of the calculated values. The PMT-substituted compounds were generously provided by Dr. J. W. Gates, Jr.[7,15]

The position of substitution in the 2-methyl-1,4-benzoquinone addition of *p*-toluenethiol, benzenesulfinate, and HPMT was established by the characteristic nmr pattern, as previously described for the PMT derivative.[15]

We found that the easily oxidized *p*-tolyl hydroquinone sulfides could be recrystallized by solution in a very small volume of chloroform followed by the addition of a large excess of ligroin (63-75°).

Acknowledgment.—We wish to express our appreciation to Dr. T. H. Regan for the nmr spectra and Mr. D. F. Ketchum for the microanalyses. Mr. G. J. Brien assisted by making several of the electrochemical determinations.

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[15] H. S. Wilgus III, E. Frauenglass, E. T. Jones, R. F. Porter, and J. W. Gates, Jr., *J. Org. Chem.*, **29**, 594 (1964).

The Condensation of Acetone with Methylcyclopentadiene. The Use of Tetracyanoethylene Adducts for Structure Proofs

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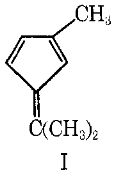
The condensation of methylcyclopentadiene with acetone has been shown to yield 2,6,6-trimethylfulvene as the major product. The structure of the molecule was established uniquely by the nmr spectrum of the tetracyanoethylene adduct. The spectra of several other TCNE adducts were analyzed and found to provide a convenient method for structure assessment of cyclic dienes.

The chemical shift assignments of the ring protons in 6,6-dimethylfulvene are open to question since they are based mainly on arguments regarding long-range couplings between the exocyclic methyls and the ring protons.[2] In an effort to clarify this issue we became interested in preparing the ring-methylated derivatives of 6,6-dimethylfulvene. While the initial goal was not achieved using these compounds as will become evident, the proof of structure of the condensation products proved an interesting exercise.[3]

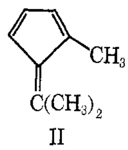
Results and Discussion

The reaction of methylcyclopentadiene with acetone was carried out by the method of Crane, Boord, and Henne.[4] The complex reaction product was fractionated by vpc and gave two compounds which had the proper nmr spectra and mass spectra for trimethylfulvenes. The major isomer was eluted first and was formed in about three times the amount of the minor. The total yield of both was estimated as 40-50% of the starting methylcyclopentadiene by the vpc analysis.

The condensation of acetone with methylcyclopentadiene most reasonably may lead to either I, II, or both. The nmr spectra of both products were made extremely complex by long-range couplings to all methyls on the part of the ring protons. Furthermore, the methyl groups had such similar chemical shifts that no selective decoupling of the methyl protons could be carried out. However, decoupling of all methyl protons gave typical ABC patterns for both major and minor isomers. The major isomer (CCl_4) gave $J_{AB} = 5.2$, $J_{AC} = 1.8$, $J_{BC} = 2.1$ Hz and δ (ppm) 6.00, 6.14, and 6.31, respectively.[5] The minor isomer essentially gave the same coupling constants with chemical shifts at δ 5.99, 6.09, and 6.24, respectively.[5] Consideration of typical fulvene nmr parameters[2] allows no decision between I and II.

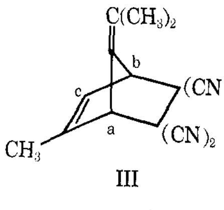


I

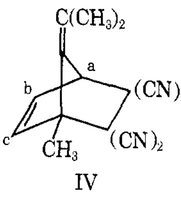


II

Subsequently the major isomer was allowed to react with tetracyanoethylene, and the product was analyzed. Again, the likely structures are III or IV. The TCNE adduct of the major fulvene isomer showed only one olefinic proton but two bridgehead protons, thus ruling in favor of III *vs.* IV and confirming the structure of the major isomer as I. The TCNE adduct of the minor isomer gave an extremely complex nmr spectrum which suggested that polymerization or decomposition had occurred. The minor isomer is tentatively assigned the structure II on the basis of its mass spectrum and nmr evidence.



III



IV

Nmr Spectra of the TCNE Adducts.—The use of TCNE to derivatize dienes has been known for some years.[6] We have found the use of perdeuterioacetonitrile to be particularly convenient as a solvent for these systems and often prepared them *in situ* in the nmr tube.

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[1] Taken in part from the Senior Honors paper of S. Biesemeier.

[2] (a) W. B. Smith and B. A. Shoulders, *J. Amer. Chem. Soc.*, **86**, 3118 (1964); (b) M. L. Heffernan and A. J. Jones, *Aust. J. Chem.*, **19**, 1813 (1966).

[3] We have recently arrived at a satisfactory solution to this problem by spin decoupling experiments on 2-(dimethylmethylol)-6,6-dimethylfulvene: W. B. Smith and C. Gonzalez, *J. Org. Chem.*, **28**, 3541 (1963). When the 6,6-dimethyl protons are decoupled, the three ring protons form an ABC pattern which was analyzed to give $J_{13} = 1.73$, $J_{14} = 2.29$, $J_{34} = 5.43$ Hz, and δ_1 (CCl_4) 6.15, δ_3 6.51, δ_4 6.45. The fact that on decoupling only the lines associated with one proton sharpen confirms that long-range coupling of the exocyclic methyls in dimethylfulvene is stronger to H-2 and H-3 than to the nearer H-1 and H-4 in agreement with ref 2b.

[4] G. Crane, E. Boord, and A. L. Henne, *ibid.*, **67**, 1237 (1945).

[5] The results were obtained by J. L. Roark of these laboratories to whom we express our appreciation.

[6] W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *J. Amer. Chem. Soc.*, **80**, 2783 (1958).

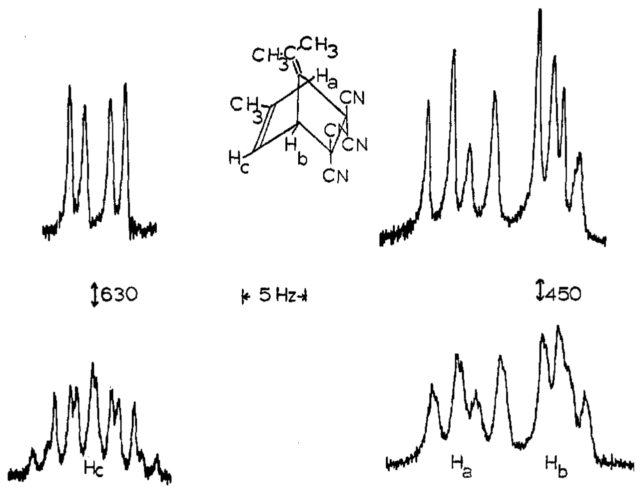


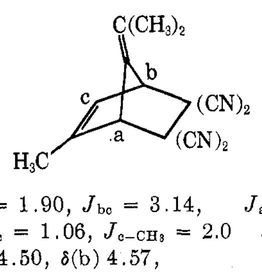
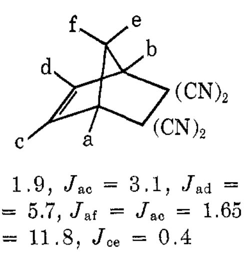
Figure 1.—100-MHz spectrum of the adduct shown. The bottom spectrum is the normal scan, while the top shows the bridgehead and olefinic protons with the methyl group decoupled.

The spectra of the adducts of 6,6-dimethylfulvene and 6,6-diphenylfulvene both consisted of three sets of nmr bands. A sharp methyl singlet at δ 1.67 and the phenyl "Christmas tree" at δ 7.4 were as expected. The bridgehead protons at δ 4.71 and 4.60 and the olefinic protons at δ 6.82 and 6.91, respectively, appeared on a broad scale as 1:2:1 triplets. However, when scale expanded the center band was slightly split into two bands of equal intensity. The significance of this is discussed below.

The details of the spectrum of I are shown in Figure 1 and, as expected, coupling to the ring methyl is evident. When spin decoupled from the methyl the olefinic proton and the two bridgehead protons formed a well-defined ABX system which was analyzed according to Becker,[7] then refined by computer. These results are in Table I.

TABLE I

NMR PARAMETERS OF THE TCNE ADDUCTS[a]

	
J_{ab} = 1.90, J_{bc} = 3.14, J_{ac} = 1.06, J_{c-CH_3} = 2.0 δ(a) 4.50, δ(b) 4.57, δ(c) 6.30, $\delta(CH_3)$ 2.07 (doublet), $\delta(CH_3)_2$ 1.74 (singlet)	J_{ab} = 1.9, J_{ac} = 3.1, J_{ad} = 0.9, J_{cd} = 5.7, J_{af} = J_{ae} = 1.65, J_{ef} = 11.8, J_{ce} = 0.4 δ_a 4.14, δ_c 6.65, δ_e 2.07, δ_f 2.13

[a] *J* values given in hertz.

There are a number of different ways that the lines in an ABX system may be assigned but invariably we were forced to conclude that J_{ab} in I is 1.90 Hz if the other coupling constants were to agree with the usual results in norbornenes.[8]

The question of whether the coupling between bridgehead hydrogens is real or not appears to be unsolved to date. King and Butler[9] first reported a J_{ab} value of ±1.4 Hz for some derivatives of 7-isopropylidenenorborene. Similar values have been reported for some oxanorbornanes.[10] However, Laszlo and Schleyer[8] have examined a number of substituted norbornenes and concluded that J_{ab} was not greater than 0.5 Hz. They reported a partial analysis of the TCNE adduct of cyclopentadiene. Because of our observations on J_{ab} we also have examined the cyclopentadiene adduct.

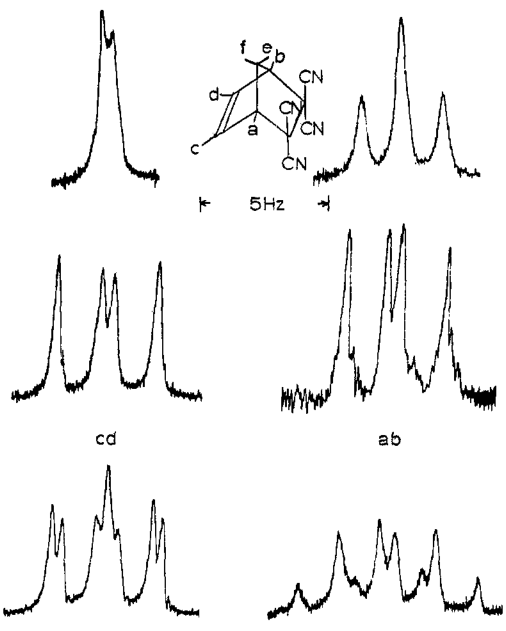


Figure 2.—100-MHz spectrum of compound shown. The normal spectrum of the olefinic (left) and bridgehead protons (right) is shown at the bottom. In the middle the scan is repeated with decoupling of the methylene protons. The top left shows c–d while decoupling a–b. The top right shows a–b while decoupling c–d.

The spectrum of the TCNE adduct of cyclopentadiene has been published in part previously.[8] However, the 100-MHz high-resolution spectrum reveals many more details. The bridgehead and olefinic protons are shown in Figure 2. Decoupling of these protons reduced the bridging methylene to a simple AB system. Similarly, decoupling of the methylene protons gave an AA'XX' spectrum for the bridgehead and olefinic protons. The splitting patterns here were virtually superimposable on the spectra for the dimethyl and diphenylfulvene adducts.

The AA'XX' spectra for the olefinic and bridgehead protons are deceptively simple. Under the conditions in which the center band is somewhat split the separation is given by $L^2/2\,J_{dc}$ where L is $(J_{ac} - J_{ad})$.[11] Under these conditions if J_{dc} is assigned a value all other parameters may be determined. The value of J_{dc} was taken as 5.7 Hz[8] and all lines were assumed to fall under one of the eight observable lines. From this treatment one obtains J_{ac} = 3.17 J_{ad} = 0.83, and J_{ab} = 0.0 Hz. However, exploration of the possibilities of J_{ab} equal to 1.9 Hz revealed the quartet pattern to be fit equally well with the parameter set in Table I. Furthermore,

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[7] E. D. Becker, "High Resolution NMR," Academic Press, New York, N. Y., 1969, p 152.

[8] P. Lasslo and R. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964).

[9] R. W. King and P. E. Butler, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., 1962, Abstracts, p 84Q.

[10] I. Gagnaire and E. Payo-Subiza, *Bull. Soc. Chim. Fr.*, 2623 (1963).

[11] (a) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961); (b) J. N. Shoolery and B. Crawford, Jr., *J. Mol. Spectrosc.*, **1**, 270 (1957).

these values lead to the prediction of four weak lines spaced in two pairs about the center of each quartet. These are not present when J_{ab} is nil. Reexamination of the spectrum under high amplitude showed the weak lines to be present exactly as predicted. The same lines were found to be present in the spectra of the adducts from dimethyl and diphenylfulvene. Thus, *all our systems have been shown to have* a bridgehead to bridgehead proton coupling constant of ~1.9 Hz.

Conclusions

The condensation of acetone with methylcyclopentadiene yields as the major product 2,6,6-trimethylfulvene which is readily characterized by the TCNE adduct. The nmr spectra of cyclopentadiene and fulvene TCNE adducts are extremely useful for structure determination work since they are readily prepared *in situ* and display large chemical shift differences between the various types of protons.

Experimental Section[12]

Reaction of Methylcyclopentadiene with Acetone.—Methylcyclopentadiene dimer (Enjay) was cracked by distillation. The product was then redistilled to give a mixture of methylcyclopentadienes. This material (20 ml) was mixed wth 17.5 ml of acetone, and 7.5 ml of 20% potassium hydroxide in ethanol was added in 2-ml portions with swirling and cooling. The mixture was stored cold overnight and poured into water (75 ml), and the oily layer was collected. Steam distillation separated the more volatile components (about 25 g) from some tar. The distilled oil was dried over anhydrous $MgSO_4$.

Vacuum distillation caused an appreciable polymerization of the products which appear to be less stable than dimethylfulvene in all respects. Fractionation was effected by vpc over 20% Carbowax on Celite. Six bands were observed which, by retention times, appeared to be methylcyclopentadiene, acetone, dimethylfulvene, and the methylcyclopentadiene dimer(s), and a major and minor band of product. The latter two bands comprised *ca.* 50% of the mixture. The major and minor bands were trapped readily from the vpc and characterized as below.

The major isomer gave nmr (CCl_4) δ 1.99 (3 H, s, CH_3), 2.08 (6 H, s, $C(CH_3)_2$), and 6.08–6.58 (3 H, multiplet, ring H); mass spectrum *m/e* (rel intensity) 120 (43), 105 (100), 91 (34), 80 (34), 79 (60), 77 (45), 51 (44), 41 (38), 39 (65), and 27 (42).

The minor isomer was characterized by nmr (CCl_4) δ 2.19 with shoulder at 2.21 (9 H, s, CH_3 and $C(CH_3)_2$) and 6.03–6.53 (3, H, multiplet, ring H); mass spectrum *m/e* (rel intensity) 120 (45), 105 (100), 91 (36), 79 (45), 77 (41), 51 (42), 41 (39), 39 (64), and 27 (39).

Under the same conditions dimethylfulvene gives δ 2.13 (6 H, s, $C(CH_3)_2$) and 6.30 (4 H, s, ring); mass spectrum *m/e* (rel intensity) 106 (49), 91 (100), 66 (23), 65 (28), 51 (28), 50 (20), 41 (21), and 39 (53).

No attempt was made to obtain C and H analyses on the products due to their avidity for oxygen.

TCNE Adducts were prepared by reacting small amounts of the fulvene or cyclopentadiene with an excess of TCNE in either tetrahydrofuran or acetonitrile at room temperature. Sometimes the reaction was carried out in the nmr tube in the probe. Recrystallization was from a benzene–ether mixture.

Melting points were determined in sealed capillary tubes and were difficult to ascertain because of decomposition. The onset of melting for the TCNE adducts of the major isomer, minor isomer, and dimethylfulvene were 118, 127, and 133°, respectively.

Carbon, hydrogen, and nitrogen analyses were as follows.

Anal. Calcd for $C_{15}H_{12}N_4$ (major isomer): C, 72.56; H, 4.87; N, 22.57. Found: C, 72.26; H, 4.73; N, 22.53.

Anal. Calcd for $C_{15}H_{12}N_4$ (minor isomer): C, 72.56; H, 4.87; N, 22.57. Found: C, 72.34; H, 4.71; N, 22.39.

Anal. Calcd for $C_{14}H_{10}N_4$ (6,6-dimethylfulvene): C, 71.78; H, 4.30; N, 23.92. Found: C, 72.01; H, 4.31; N, 23.84.

The mass spectral data for the adducts in all three cases consisted of that for the parent hydrocarbon plus that for TCNE. No parent ion peak for the adduct could be observed.

Registry No.—I, 30953-08-3; II, 30883-04-6; III, 30883-05-7; IV, 30883-06-8; 6,6-dimethylfulvene, 2175-91-9, 30883-08-0 (TCNE adduct); acetone, 67-64-1; methylcyclopentadiene, 26519-91-5.

Acknowledgment.—We wish to express our appreciation to The Robert A. Welch Foundation for the support of this work and to the National Science Foundation for a grant for the HA-100.

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[12] Melting points are uncorrected. Nmr spectra were determined in carbon tetrachloride solutions for the fulvenes and perdeuterioacetonitrile for the TCNE adducts on Varian A-60A and HA-100 instruments. Spectral analysis was aided by the Laocoon computer program of S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964). Mass spectra were determined on a Finnegan 1015/SL. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Hydroazulenes. I. A Thermal Epoxide Rearrangement

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The epimeric 1,2-epoxy-2-methyl-3-methylenebicyclo[4.4.0]decanes **1** and **2** have been prepared and their thermal rearrangements studied. Pyrolysis of **1** gives a 75% yield of *cis*-1-methyl-10-methylenebicyclo[5.3.0]-decan-2-one (**10a**) while its epimer **2** affords 1-methyl-9-methylenebicyclo[4.3.1]decan-10-one (**9a**) in 47% yield. Magnesium bromide catalyzed rearrangement of **2** failed to yield **9a**.

Until recently, the hydroazulenic sesquiterpenes have represented one of the more neglected areas of study in terpene chemistry. In recent years, however, these compounds have attracted more attention and the number of sesquiterpenes known to contain the hydroazulene ring system has increased substantially.[2] As a part of our work in sesquiterpene synthesis, we have been concerned with techniques for the stereoselective preparation of functionalized and highly substituted hydroazulenes. A few solutions to this problem have been reported,[3] but unfortunately, a wide selection of methods is not yet available to meet the diversity of

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[1] National Science Foundation College Teacher Research Participant, summer 1969 and 1970.

[2] T. Nozoe and S. Itô, *Progr. Chem. Org. Natur. Prod.*, **19**, 32 (1961); J. Romo and A. R. de Vivar, *ibid.*, **25**, 90 (1967); W. Parker and J. S. Roberts, *Quart. Rev., Chem. Soc.*, **21**, 331 (1967); G. Ourisson, S. Munavalli, and C. Ehret, "Sesquiterpenoids," Pergamon Press, Oxford, 1966; J. Romo, *Pure Appl. Chem.*, **21**, 123 (1970).

[3] *Cf.* J. A. Marshall and W. F. Huffman, *J. Amer. Chem. Soc.*, **92**, 6358 (1970); J. A. Marshall, N. H. Andersen, and P. C. Johnson, *J. Org. Chem.*, **35**, 186 (1970); J. A. Marshall and J. J. Partridge, *Tetrahedron*, **25**, 2159 (1969); C. H. Heathcock and R. Ratcliffe, *Chem. Commun.*, 994 (1968); J. B. Hendrickson, C. Ganter, D. Dorman, and H. Link, *Tetrahedron Lett.*, 2235 (1968); E. H. White and J. N. Marx, *J. Amer. Chem. Soc.*, **89**, 5511 (1967); G. Büchi, W. Hofheinz, and J. V. Paukstelis, *ibid.*, **88**, 4113 (1966).