*. A soln of **3** (0.269 g; 1.05 mmol) in dry THF (2.5 ml) and n-hexane (5 ml) was added dropwise to 6 ml of an ice-cooled soln (0.63 N) of n-BuLi in hexane with stirring under N_2. After stirring at 0° for 1 hr and subsequently at room temp. for another 1 hr, the deep red-violet soln was hydrolyzed and worked up to give 0.444 g of the mixture, which showed three main spots (R_f 0.68, 0.58, and 0.06–0.0) on a SiO_2 thin-layer chromatoplate developed with n-hexane–benzene (9:1). By means of two repeated preparative TLC, a component with R_f 0.68 was isolated as a colorless oil (0.0442 g; 13.4% yield), and identified as **9** on the basis of the NMR (Table 3) and UV spectral data; UV λ_{max}^{MeCN} 245 nm (log ϵ 3.75), 302 (4.00). Similarly, a component with R_f 0.58 was isolated as a colorless oil (0.149 g; 45.0% yield), and identified as **8**; UV λ_{max}^{MeCN} 261 nm (log ϵ 3.67); the NMR spectral data are shown in Table 3. (Found: C, 91.92; H, 8.54. Calc. for $C_{24}H_{26}$: C, 91.66; H, 8.34%).

In a duplicate run in which the mixture was hydrolyzed with D_2O, the incorporation of deuterium was observed at the 7-methylene carbon in **9** and at the methine carbon of the benzhydryl group in **8**, by the NMR analysis on the products isolated in the same way as above.

Reaction of **2** *with TCNE*. To a stirred soln of **2** in dry benzene (*ca.* 20 ml), prepared from benzyltropylium perchlorate (1.465 g; 5.22 mmol) and purified as described previously, there was added dropwise a soln of TCNE (0.361 g, 2.82 mmol) in benzene (75 ml). After stirring for 20 hr at room temp. under N_2, the mixture was evaporated *in vacuo* to give 0.916 g of the product mixture. Two repeated preparative TLC on this mixture over SiO_2 with benzene as the solvent afforded a yellowish oil (0.0662 g; 7.6% yield based on TCNE), which was tentatively assigned as the cycloadduct **10** on the basis of the following spectral properties;

IR (CCl_4) ν_{CN} 2255 cm^{-1}; NMR ($CDCl_3$) τ 2.75 (m, 5H, Ph), 3.29 (t, 1H, H^4), 3.57 (m, 2H, $H^3 + H^5$), 3.90 (br m, 1H, H^2), 4.48 (dd, 1H, H^1), 5.04 (s, 1H, $\rangle$C$\underline{\mathrm{H}}$Ph), 6.88 (br d, 1H, H^7). Any attempt to purify this compound was always accompanied by the formation of some decomposition product, thus, further verification of its structure was unsuccessful.

Reaction of **3** *with TCNE.* A soln of TCNE (0.159 g; 1.24 mmol) in dry benzene (20 ml) was added dropwise to a stirred soln of **3** (0.287 g; 1.12 mmol) in dry benzene (9 ml). After stirring for 4.5 hr at room temp. under N_2, the soln was evaporated *in vacuo* to give 0.446 g of a brownish solid, which was then subjected to preparative TLC over SiO_2 developed with benzene. A component with R_f 0.56 was isolated as a white powder (0.266 g; 61.8% yield) and identified as the [4+2]-cycloadduct **11** on the basis of the spectral properties described below; m.p. (after recrystallization from CCl_4) 176.0–178.0° (dec); IR (KBr) ν 3080 w, 3020 w, 2985 w, 2260 w, 1640 m, 1570 m, 1545 m, 1490 m, 1440 s, 1400 w, 1335 m, 1320 m, 1305 s, 1260 m, 1160 m, 1080 m, 1035 m, 1000 w, 960 w, 950 w, 935 w, 900 m, 880 s, 810 s, 780 s, 765 s, 730 s, 705 vs, 680 m cm^{-1}; UV λ_{max}^{MeCN} 234 nm (log ϵ 4.31), 297.5 (4.33) (lit. value for 1,1-diphenyl-1,3-butadiene, $\lambda_{max}^{cyclohexane}$ 236 sh nm (log ϵ 3.71) 297 (4.26)[17]); NMR (CD_3CN–$CDCl_3$ (1:1)) τ 2.75 (m, 10H, Ph), 3.31 (sept, 1H, H^6; $J_{6,7} = 8.6$ Hz, $J_{6,5} = 6.6$ Hz, $J_{6,1} = 1.4$ Hz), 3.51 (sept, 1H, H^7; $J_{7,1} = 6.8$ Hz, $J_{7,5} = 1.4$ Hz), 3.74 (dq, 1H, H^3; $J_{3,4} = 11.0$ Hz, $J_{3,1} = 1.6$ Hz, $J_{3,5} = 0.8$ Hz), 4.12 (dd, 1H, H^4; $J_{4,5} = 8.0$ Hz), 5.73 (dt, 1H, H^1), 5.98 (tm, 1H, H^5); *m/e* 256 (3, 100%), 179 (63%), 178 (65%), 128 (TCNE, 84%). (Found: C, 81.42; H, 4.69. Calc. for $C_{26}H_{16}N_4$: C, 81.23; H, 4.19%).

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