[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TEXAS CHRISTIAN UNIVERSITY, FORT WORTH, TEXAS]

The Proton Magnetic Resonance Spectra of Three Fulvenes

BY WILLIAM B. SMITH AND BEN A. SHOULDERS

RECEIVED FEBRUARY 27, 1964

The proton magnetic resonance spectra of 6,6-dimethylfulvene, 6,6-dibenzylfulvene, and 6,6-diphenylfulvene have been studied in some detail, and the relevant chemical shifts and coupling constants have been determined. As might be expected, the ring proton coupling constants do not vary widely. However, the chemical shifts between the protons on the ring show a marked increase in the order given above.

The bright colors and considerable chemical reactivity of the fulvenes have aroused the interests of chemists for a number of years, and the synthesis and properties of a number of fulvenes have been reported.[1] The fact that these substances readily undergo the Diels–Alder reaction and show both addition and substitution reactions with halogens suggests that chemically the fulvenes belong on the borderline between the conjugated dienes and true aromatic compounds.

For the physical chemist, the fulvenes have been of great interest because they represent relatively simple, nonalternate hydrocarbons which are readily amenable to quantum mechanical treatment by either the valence bond or molecular orbital treatment. Thus, the rather large dipole moments found for 6,6-dimethylfulvene and 6,6-diphenylfulvene have been accounted for by several different refinements on HMO type calculations on fulvene itself.[2–4] Depending on the degree of approximation which one is willing to accept, one may pick any of a variety of values for not only the calculated dipole moments but also for such quantities as the charge densities and π-bond orders around the fulvene ring. These calculations agree on one point, *i.e.*, that the dipole moment of the fulvenes is a direct consequence of the electronic structure of the fulvene system, and that the moment is directed with the negative pole toward the ring.

Calculations of the delocalization energy of fulvene itself give a value which is considerably above the experimental values, as calculated from the heats of combustion, of 6,6-dimethylfulvene and 6,6-diphenylfulvene.[5,6] Dauben, however, has suggested that the difference is due primarily to a ring strain effect and has estimated a correction factor which largely reconciles the experimental and calculated values.[7] In any event, the resonance energy of the fulvene ring system of 11–12 kcal. again suggests that the fulvenes fall on that interesting borderline between the cyclic dienes (R.E. 3–5 kcal.) and true aromatic substances such as benzene (R.E. 36 kcal.).

The above considerations suggest that the proton magnetic resonance spectra of a representative group of fulvenes should be informative regarding the structures and properties of the fulvenes. It has now been well established that chemical shifts and coupling constants are a function of the π-electron densities on the carbon atoms to which the protons are attached. Consequently, we have examined in some detail the spectra produced by 6,6-dimethylfulvene, 6,6-dibenzylfulvene, and 6,6-diphenylfulvene.

Experimental

The fulvenes used in this study were prepared by the method of Crane, Boord, and Henne[8] from cyclopentadiene and the appropriate ketones. 6,6-Dimethylfulvene was carefully purified by vacuum distillation and was subsequently redistilled in an evacuated H-tube before each determination. 6,6-Diphenylfulvene was prepared in the same fashion and was carefully recrystallized from methanol before use; m.p. 80–80.5 (reported[9] m.p. 80–80.5°). The preparation of 6,6-dibenzylfulvene has not previously been reported in the literature. The same method[8] was used starting from cyclopentadiene and 1,3-diphenylpropanone. The product was crystallized several times from methanol to give yellow crystals m.p. 84–85°.

Anal. Calcd. for $C_{20}H_{18}$; H, 7.02. Found: H, 6.65 by means of p.m.r.[10,10a]

All p.m.r. spectra were determined using a Varian A-60 at the normal operating temperature of the probe (*ca.* 43°). All samples were degassed. The resolution of the instrument was found consistently to be 0.3 c.p.s. Dimethylfulvene was run as the pure liquid and in solutions of carbon tetrachloride and dimethyl sulfoxide using tetramethylsilane as an internal standard. The chemical shifts are given in Table I and the pertinent coupling constants in Table II. All line positions used in the calculations were the averages of four to six different determinations. The chemical shifts of related compounds as determined by us are also included in Table I as well as certain pertinent values taken from the literature. Pure liquid dimethylfulvene was used for the C^{13}–H results, and concentrated solutions of dibenzylfulvene in carbon tetrachloride were used also. These results are reported in the text.

Results

The proton magnetic resonance spectrum of 6,6-diphenylfulvene consists of two regions corresponding to an absorption due to the phenyl groups and another due to the ring protons. The latter displayed the characteristic symmetry expected of an A_2B_2 system. The downfield portion of the ring spectrum in dimethyl sulfoxide solution is shown in Fig. 1.

The details of the treatment of A_2B_2 spectra have been amply covered elsewhere and will not be repeated here.[11–13] The pertinent terms to be considered and the structure and numbering of the fulvene ring are given:

---

(1) For reviews on fulvene chemistry see (a) J. H. Day, *Chem. Rev.*, **53**, 167 (1953); (b) E. D. Bergman in "Progress in Organic Chemistry," Vol. 3, J. W. Cook, Ed., Butterworth Scientific Publications, London, 1955.

(2) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).

(3) G. Berthier, *ibid.*, **21**, 953 (1953).

(4) A. Julg and A. Pullman, *J. chim. phys.*, **50**, 459 (1953).

(5) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 243.

(6) J. H. Day and C. Oestreich, *J. Org. Chem.*, **22**, 214 (1957).

(7) H. J. Dauben, Jr., as quoted in ref. 5, p. 243.

(8) G. Crane, C. E. Boord, and A. L. Henne, *J. Am. Chem. Soc.*, **67**, 1237 (1945).

(9) E. D. Bergmann and E. F. Christiani, *Ber.*, **63B**, 2563 (1930).

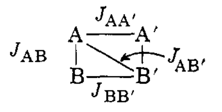
(10) W. B. Smith, *J. Chem. Educ.*, **41**, 97 (1964).

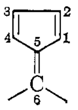
(10a) NOTE ADDED IN PROOF.—Fulvenes add oxygen rapidly. Duplicate analysis made by Galbraith Laboratories, Knoxville, Tenn. *Anal.* Calcd. for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 91.80, 91.61; H, 6.99, 6.92.

(11) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

(12) K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962.

(13) D. M. Grant, R. C. Hirst, and H. S. Gutowsky, *J. Chem. Phys.*, **38**, 470 (1963).





$$
\begin{aligned}
N &= J_{AB} + J_{AB'}\\
L &= J_{AB} - J_{AB'}\\
K &= J_{AA} + J_{BB'}\\
M &= J_{AA} - J_{BB'}\\
\Delta_{AB} &= \nu_A - \nu_B
\end{aligned}
$$

Following the suggestion of Professor Wiberg, the lines in the ring portion of the diphenylfulvene spectrum were assigned on the basis that the ring spectrum approximated an A_2X_2 system. This assignment is shown in Fig. 1 for the downfield half of the ring spectrum. The sum and difference relationships for the lines 1 and 3 gave values of N and Δ_{AB} directly.[11-13] Similarly, L and M were determined from the sum and difference relationships of lines 9 and 11. The value of K was approximated from the frequency difference of lines 5 and 6,[13] and these values were used in setting up the 4 × 4 matrix which appears in the solution of the A_2B_2 case. The eigenvalues and eigenvectors were then determined using an IBM 1620 computer. A check between line positions and intensities for the calculated and experimental values showed that a very satisfactory fit had been achieved in this fashion with all line positions being found to check out to 0.1 c.p.s. or better. Values of $J_{AA'}$, J_{AB}, $J_{BB'}$, and $J_{AB'}$ were then obtained. These coupling constants were then assigned to the appropriate hydrogen nuclei on the assumption that the fulvene ring system approximated the situations found in thiophene, furan, and pyrrole.[13,14] The J-values are given in Table II along with the values of Δ_{AB}.

In the subsequent calculations on dimethyl- and dibenzylfulvene all calculations were carried out with the aid of the 1620 computer using the FREQUINT A 1620 program.[15] A check of the program was made using the data for diphenylfulvene. The computer results and the calculations above agreed exactly.

Two items of interest should be mentioned regarding the spectrum of diphenylfulvene. First, the spectrum of the ring portion of diphenylfulvene was completely unaltered on examination in dimethyl sulfoxide at 100°. Second, when the spectrum was determined in carbon tetrachloride solution the major alteration was in Δ_{AB} which decreased to a value of 17.0 ± 0.1 c.p.s. Rough calculations on the spectrum in this solvent revealed little or no change in the value of the coupling constants.

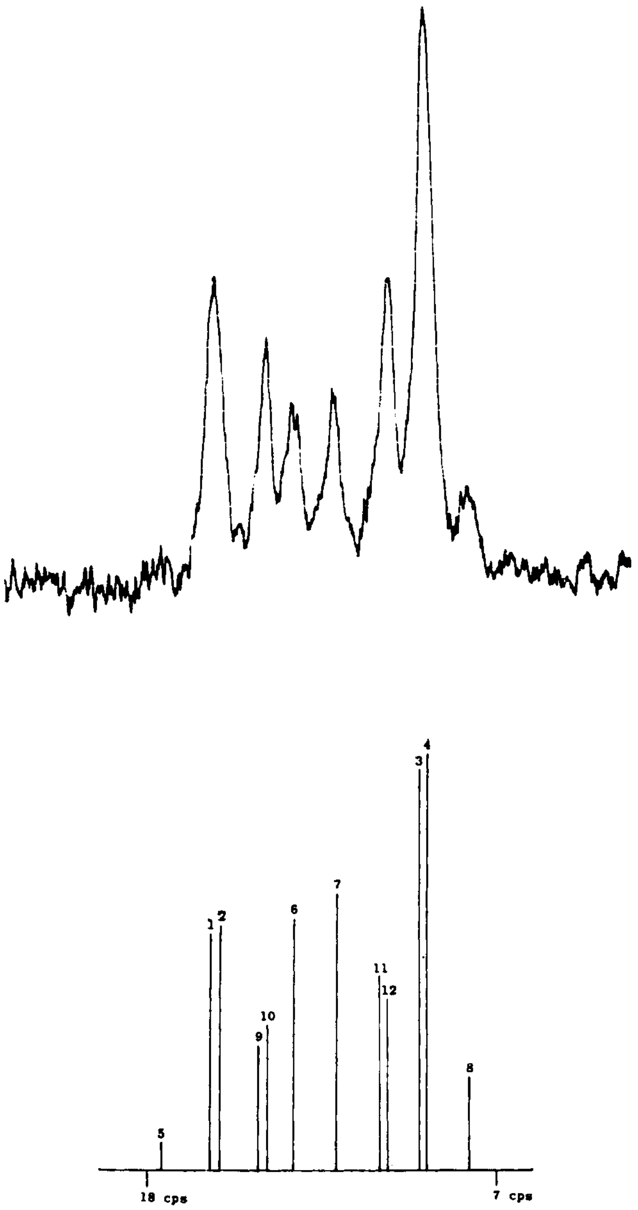


Fig. 1.—The downfield portion of the ring proton spectrum of 6,6-diphenylfulvene in dimethyl sulfoxide. Frequencies are given in c.p.s. downfield from the line of centers in the A_2B_2 spectrum.

The p.m.r. spectrum of dimethylfulvene was consiberably different from that for diphenylfulvene. Both the pure liquid and solutions in carbon tetrachloride showed only two bands characteristic of the ring protons and those of the methyl groups (chemical shifts given in Table I). On dilution with dimethyl sulfoxide the ring proton spectrum of dimethylfulvene splits into two halfs which are only roughly symmetrical (Fig. 2). While the downfield portion shows well defined band structure, the upfield portion is badly washed out. The fact that splitting occurs in polar dimethyl sulfoxide but not in carbon tetrachloride is indicative of a strong dipole–dipole interaction in the former solvent. On continued dilution the position of the downfield portion remains constant while the upfield portion moves slightly further upfield.

The washing out of the upfield portion is most likely due to a long range coupling between the protons at C-1 and -4 on the ring with the methyl protons. Such long range couplings through five bonds in unsaturated systems are now well established. Substantiation for this contention was obtained by the observation that the methyl group was broadened and split slightly into a triplet when the spectrum was run in pyridine (the absorption of dimethyl sulfoxide obscures the methyl absorption in the fulvene).

Properly speaking, the spectrum for dimethylfulvene should be treated as an $A_2B_2X_6$ system. Such a task would be quite formidable being beyond the capacity of our four-spin computer program. We have, therefore, treated the downfield portion of the dimethylfulvene ring spectrum as though it were half of a true A_2B_2

---

(14) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 905 (1961).

(15) We wish to express our gratitude to Professor P. C. Lauterbur who provided us with the FREQUINT A 1620 program. The aid of the staff of the T. C. U. Computer Center is also gratefully acknowledged.

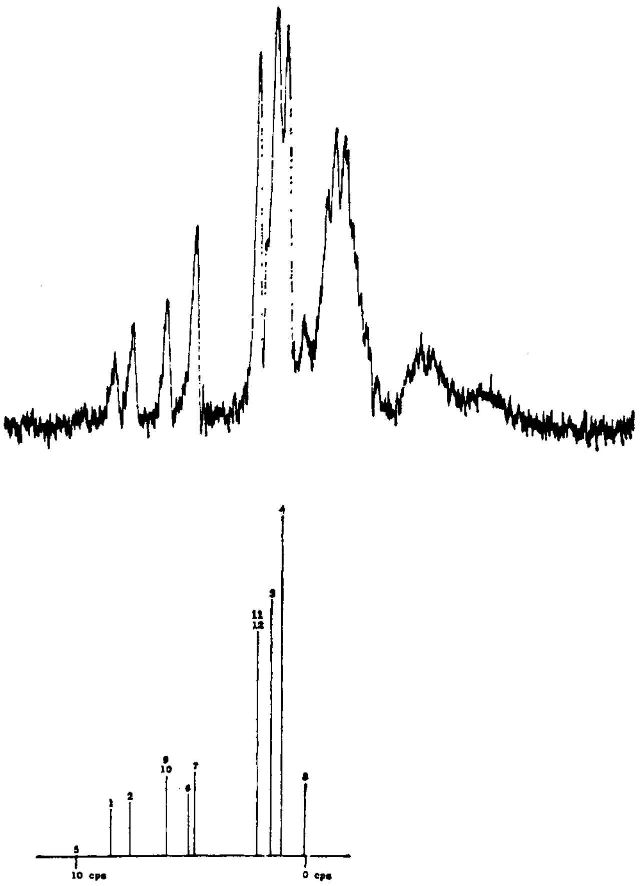


Fig. 2.—The ring proton spectrum of 6,6-dimethylfulvene in dimethyl sulfoxide solution.

system. Such an approximation is reasonable for the perturbation of the spins on C-2 and -3 due to the methyl protons should be slight.

The most noticeable difference in comparing the spectra of diphenylfulvene and dimethylfulvene is an alteration in Δ_{AB}. The results of such a change using the coupling parameters for diphenylfulvene is shown in Fig. 3. As can be seen, reduction of Δ_{AB} causes a progressive shift of the spectrum toward the line of centers in the A_2B_2 spectrum. As Δ_{AB} is reduced, lines 6 and 7 move together and at lower values of Δ_{AB} cross over each other. At the same time, line 8 moves toward the center and ultimately crosses.

TABLE I

CHEMICAL SHIFTS (τ) IN CARBON TETRACHLORIDE

Compound	$CH_2(CH_3)$	Ring[a]	Phenyl[b]
Dimethylfulvene	7.87	3.70	. .
Dibenzylfulvene	6.34	3.48	2.85
Diphenylfulvene	. .	3.70	2.72
Isobutylene	8.30[c]	. .	. .
Acetone	7.91	. .	. .
Diphenylethylene	. .	. .	2.82
Benzophenone	. .	. .	2.51
Allylbenzene	6.70	. .	2.91
Benzene	. .	. .	2.75
Toluene	7.66	. .	2.90
Cyclopentadiene	. .	3.58[c]	. .
Spiro[2.4]heptadiene-1,3	. .	3.78[d]	. .

[a] Taken from the center of the band where splitting occurs. [b] Taken from the strongest peak where splitting occurs. [c] G. V. D. Tiers, "Characteristic Nuclear Magnetic Shielding Values, etc.," Minnesota Mining and Manufacturing Co., 1958. [d] Reference 24.

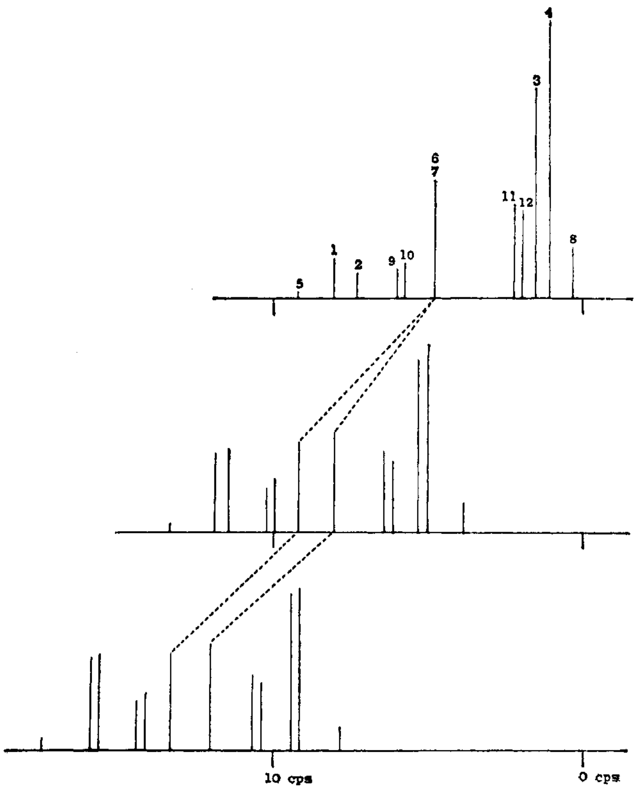


Fig. 3.—The effect of changing Δ_{AB} on the A_2B_2 spectrum (downfield half only shown). The coupling constants are those for 6,6-diphenylfulvene. The chemical shifts are: 24.8 c.p.s. (lower); 15 c.p.s. (middle); and 7 c.p.s. (upper).

Since no major alteration of coupling constants would be expected in going from diphenylfulvene to dimethylfulvene, lines in the dimethylfulvene spectrum were assigned from Fig. 3. Using the sum and difference relationships for lines 1–3 and 9–11, respectively, gave two slightly different values for Δ_{AB}. Consistent values were obtained by displacing the center line slightly downfield from the geometric center of the spectrum. In view of the effect exerted by the solvent on the upfield portion of the spectrum this seems justifiable. Values of N, L, M, and K were then determined as before. The values given in Table II gave a good fit for the experimental spectrum (Fig. 2) with all lines but 5 matched by 0.1 c.p.s. or better. As can be seen, line 5 is rather ill defined and the fit here was estimated to be off by 0.3 c.p.s.

TABLE II

SPECTRAL PARAMETERS IN DIMETHYL SULFOXIDE[a]

Compound	Δ_{AB}	J_{12}	J_{23}	J_{14}	J_{13}
Dimethylfulvene	7.30	5.45	2.40	2.40	1.50
Dibenzylfulvene	14.66	5.24	1.97	1.94	1.90
Diphenylfulvene	24.54	5.17	2.21	1.94	1.38
Spiro[2.4]heptadiene-1,3[24] (CCl_4)	24.8	5.2	2.1	2.0	1.5

[a] All values in c.p.s. at 60 Mc./sec.

The spectrum of dibenzylfulvene resembles that of dimethylfulvene. Analysis by the method above indicated a value of Δ_{AB} intermediate between the two previous cases. The parameters given in Table II fit the spectrum quite well. However, lines 4 and 6 were off by 0.4–0.5 c.p.s. Further adjustment of the parameters did not improve the fit, and it was assumed that a perturbation introduced by the methylene groups was responsible for this minor discrepancy.

The C^{13}–H splitting for the methyl groups and ring protons in dimethylfulvene were determined on the pure liquid to be 127.1 and 167 c.p.s., respectively. The ring proton–C^{13} bands were broad, and the value given here was taken as the difference between the centers. Similar measurements on the methylene band in dibenzylfulvene were made on concentrated solutions of the fulvene in carbon tetrachloride. A value of 128.5 c.p.s. was obtained. For comparison, the C^{13}–H splitting of the methylene group in allylbenzene was determined as 127.4 c.p.s. The values given here were the average of several determinations and are good to ±0.5 c.p.s.

Discussion

The chemical shifts of the ring protons in the fulvenes are a function of a variety of affects, some operating in direct opposition to each other. The various molecular orbital calculations on fulvene itself suggest that there is an appreciable drift of electrons from the exocyclic double bond into the ring. This accounts for the dipole moment of the fulvenes and the enhanced resonance energy of these compounds over cyclopentadiene. On one hand, this drift suggests that the protons on the ring should experience an increased shielding due to this greater electron density. On the other hand, a counteracting deshielding due to the increased significance of ring current effects would also be expected.

The latter effect should be of relatively minor importance, however. Fraenkel and co-workers[16] have measured the shift of cyclopentadiene and sodium cyclopentadiene relative to benzene and have concluded that the charge effect is considerably more important than ring current effects. Thus, one might conclude that the upfield shift of the ring proton absorption in dimethyl- and diphenylfulvene from cyclopentadiene reflects the greater electron density in the fulvene ring. The fact that the absorption due to the ring protons in dibenzylfulvene is downfield from cyclopentadiene, however, suggests that this premise alone may not account for the result. Unfortunately, the dipole moment and resonance energy for dibenzylfulvene have not been measured.

The molecular orbital calculations on fulvene itself have been reviewed in the literature.[1] All of the various approximations used indicate an excess of charge in the ring, and most predict that C-1 will be slightly more negative than C-2. Fraenkel and coworkers[16] and Shaefer and Schneider[17] have concluded that shifts of about 10 p.p.m. per electron are to be expected. The results on dimethylfulvene indicate that there is no perceptible charge differences among the ring protons in this compound since no difference in chemical shift was observed between the pure liquid and solutions in carbon tetrachloride. Of the results reported for fulvene, this observation accords best with the SCF calculations of Berthier[3] which predict a charge difference of only 0.001 between C-1 and C-2. Since the methyl group in toluene causes no difference in chemical shifts among the phenyl protons, one may assume that no serious perturbation due to the methyl groups occurs in dimethylfulvene.[17a]

While the center of the ring absorption for diphenylfulvene occurs at the same frequency as that of dimethylfulvene, the ring protons show considerably different chemical shifts. This observation may be accounted for on the basis of a difference in shielding introduced by the diamagnetic anisotropy of the phenyl groups. Coates and Sutton[19] have determined by dipole moment measurements that the phenyl groups in 1,1-diphenylethylene are inclined at about a 30° angle to the plane of the double bond. Presumably, the same geometry would be found in diphenylfulvene. If so, then the hydrogens on the fulvene ring will experience a difference in shielding due to the phenyl groups. Using Dreiding models as a measure of the appropriate distances, the difference in shielding between the C-1 proton and the C-2 proton were calculated using the method of Waugh and Fessenden[20] and that of Johnson and Bovey.[21] The two methods gave chemical shift differences of 12 and 25 c.p.s., respectively, results in good agreement with the measured 17 c.p.s. in carbon tetrachloride.

In dibenzylfulvene the phenyl groups have a considerably greater amount of freedom to rotate (at least from inspection of the Dreiding model). Consequently, no meaningful calculations can be carried out. However, it may be assumed that the difference in chemical shifts in the ring protons is again due to an anisotropic effect from the phenyl groups. The fact that the value is intermediate between dimethyl- and diphenylfulvene is probably fortuitous.

It now seems well established that vicinal coupling constants reflect the aromaticity of the bond joining the carbons. Thus various cyclohexenes show olefinic proton couplings of 9–11 c.p.s.[22] while *ortho* coupling constants in substituted benzenes range from 5–9 c.p.s.[11] A similar diminution has been noted in the five-membered rings. The olefinic coupling in cyclopentene is 5.1–5.4 c.p.s.[23,24] The appropriate coupling constant in a substituted cyclopentadiene, spiro[2,4]-heptadiene–1,3, has been reported as 5.2 c.p.s.[25] In contrast, the *ortho* coupling constant in the five-membered ring in azulene has been determined as 3.5 c.p.s.[11] and the coupling in the pentalenyl dianion as 3.0 c.p.s.[26]

It is apparent from the values in Table II that the coupling constants in the three fulvenes reported here are in close agreement with the results reported for the diene of Dischler and Englert.[25] As far as the coupling

---

[16] G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960).

[17] T. Shaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

[17a] NOTE ADDED IN PROOF.—Several weeks after this manuscript was accepted, Professor E. Heilbronner of Zurich kindly sent us a copy of the spectrum of fulvene itself which had been obtained by his associates. Subsequently, Mr. John Wyss of this laboratory prepared fulvene from cyclopentadiene and formalin and isolated the pure material by v.p.c. The methylene absorption and the center of the ring proton absorption appeared at τ 4.00 (4.01) and 3.66 (3.56) in carbon tetrachloride (dimethyl sulfoxide). Both the ring-proton bands and the methylene band showed a complex pattern due to the long-range coupling effects. The value of Δ_{AB} was estimated as 16–18 c.p.s. in each solvent. Thus, the strong solvent effect observed with the three fulvenes above was absent in fulvene itself. The conclusions of the above paragraph need to be reconsidered in the light of this more recent information.

The value of the C^{13}–H coupling for the methylene group was determined as 170 ± 1 c.p.s., a value in keeping with the positive nature of C-6.[18]

[18] C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2198 (1962).

[19] G. E. Coates and L. E. Sutton, *J. Chem. Soc.*, 567 (1942).

[20] J. W. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79**, 846 (1957).

[21] C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

[22] O. L. Chapman, *J. Am. Chem. Soc.*, **85**, 2014 (1963).

[23] G. V. Smith and H. Kriloff, *ibid.*, **85**, 2016 (1963).

[24] P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2017 (1963).

[25] B. Dischler and G. Englert, *Z. Naturforsch.*, **16a**, 1180 (1961).

[26] T. J. Katz and M. Rosenberger, *J. Am. Chem. Soc.*, **84**, 865 (1962).

constants are concerned, it is evident that the fulvenes are better treated as dienes than as aromatic systems.

The C^{13}–H spin coupling results are informative regarding the molecular orbital predictions that the exocyclic carbon-6 in the fulvene structure should bear a positive charge. Juan and Gutowsky[18] have derived relationships between J_{CH}, the s-character of the hybrid orbitals of the C–H bond (a_H^2), and a term Δ_X which measures the "affinity" of a substituent X for the carbon 2s-character. They have shown that the value of Δ_X increases with the electronegativity of the substituent and that the effects of multiple substituents on a_H^2 are additive. Using their relationships and the value of the J_{CH} for the methyl group in dimethylfulvene one calculates a value of Δ_X of 0.0168 for the fulvene residue. Using their additivity relationship and their value for a phenyl group gives a calculated value for the methylene group in dibenzylfulvene of a_H^2 of 0.257 which agrees well with the experimental value of 0.256.

A similar set of calculations was carried out using J_{CH} for the methyl group in isobutylene (126 c.p.s.)[27] and our values for allylbenzene. The value of Δ_X for the olefin substituent was found to be 0.008. Calculated and observed values for the allylbenzene methylene were a_H^2 0.254 and 0.255, respectively.

The values of Δ_X of 0.0168 for the fulvene residue and 0.008 for the olefin residue point up the greater electronegativity of the former group, a result in keeping with the enhanced positive character of C-6.

Acknowledgment.—We wish to acknowledge the generous financial aid of the Robert A. Welch Foundation in support of this work. The helpful suggestions of Dr. K. B. Wiberg, Dr. Wallace Brey, Jr., and Dr. J. N. Shoolery are also gratefully acknowledged.

---

[27] N. Muller and D. E. Pritchard, *J. Am. Chem. Soc.*, **31**, 1471 (1961).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO, BOULDER, COLO.]

Bridged Polycyclic Compounds. XXVI. The Solvolysis of Some 4-Chlorodibenzobicyclo[3.2.1]octadienes[1]

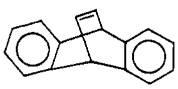
BY STANLEY J. CRISTOL AND DENNIS D. TANNER

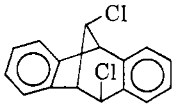
RECEIVED FEBRUARY 24, 1964

The solvolyses of *exo*- (II) and *endo*-4-*syn*-8-dichlorodibenzobicyclo[3.2.1]octadiene (III) and of *exo*-4-chlorodibenzobicyclo[3.2.1]octadiene (V) have been studied. Acetolysis of III and V proceeds with good first-order kinetics to give the *exo*-acetate IV and its dichloro analog, respectively. The acetolysis of II to IV is accompanied by epimerization to III, involving ion-pair intermediates. Solvolysis of II in pivalic acid gives the *endo*-pivalate. Various carbonium ions are considered as intermediates, and it is concluded that a classical benzylic carbonium ion can accommodate the results.

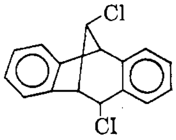
Introduction

In a recent study[2] of the ionic chlorination of 9,10-dihydro-9,10-ethenoanthracene (I) the sole products of the reaction were found to be *exo*- and *endo*-4-*syn*-8-dichlorodibenzobicyclo[3.2.1]octadiene (II and III).


I



II

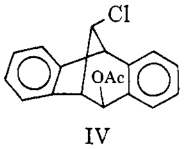


III

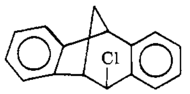
The major isomer, compound II, produced in 88% yield, was shown to be the less stable of the two dichlorides. In view of our interest in such compounds, we have investigated the rates and products of solvolysis of the two isomers.

Results

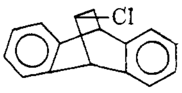
Solvolysis rates were followed in dry acetic acid, with added potassium acetate. A plot of the experimental data for the acetolysis of the *endo* isomer III at 74.74° gave a constant first-order rate which showed no observable trends. Only one product was obtained from solvolysis of III; this product was identified as *syn*-8-chlorodibenzobicyclo[3.2.1]octadien-*exo*-2-yl acetate (IV).[2] The specific rate constant obtained graphically was 1.68×10^{-6} sec.$^{-1}$. An average of three kinetic runs was used to obtain this value.



IV



V



VI

When the *exo* isomer II was solvolyzed, a first-order plot of the experimental data showed a considerable downward drift. The steadily decreasing rate was shown to be caused by the concomitant isomerization of the *exo* to the *endo* isomer during the course of the solvolysis. Thus, when a sample of the *exo* isomer was allowed to react to about 50% completion, the remaining (46%) dichloride which was recovered was the *endo* isomer III. The acetolysis product appeared to be entirely *syn*-8-chlorodibenzobicyclo[3.2.1]octadien-*exo*-2-yl acetate (IV), the same product obtained from the solvolysis of III.

This behavior is analogous to that observed in the acetolysis of α,α-dimethylallyl chloride,[3] and the same kinetic procedure was used in this work to calculate the specific rate of solvolysis for II and the rate of isomerization of II to III, except that an analytical procedure, rather than a graphical one, was used to calculate the specific reaction rate constants.[4]

---

[1] Previous paper in series: S. J. Cristol and D. I. Davies, *J. Org. Chem.*, **29**, 1282 (1964). This work was reported at the 18th National Organic Symposium of the American Chemical Society, Columbus, Ohio, June, 1963.

[2] S. J. Cristol, R. P. Arganbright, and D. D. Tanner, *J. Org. Chem.*, **28**, 1374 (1963).

[3] W. G. Young, S. Winstein, and H. L. Goering, *J. Am. Chem. Soc.*, **73**, 1958 (1951).

[4] Details of this procedure are given in the Ph.D. Thesis of D. D. Tanner, University of Colorado, 1961.