If the out-of-plane bending force constant is indeed especially small in free radicals, as above suggested, then the effect does not seem to persist with larger distortions, as found in the 1-norbornyl radical. The latter is about 6.7 kcal. less stable than the 1-bicyclo[2.2.2]octyl radical (Table II), whereas in the carbonium ion series, an energy difference of just 5.6 kcal. (in $\Delta\Delta H^*$ of solvolysis) has been proposed[3] and seems reasonable, although the data on the 1-norbornyl system here are too scanty to make much of the comparison. The present data are certainly enough, however, to make the point that whereas the data on the 1-bicyclo[2.2.2]octyl radical show *no steric destabilization*, the data on the *1-norbornyl radical show major destabilization*.

A curious contrast with the results given by this work is presented by some recent findings of Baker, Holtz, and Stock,[51] who reported that the 1-bicyclo[2.2.2]octyl radical, as generated by the Cristol–Firth modification of the Hunsdiecker reaction, abstracts chlorine from either carbon tetrachloride or bromotrichloromethane in competition with elemental bromine. Such behavior is unexpected for a radical as stable as *t*-butyl. No explanation will be offered here.

A possible source of difficulty in the interpretation of the decarbonylation results described above is that the rate constant k_2 may be neither invariant nor smoothly variant with k_1. The result would be a failure of the linear correlation of $\ln (k_1/k_2)$ with $D(\mathrm{R{-}H})$, and the values of $D(\mathrm{R{-}H})$ in Table II would then be worthless. This possibility cannot be ruled out rigorously, but against it can be raised the following arguments. (1) If steric effects in any of the systems considered here are to affect k_2 materially, then the effect should be evident in the three aliphatic model compounds, which should therefore not give the linear correlation observed. (A steric effect would presumably lower k_2 for pivaloyl as much as it would for any of the bridgehead cases.) (2) A fairly good model reaction, $\mathrm{RCHO + CH_3 \rightarrow RCO + CH_4}$, is known to go at almost exactly the same rate at 135° for acetaldehyde, propionaldehyde, *n*-butyraldehyde, isobutyraldehyde, pivaldehyde, and others.[52] If either steric or electronic effects were going to cause variations in k_2, then it might have been expected that the same effects would appear in the reaction of aldehydes with methyl. (3) The activation energies for abstraction of tertiary hydrogen by methyl from isobutane, 2,3-dimethylbutane, and 2,3,4-trimethylpentane are 7.6, 7.8, and 7.9 kcal., respectively,[53] indicating again a very small effect of β-substituents on an incipient free radical. (4) It is known that the acidities of acyl *cations* are rather insensitive to α-alkyl substituents,[54] so that even a polar contribution to the transition state for reaction of acyl radical with carbon tetrachloride cannot be expected to produce significant variation in k_2.

(51) F. W. Baker, H. D. Holtz, and L. M. Stock, *J. Org. Chem.*, **28**, 514 (1963).

(52) R. N. Birrell and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 2059 (1960).

(53) (a) A. F. Trotman-Dickenson, J. R. Birchard, and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 163 (1951); (b) H. O. Pritchard and G. O. Pritchard, *Can. J. Chem.*, **41**, 3042 (1963).

(54) N. C. Deno, C. U. Pittman, Jr., and M. J. Wisotsky, *J. Am. Chem. Soc.*, **86**, 4370 (1964).

Heptaphenylcycloheptatrienyl Anion[1]

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Reduction of heptaphenyltropylium bromide with potassium produces potassium heptaphenylcycloheptatrienide, an anion for which a possible triplet ground state is predicted. However, various magnetic studies show that the species is a singlet. The anion reacts with the original tropylium ion to produce heptaphenylcycloheptatrienyl radical, while reduction of the anion with potassium leads to fragmentation to stilbene and pentaphenylcyclopentadienyl anion.

Introduction

The possibility that certain derivatives of cyclic 4n π-electron systems could have triplet ground states is one of the most intriguing predictions made by simple m.o. theory.[2] This is based on the degeneracy of the highest occupied molecular orbitals, which are half-filled, together with the usual[3] electronic advantage of triplet states in such situations. A number of stable organic and inorganic triplets are known.[4] However, the prediction[2] that the cyclobutadiene molecule, for instance, might be more stable with only one double bond and two unpaired electrons is relatively unusual; only in species such as O_2 and S_2 were cases known in which the structural principle[5] of maximum bonding was violated, and special explanations[6] had been offered here. Accordingly, it was of considerable interest to explore the possibility of triplet ground states for symmetrical 4n π-electron systems.

The first[7] examples of such systems, heptaphenyl-

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(1) This work was supported in part by the National Science Foundation and the Sloan Foundation. For a preliminary communication of some of these results, see R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **84**, 1484 (1962).

(2) *Cf.* A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961, especially Chapter 10.

(3) C. Coulson, "Valence," 2nd Ed., Oxford University Press, London, 1961, p. 36.

(4) See for instance, E. Wasserman, L. Barash, A. M. Trozzolo, R. W. Murray, and W. A. Yager, *J. Am. Chem. Soc.*, **86**, 2304 (1964), and references therein.

(5) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 21.

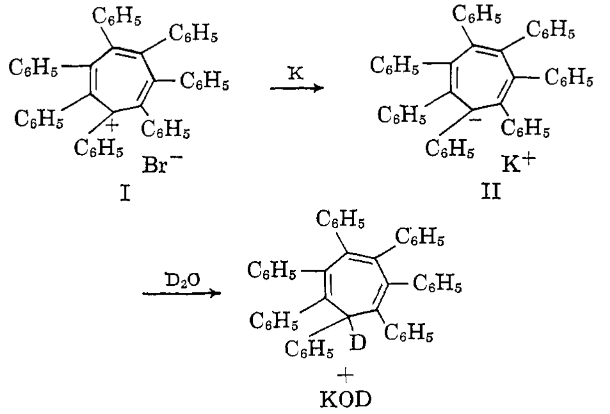
(6) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 351 ff.

(7) Cyclooctatetraene would be such a system if it were planar.

cycloheptatrienyl anion[1] and the tetrapotassium salt of tetrahydroxybenzoquinone,[8] proved to be singlets. However, subsequent work has uncovered several systems of this type with detectable triplet states: triphenylbenzene dianion and decacyclene dianion,[9] pentaphenylcyclopentadienyl cation and related compounds,[10] and pentachlorocyclopentadienyl cation,[11] the latter with a triplet ground state. In this paper we wish to describe our work with the heptaphenylcycloheptatrienyl anion.

Results and Discussion

When heptaphenyltropylium bromide (I)[12] was suspended in ether with an excess of potassium metal, it afforded a bluish purple suspension of potassium heptaphenylcycloheptatrienide (II), which yielded heptaphenyltropylidene[12] on quenching with water. Solutions of II were prepared by treating I with potassium in dimethoxyethane. Quenching of such a solution in D_2O afforded heptaphenylcycloheptatriene-7-*d* and potassium deuteroxide, determined by titration.



The solution of II in dimethoxyethane showed a number of peaks in the aromatic region of the n.m.r. (Figure 1). Although we find that the n.m.r. spectrum of pentaphenylcyclopentadienyl anion has a single sharp peak, triphenylmethyl anion and related compounds[13] show broad spectra related to that of II. However, the critical point is that II exhibits a standard spectrum, in contrast to the situation in pentaphenylcyclopentadienyl cation[10] where the aromatic proton spectrum is completely lost because of equilibrium with a triplet state. Further evidence that II is a singlet comes from e.s.r. studies of the frozen solution; no triplet signals could be detected under conditions which were successful[4,10,11] in detecting other triplets. The solvent line in the n.m.r. was not broadened in solutions of II, but if I was added to II to produce heptaphenylcycloheptatrienyl radical (III)[14] the resulting solution showed solvent line broadening, due to paramagnetic relaxation effects,[15] and the phenyl protons vanished. Finally, solutions of II were examined in the Gouy balance. The anion II was slightly diamagnetic, after correction for solvent diamagnetism, while the radical III showed easily detectable net paramagnetism.

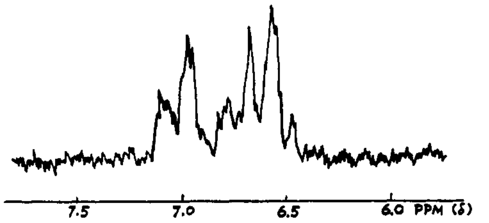
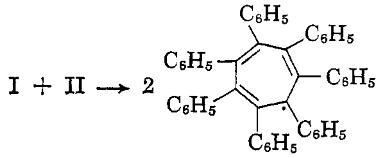


Figure 1. The n.m.r. spectrum of heptaphenylcycloheptatrienyl anion in dimethoxyethane, referred to internal TMS. The only other signals are derived from solvent protons and are not shown here.



III

Accordingly it seems clear that II is in a singlet electronic state and that the triplet state is not as thermally accessible as it is in pentaphenylcyclopentadienyl cation. The triplet prediction is based on the idea that the molecule is heptagonally symmetrical, with the seven-membered ring in a plane and all phenyls equally tipped. If this is true then the highest occupied orbitals can indeed be half-filled, with two unpaired electrons. However, the Jahn–Teller principle[16] indicates that the *orbital* energy of such a 4n π-electron system can always be lowered by a distortion away from perfect polygonal symmetry. Presumably, the molecule will be a ground-state triplet only if the triplet–singlet energy difference,[17] which favors a symmetrical system with unpaired electrons, is greater than the stabilization by Jahn–Teller distortion of the singlet state.

The nature of the distortion in II is not easily specified. It seems unlikely that it is caused by ion pairing in an unsymmetrical way, since the potassium ion is well solvated in dimethoxyethane[18] and the organic anion is too bulky for close approach to seem reasonable. However, puckering of the seven-membered ring, unsymmetrical tipping of the phenyls, or bond-length alternations are possibilities. In smaller molecules the possibilities for distortion are more limited and the electrons are closer, so the triplet–singlet energy difference will be larger.[19] Thus it was predicted that in suitable species smaller than II the triplet state would be more stable and this has been confirmed.[10,11]

[8] R. West and H. Y. Niu, *J. Am. Chem. Soc.*, **84**, 1324 (1962).

[9] R. Jesse, P. Biloen, R. Prins, J. van Voorst, and G. Hoijtinck, *Mol. Phys.*, **6**, 633 (1963).

[10] R. Breslow, H. W. Chang, and W. A. Yager, *J. Am. Chem. Soc.*, **85**, 2033 (1963), and later work.

[11] R. Breslow, R. Hill, and E. Wasserman, *ibid.*, **86**, 5349 (1964).

[12] M. A. Battiste, *Chem. Ind.* (London), 550 (1961); *J. Am. Chem. Soc.*, **83**, 4101 (1961).

[13] V. R. Sandel and H. H. Freedman, *ibid.*, **85**, 2328 (1963).

[14] *Cf.* also M. Battiste, *ibid.*, **84**, 3780 (1962).

[15] J. Pople, W. Schneider, and H. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 207.

[16] H. Jahn and E. Teller, *Proc. Roy. Soc.* (London), **A161**, 220 (1937).

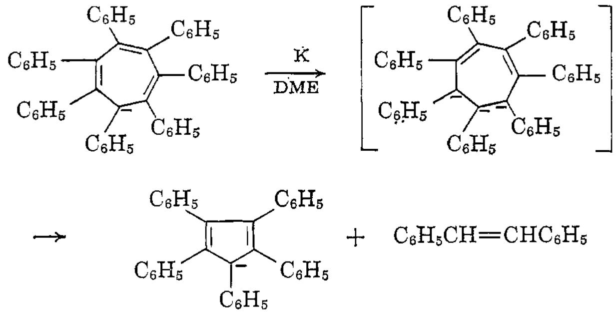
[17] For some quantitative illustrations of the magnitude of the energy advantage of triplets relative to corresponding singlets, see M. Kasha, *Radiation Res., Suppl.*, **2**, 243 (1960), and C. Reid, "Excited States in Chemistry and Biology," Academic Press Inc., New York, N. Y., 1957, p. 90.

[18] A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p. 318.

[19] *Cf.* C. K. Jørgensen, *Progr. Inorg. Chem.*, **4**, 112 (1962).

The pK_a of heptaphenylcycloheptatriene was determined as an indication of the stability of II. Treatment of the cycloheptatriene with either potassium amide in ammonia or potassium *n*-propylamide in *n*-propylamine gave the deep bluish purple color of II; in semiquantitative experiments it was observed that the color of II, in *n*-propylamine, was quenched[20] by fluorene (pK_a = 25),[21] triphenylmethane (pK_a = 33),[21] or diphenylmethane (pK_a = 35).[21] Thus the pK_a lies between that of diphenylmethane and ammonia, *ca.* 36. Dauben has recently[22] prepared cycloheptatrienyl anion in solution; his estimate for the pK_a (36) indicates remarkably little help in II from the seven (noncoplanar) phenyls.[23]

The possibility of reducing II further was investigated. Addition of two more electrons might afford heptaphenylcycloheptadienyl trianion, a derivative of a potentially aromatic system.[24] However, when the solution of II was allowed to stir for a longer time over potassium metal it was converted to pentaphenylcyclopentadienyl anion and stilbene, whose two protons are derived from dimethoxyethane. No intermediates could be detected at shorter times, so the precise path of fragmentation must remain speculative.



Experimental

Heptaphenyltropylidene.[12] Triphenylcyclopropene (29.03 g., 0.108 mole) and tetracyclone (41.5 g., 0.108 mole) were heated under N_2 at reflux in 300 ml. of xylene for 24 hr. On cooling, the solution deposited 67 g. (99.5% yield) of *heptaphenyltropylidene*, m.p. 284–285° (lit.[12] 75% yield, m.p. 285–287.5°). The infrared and ultraviolet spectra were as reported; in the n.m.r. (CS_2 *vs.* Me_4Si) the phenyl protons were found between τ 2.10 and 3.85, and a single proton appeared at 4.73.

Heptaphenyltropylium Bromide.[12] The above compound liberated HBr slowly over 5 days on stirring with 2 moles of Br_2 in CCl_4 solution. The yellow solid was collected and digested with acetonitrile–acetone as described[12] to afford a 61% yield of heptaphenyltropylium bromide, m.p. 266–270° dec. (lit. 265–270° dec.). In the n.m.r. (CF_3CO_2H) the compound showed a single sharp peak at 0.42 p.p.m. higher field than an internal benzene standard.

Heptaphenyldeuteriotropylidene. Heptaphenyltropylium bromide (600 mg.) was treated with 50 mg. of $LiAlD_4$ in 75 ml. of ether for 2 hr. Aqueous work-up afforded a 98% yield of the deuteriotropylidene, m.p. 282–283°, raised to 284–285° on recrystallization. In the infrared this was essentially identical with the undeuterated compound, except for the presence of a C–D stretching band at 4.4 μ. In the n.m.r. the τ 4.73 band was absent.

Heptaphenylcycloheptatrienyl Anion. Treatment[25] of heptaphenyltropylium bromide (1.00 g.) with excess potassium metal (0.5 g.) suspended in 25 ml. of dry ether under argon for 3 hr. afforded a bluish purple precipitate of the potassium salt. This suspension was decanted from excess potassium (under N_2) into wet ether, when it instantly decolorized. Chromatography afforded 0.865 g. (98%) of heptaphenyltropylidene, m.p. 280–283°, raised to 284–285° by recrystallization; the substance was identified by infrared and mixture melting point comparisons.

When 0.50 g. (0.71 mmole) of heptaphenyltropylium bromide in 15 ml. of dimethoxyethane was stirred with 0.2 g. of potassium for *ca.* 30 min. in a sealed, degassed all-glass, Schlenkrohr,[25] a deep blue solution was formed. As soon as the initial purple tint had changed to blue, this was filtered through glass wool into a side-arm n.m.r. tube and a side-arm bulb, and both of these were sealed and removed. The n.m.r. spectrum (Figure 1) of the solution showed a broad (45 c.p.s.) multiplet at τ 3.25 in addition to solvent protons. The solution in the bulb was quenched in D_2O–ether under N_2 (by crushing the bulb) and 0.367 g. of organic material was isolated. This was chromatographed to yield 0.328 g. (89%) of heptaphenylcycloheptatriene-1-*d*, m.p. 281–283°, identified by infrared, mixture melting point, and n.m.r. (no signal at τ 4.73). A run on the same scale was performed in which the entire solution was filtered into the bulb, and a total of 0.409 g. of organic material (0.65 mmole if pure cycloheptatriene) was isolated after quenching, m.p. 265–276°. Titration of the aqueous solution with 0.100 *N* HCl required 6.40 ml. to a phenolphthalein end point, so 0.64 mmole of base had been formed.[26]

pK_a of Heptaphenylcycloheptatriene. When the cycloheptatriene was treated with potassium propylamide in propylamine under argon in a sealed system[25] the characteristic bluish purple color of the anion was produced, λ_{max} 563 mμ. A similar strong color was observed with potassium amide in ammonia. However, the anion color was quenched by fluorene, triphenylmethane, or diphenylmethane. The following is a typical experiment.

A solution of approximately 0.20 mmole of potassium *n*-propylamide was produced in 15 ml. of propylamine in one bulb of an all-glass sealed evacuated apparatus. This was then poured through a plug of glass wool into a second bulb containing 0.16 g. (0.256 mmole) of heptaphenylcycloheptatriene, when the deep bluish purple color of the anion developed. This was then tipped into a third bulb containing 0.0433 g. (0.26 mmole) of diphenylmethane; the purple color faded and was replaced with the yellowish orange of diphenylmethide ion. As a control, an excess of potassium propylamide (*ca.* 1.0 mmole) was then ad-

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(20) The propylamine acted as proton carrier, so equilibration was rapid.

(21) W. K. McEwen, *J. Am. Chem. Soc.*, **58**, 1124 (1936).

(22) H. J. Dauben, Jr., and M. R. Rifi, *ibid.*, **85**, 3041 (1963).

(23) This surprising result is reasonable only if the acid-strengthening inductive effect of seven phenyls is counterbalanced by poorer solvation in the large ion.

(24) R. Breslow and E. Mohacsi, *J. Am. Chem. Soc.*, **85**, 431 (1963).

(25) The experimental technique involved use of an interconnecting set of glass bulbs with side arms for n.m.r. tubes, etc. After charging with appropriate reagents, the entire system was evacuated and sealed.

(26) A control showed that over this time period potassium in the solvent alone does not generate an appreciable base titer.

mitted through a break seal, and the purple color (mixed with orange) was restored.

Heptaphenylcycloheptatrienyl Radical.[14] A solution of this radical was obtained by filtering the solution of heptaphenylcycloheptatrienyl anion (*vide supra*) from 0.3 g. of the tropylium bromide in 10 ml. of dimethoxyethane into a second bulb containing another 0.5 g. of heptaphenyltropylium bromide in 5 ml. of dimethoxyethane. The bluish purple color was replaced by russet; the radical was used for the paramagnetic studies below. Quenching of this solution gave neither base (titration) nor tropylidene (thin plate), but a complex mixture of organic products was formed.

Magnetic Properties. The radical solution showed the expected strong e.s.r. signal, as reported,[14] but the anion solution (from 0.5 g. of cation in 16 ml. of dimethoxyethane) showed no triplet e.s.r. signals over a temperature range of 78 to 200°K. under conditions[4,10,11] in which ground-state or low-lying triplets have been easily detected.

In the n.m.r. the anion solution above (0.045 *M* if conversion is 100%) showed phenyl hydrogens (Figure 1) and unbroadened solvent lines (half-width of τ 6.74 peak = 0.6 c.p.s., as in control). By contrast the radical solution (from a total of 0.6 g. of cation in 15 ml. of dimethoxyethane; 0.057 *M* if 100% conversion) showed no phenyl protons, and the solvent line showed 0.3 c.p.s. broadening (half-width). A 0.02 *M* solution of di-*t*-butylnitroxyl[27] in dimethoxyethane caused 0.3-c.p.s. solvent line broadening, while a 0.04 *M* solution had 0.6-c.p.s. increase in half-width.

A series of 6-ml. solutions were examined in sealed tubes on a standard Gouy balance,[28] with a 4000-gauss magnet. Di-*t*-butylnitroxyl (0.035 g. in 6 ml. of dimethoxyethane) was 8.08 ± 0.05 mg. diamagnetic, while the solvent blank was 8.67 ± 0.05 mg. diamagnetic, so 0.59 ± 0.07 mg. of paramagnetism was easily detected. A solution of the heptaphenylcycloheptatrienyl radical, prepared as described above, was tipped into a side arm up to a 6-ml. mark, and the tube was sealed off. It showed 9.58 ± 0.03 mg. of diamagnetism, while the same tube in which the solution was replaced with pure solvent showed 9.88 ± 0.03 mg. of diamagnetism. Accordingly the radical is 0.30 mg. net paramagnetic. When the above described heptaphenylcycloheptatrienyl anion solution was examined similarly, it was 0.09 ± 0.04 mg. more diamagnetic than the solvent blank in the same tube; the same blank was obtained by simply quenching the anion with a drop of water.

Reaction of Heptaphenylcycloheptatrienyl Anion with Potassium. When heptaphenyltropylium bromide (1.4 g., 0.002 mole) was stirred in a sealed evacuated apparatus with 0.5 g. of potassium in 80 ml. of dimethoxyethane, the initial orange cation went to purple anion in about 20 min. and this then slowly turned reddish brown. At the end of 4 hr. the solution was filtered into a glass bulb which was sealed off, and this was then cracked under (oxygen-free) ether–water in a nitrogen box. Titration of the aqueous solution showed, after correction for a small amount of base formed from solvent and potassium under these conditions, that 4.9 equiv. of KOH per mole of tropylium bromide had been formed. The organic phase afforded, on chromatography, 0.838 g. (94%) of pentaphenylcyclopentadiene, m.p. 250–251°, identical with an authentic sample in all respects, and 0.145 g. (39%) of 1,2-diphenylethane, m.p. 47–49°. When this experiment was repeated, with quenching in D_2O, the pentaphenylcyclopentadiene was deuterated in its aliphatic hydrogen (n.m.r. τ 4.88) and the diphenylethane had two aliphatic deuterons (n.m.r. ratio of τ 2.95 to 7.17 was 10:1.97).

The same experiment was run for a shorter time with 1.2 g. (0.0017 mole) of cation, filtering 10 min. after the first appearance of the blue anion color when the solution was reddish purple. Only 2.4 equiv. of base were formed, and 0.649 g. (85% yield) of pentaphenylcyclopentadiene, 0.168 g. (55% yield) of *trans*-stilbene, along with a trace of diphenylethane and of heptaphenylcycloheptatriene and 0.066 g. of hexaphenylbenzene. When the quenching was performed with D_2O, the stilbene protons were still protium (τ 2.94 to 3.21 ratio was 10:1.9) but the aliphatic cyclopentadiene proton was a deuteron. *trans*-Stilbene (0.683 g., 0.00378 mole) in 40 ml. of dimethoxyethane with 0.3 g. of potassium for 4 hr., quenched (after filtering as above) in D_2O, afforded diphenylethane (0.652 g., 0.00358 mole) with two aliphatic deuterons (τ 2.95, 7.17 was 10:2). Treatment of hexaphenylbenzene with potassium under the standard conditions afforded a mixture which contained no detectable (thin layer chromatography) pentaphenylcyclopentadiene.

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(27) A. K. Hoffman and A. T. Henderson, *J. Am. Chem. Soc.*, **83**, 4671 (1961).

(28) Repeated measurements and several runs were performed with good agreement in each case.