Pentatriafulvalene Syntheses by Condensation of Alkoxycyclopropenium Salts with Substituted Cyclopentadienides

Andrew S. Kende, Patrick T. Izzo, and Paul T. MacGregor

Contribution from the Organic Chemical Research Section, Lederle Laboratories Division, American Cyanamid Company, Pearl River, New York.

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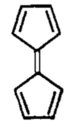
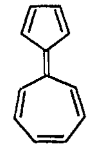
Abstract: Condensation of a mixture of sodium 1,2-dicarbomethoxy- and 1,3-dicarbomethoxycyclopentadienides with di-*n*-propylcyclopropenone in hot acetic anhydride yields the pentatriafulvalene diesters VIII and X in trace amounts. In contrast, reaction of the dicarbomethoxycyclopentadienides with di-*n*-propylethoxycyclopropenium fluoroborate (XI, R = *n*-C_3H_7) gives the diesters VI and VII in 41 and 10% yields, respectively; the diphenyl cation XI (R = C_6H_5) reacts similarly to form the diester XII in 24% yield. Whereas 1-benzoyl-6-hydroxy-6-phenylfulvene (XIII) gives only the unsymmetrical product XIV by the acetic anhydride method, its sodium enolate reacts with the dipropyl cation XI (R = *n*-C_3H_7) to give both the symmetrical and unsymmetrical diketones XV and XIV, the former predominating. By action of sodium formylcyclopentadienide upon the cation XI (R = *n*-C_3H_7) the pentatriafulvalene aldehyde XVI is obtained, and sodium tetrachlorocyclopentadienide leads to the tetrachloro product XVIII. Attempts to produce isolable pentatriafulvalene hydrocarbons by this technique have failed; indolemagnesium iodide as nucleophile has given the indolylcyclopropenium cation XX as the iodide. All of the pentatriafulvalenes so far examined exhibit strong infrared maxima near 5.4 and 6.5 to 6.9 μ; the ultraviolet absorption spectra show a characteristic maximum in the 300–360-mμ region. Nmr spectra of the stable pentatriafulvalenes indicate considerable electron transfer from the three- to the five-membered ring. An appreciable contribution of a dipolar canonical form (*e.g.*, XXVIII) to the ground state of the aldehyde XVI is shown by comparison of vicinal coupling constants in XVI with those of the analogous fulvene XXIV.

It has been clear since the elegant synthetic studies of Doering and Matzner that the hydrocarbon pentafulvalene ("fulvalene," I) lacks the chemical properties conventionally associated with aromatic character.[1] More recently Prinzbach has concluded, on the basis of spectroscopic and chemical studies, that heptapentafulvalene ("sesquifulvalene," II) and its simple derivatives have the properties of reactive polyolefins rather than aromatic substances.[2] Very little is known concerning the properties of the highly strained pentatriafulvalene ("calicene," III) system, the first derivatives of which were announced by three research groups early in 1965.[3] This paper describes a new synthesis which makes available certain nonannelated pentatriafulvalenes in practical yields and allows comparison of the spectroscopic characteristics of these compounds with those of related fulvene systems.


I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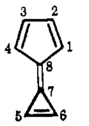
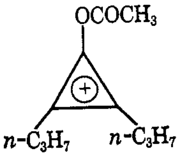
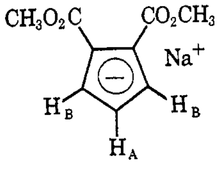


III

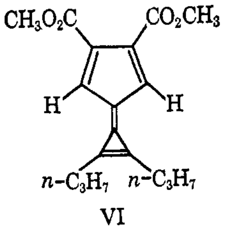
Condensation of Dicarbomethoxycyclopentadienide Anion with Di-*n*-propylcyclopropenone. The smooth formation of substituted benzo[*a*]pentatriafulvalenes from the condensation[4] of indene derivatives with di-*n*-propylcyclopropenone prompted the use of monocyclic cyclopentadienes in the form of their sodium salts in this reaction. Such salts are stable as monomers and should serve as reactive carbon nucleophiles toward the postulated acetoxycyclopropenium intermediate IV in the condensation process. The first to be examined was the salt $Na^+(C_5H_3(CO_2CH_3)_2)$, characterized by Peters as the principal product of the acylation of sodium cyclopentadienide with methyl chloroformate and assigned the 1,2-diester structure V by experimental analogy and upon its demonstrated conversion, albeit in low yield, to *cis*-cyclopentane-1,2-dicarboxylic acid upon reduction and hydrolysis.[5] This sodium salt reacted rapidly with di-*n*-propylcyclopropenone in acetic anhydride to give a tarry mixture which was subjected to elaborate chromatographic processing. Adsorption chromatography on silica gel, followed by partition chromatography over diatomaceous earth, ultimately produced minute yields of two crystalline $C_{18}H_{22}O_4$ diesters, mp 141–142° and mp 130–131°,



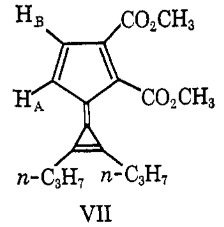
IV



V



VI



VII

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[1] W. E. Doering in "Theoretical Organic Chemistry," The Kekulé Symposium, Butterworths Scientific Publications, London, 1959, p 35.

[2] H. Prinzbach and D. Seip, *Angew. Chem.*, **73**, 169 (1961); H. Prinzbach and W. Rosswog, *Tetrahedron Letters*, **19**, 1217 (1963).

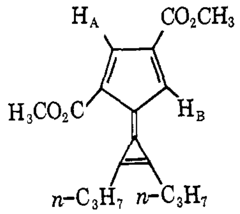
[3] W. Jones and R. S. Pyron, *J. Am. Chem. Soc.*, **87**, 1608 (1965); H. Prinzbach, D. Seip, and U. Fischer, *Angew. Chem.*, **77**, 258 (1965); A. S. Kende and P. T. Izzo, *J. Am. Chem. Soc.*, **87**, 1609 (1965). The name "pentatriafulvalene" and the numbering system depicted in III are elements of a systematic nomenclature of mixed fulvalenes proposed by Professor M. A. Battiste (University of Florida) which we shall adopt for papers in this series.

[4] A. S. Kende and P. T. Izzo, *ibid.*, **87**, 4162 (1965).

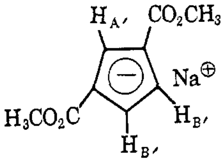
[5] D. Peters, *J. Chem. Soc.*, 1757 (1959).

identified as pentatriafulvalenes by their characteristic infrared maxima at 5.4, 6.6, and 6.9 μ.

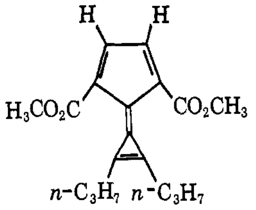
Condensation between cation IV and anion V could produce not only the symmetrical 2,3-diester VI but also the unsymmetrical 1,2-diester VII, which should be distinguishable by nmr. The 142° product showed magnetically dissimilar propyl groups and in the τ 3 region a four-line AB pattern for the two ring protons. Although this spectrum was consistent with an unsymmetrical structure such as VII the value of the observed coupling $|J_{AB}| = 2.1 \pm 0.3$ cps was abnormally low for the adjacent ring protons of VII, even assuming considerable cyclopentadienide character in the five-membered ring. Indeed, our observed 2.1-cps coupling was more nearly in line with 1,3-coupling constants among the fulvenes, which range from 1.4 to 2.8 cps.[6,7] Given all of the data, one is led to the surprising formulation VIII for the 142° diester.



VIII



IX

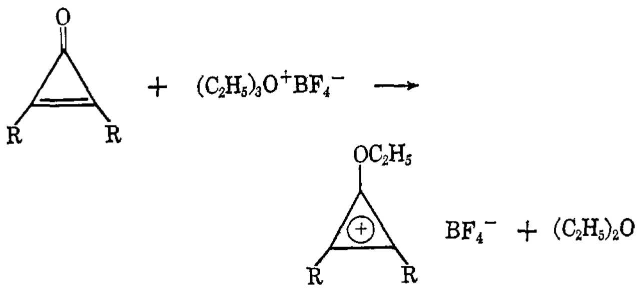


X

If structure VIII did, in fact, correspond to the 142° diester, then the sodium salt described by Peters is very probably misrepresented by structure V alone. That this was the case was dramatically revealed by the nmr spectrum of the sodium dicarbomethoxycyclopentadienide in CD$_3$CN, which in the τ 3 region exhibited not one but two AB$_2$ patterns, the stronger characterized by $|J_{AB}| = 3.5$ cps and the weaker having $|J_{A'B'}| = 2.1$ cps. These values, as well as the observed chemical shifts, signify that this salt is a mixture of the 1,2-isomer V and the 1,3-isomer IX in approximately 5:1 ratio. Thus the 142° diester VIII apparently arises from the minor component of the isomeric mixture.

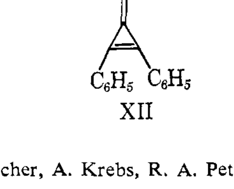
The accompanying 130–131° pentatriafulvalene diester showed magnetically equivalent propyl groups and a sharp, two-proton olefinic singlet at τ 2.95. These data were consistent with the anticipated structure VI but did not exclude the alternative 1,4-diester X which, like the 142° isomer, could arise from the minor component of the dicarbomethoxycyclopentadienide. Evidence to be described in the next paragraph established that this compound did, in fact, have the 1,4-diester structure X.

Ethoxycyclopropenium Syntheses of Pentatriafulvalene Diesters. The dismal yields experienced in the preceding synthesis of diesters VII and X led to reexamination of our synthetic method. An inherent flaw seemed to be that the postulated acetoxycyclopropenium intermediate IV was likely to act as an acylating agent as well as an alkylating agent. This feature could be overcome by use of an alkoxycyclopropenium salt (XI), a species recently prepared by the action of triethyloxonium fluoroborate on a cyclopropenone.[8] When a methylene chloride solution containing cation XI (R = n-C$_3$H$_7$), formed *in situ* from the cyclopropenone and the triethyloxonium reagent, was added to a suspension of sodium dicarbomethoxycyclopentadienide at room temperature, a mixture of pentatriafulvalene diesters was obtained in *ca.* 50% yield. The principal product (41% yield) was a new crystalline diester, mp 134–135°, shown by nmr to have the symmetry of either VI or X. The yield of this product demanded that it be derived from the major component of the sodium salt; hence structure VI was undoubtedly correct. Accompanying diester VI was a fourth isomer, mp 103–104°, showing magnetically nonequivalent propyl groups and an AB pattern in the ring-proton region. These properties defined this 104° isomer as the 1,2-diester VII, at length completing the identification of all four pentatriafulvalene diester isomers which can arise from sodium dicarbomethoxycyclopentadienide.



XI

Encouraged by the vastly improved yield of the ethoxycyclopropenium route over the anhydride method, we were led to extend this approach to the diphenyl series. Reaction of the diphenyl cation XI (R = C$_6$H$_5$) with sodium dicarbomethoxycyclopentadienide proceeded readily at room temperature to give 24% yield of a single yellow crystalline diester, mp 211–213°. The high symmetry shown in the nmr spectrum identified this product as the 2,3-diester XII; no other crystalline products could be isolated from the mother liquors of this reaction.



XII

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(6) M. Neuenschwander, D. Meuche, and H. Schaltegger, *Helv. Chim. Acta*, **47**, 1023 (1964); D. Meuche, M. Neueschwander, H. Schaltegger, and H. U. Schlunegger, *Helv. Chim. Acta*, **47**, 1211 (1964).

(7) W. B. Smith and B. A. Shoulders, *J. Am. Chem. Soc.*, **86**, 3118 (1964).

(8) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *ibid.*, **87**, 1320 (1965).

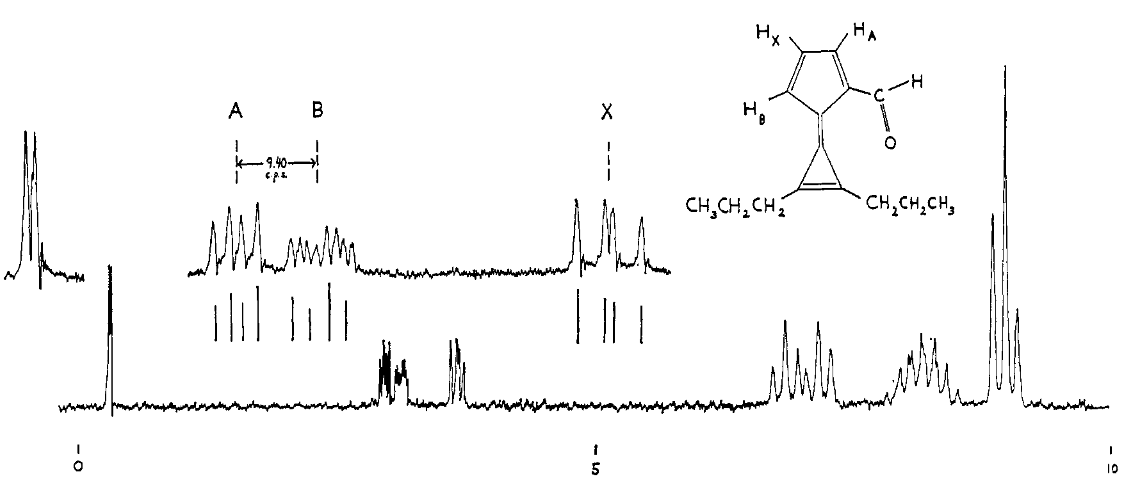
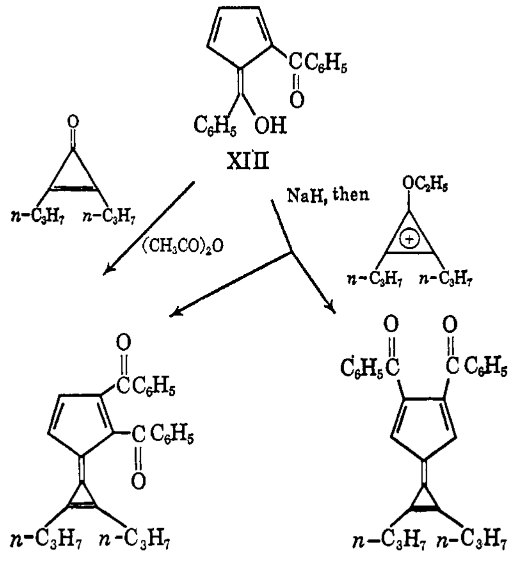


Figure 1. Nmr spectrum, taken in $CDCl_3$ solution at 60 Mc, of 1-formyl-5,6-dipropylpentatriafulvalene (XVI); abscissa in τ units. Inserts show low-field protons at fivefold scale expansion.

Pentatriafulvalene Diketones. Simple 1,2-diacylcyclopentadienes normally exist in the fulvene tautomeric form (*e.g.*, XIII) which can undergo facile ionization to an ambident anion in which the negative charge is delocalized onto the five-membered ring. That the fulvene XIII does, in fact, possess useful nucleophilic capability on carbon was shown by its reaction with di-*n*-propylcyclopropenone in acetic anhydride to give in low yield a crystalline product, mp 112–113°, shown to be a dibenzoylpentatriafulvalene (XIV or XV) by analytical data and infrared spectroscopy. When, however, the fulvene XIII was converted by sodium hydride to its anion and this was condensed with the ethoxycyclopropenium cation XI (R = n-C_3H_7), two discrete dibenzoylpentatriafulvalenes, mp 146–147° and 112–113°, were obtained in yields of 25 and 7%, respectively. The minor product was identical with the 113° material obtained by the anhydride process.



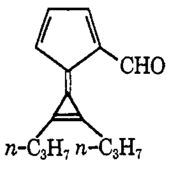
XIV

XV

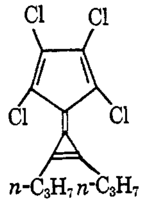
A slow scan of the nmr spectrum of the 147° isomer indicated equivalent propyl groups and a sharp singlet at τ 3.20 corresponding to two ring protons. Slow scan of the 113° compound in the τ 3 region showed a very narrow AB pattern with $|J_{AB}| = 4.5$ cps and $\Delta\nu_{AB} = 2.4$ cps. It is seen therefore that the ethoxycyclopropenium synthesis once again gives both the symmetrical and unsymmetrical diketones, whereas the anhydride method yields only the unsymmetrical isomer.[9] In this case, however, it is unnecessary to search for a subtle mechanistic rationale, since we have found that the symmetrical pentatriafulvalene XV is thermally labile above 100° and hence could not survive the conditions of the anhydride reaction. The nature of the pyrolytic transformation of XV is under study.

Extension to Simpler Pentatriafulvalenes. The ethoxycyclopropenium synthesis has been found useful in preparing still simpler pentatriafulvalenes than the derivatives cited above. While sodium formylcyclopentadienide reacted with cation XI (R = n-C_3H_7) at room temperature to give tarry materials, below 10° a clean condensation took place to give a crystalline aldehyde in 17% yield. It was anticipated that this reaction would produce the 1-formylpentatriafulvalene XVI, a prediction borne out by the nmr spectrum of this compound (Figure 1). In addition to the two nonequivalent propyl groups and the singlet aldehydic proton at τ 0.26, the ring protons near 3 exhibited an ABX pattern corresponding to the parameters $\Delta\nu_{AB} =$ 9.40 cps, $\Delta\nu_{AX} = 43.2$ cps, $\Delta\nu_{BX} = 33.8$ cps, $|J_{AB}| =$ 1.87 cps, $|J_{AX}| = 3.25$ cps, $|J_{BX}| = 4.21$ cps; the calculated spectrum is delineated below the observed ABX pattern of Figure 1. The doubling of peaks in the spectrum of the B proton arises from long-range coupling of proton B to the aldehydic proton, with $|J| = 1.06$ cps.

A synthesis of highly stable 1,2,3,4-tetrachloro-5,6-dipropylpentatriafulvalene (XVII), mp 178–179°, was smoothly achieved in 31% yield by using sodium tetra-



XVI



XVII

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[9] In our preliminary communication[3] the 113° condensation product from the Perkin reaction was erroneously assigned the symmetrical structure XV because of the apparent "singlet" at τ 3.25; this earlier conclusion is invalidated by the high-resolution data now presented.

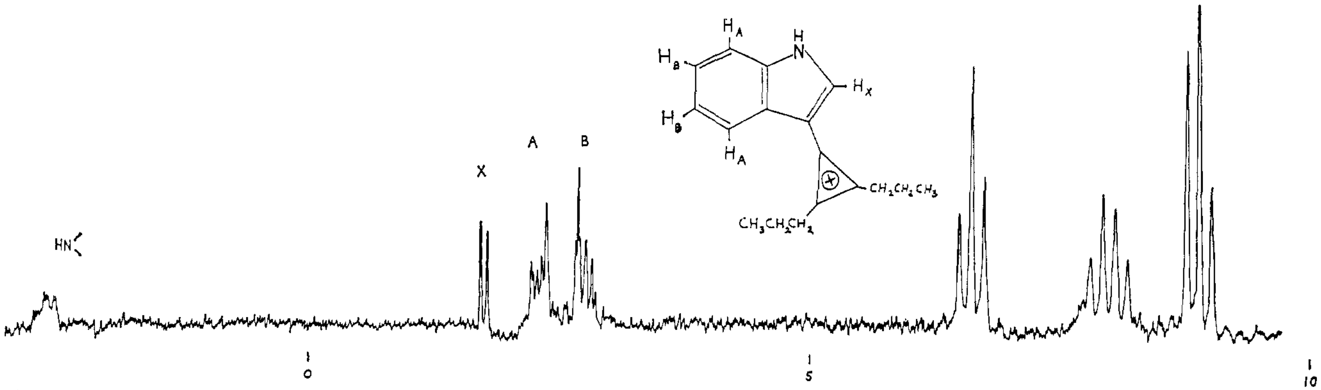
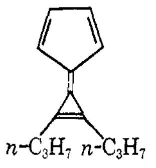


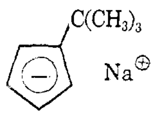
Figure 2. Nmr spectrum of azapentatriafulvalenium salt XX, measured in $CDCl_3$ at 60 Mc; abscissa in τ units.

chlorocyclopentadienide as the nucleophile toward the cation XI ($R = n\text{-}C_3H_7$).[10]

Unfortunately, the adaptation of the ethoxycyclopropenium method to the preparation of pentatriafulvalene hydrocarbons is fraught with experimental difficulties. Addition of the cation XI ($R = n\text{-}C_3H_7$) to sodium cyclopentadienide in tetrahydrofuran at −70° gave a dark solution showing an absorption maximum at 292 mμ which, in the light of the 314-mμ maximum of the tetrachloro compound XVII, might be taken to indicate formation of some of the condensation product XVIII. However, on allowing the reaction mixture to stand briefly at −20°, this peak decayed rapidly, and work-up of the reaction mixture gave no spectroscopic evidence for a pentatriafulvalene component. In the hope that this might be a result of the instability of XVIII rather than due to failure of the original condensation, the use of sodium *t*-butylcyclopentadienide (XIX)[11a] as nucleophile was explored, but with similar results. Evidently the success of the alkoxycyclopropenium synthesis requires at least one electron-withdrawing substituent on the five-membered ring.[11b]

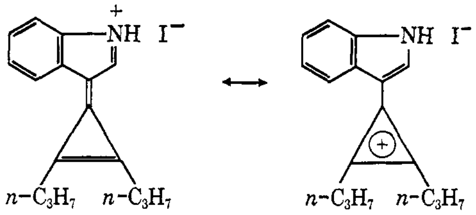


XVIII



XIX

Replacement of a carbon by nitrogen in the five-membered ring was not sufficient to allow isolation of an azapentatriafulvalene, although the intermediate conjugate acid was obtained. Thus the action of indolemagnesium iodide on ethoxydipropylcyclopropenium fluoroborate (XI, $R = n\text{-}C_3H_7$) in ether, followed by anhydrous work-up, gave a crystalline $C_{17}H_{20}NI$ product which was shown by nuclear magnetic resonance data (Figure 2) and ultraviolet and infrared spectra to be the azapentatriafulvalenium salt XX. The large chemical shift difference between the α and β methylenes in the nmr spectrum of XX reveals that there is relatively little positive charge on nitrogen, so that this substance is more precisely described as a 3-indolylcyclopropenium cation. Treatment of the salt XX with triethylamine in



XX

nominally anhydrous solvents caused decay of the 320-mμ chromophore but produced no spectroscopic evidence of azapentatriafulvalene formation.

Infrared and Ultraviolet Spectra. All of the pentatriafulvalenes examined in this laboratory exhibit characteristic infrared maxima at 5.4 and in the region 6.5 to 6.9 μ, the latter normally in the form of two intense peaks separated by 0.05 to 0.35 μ. The 5.4-μ peak is found in most cyclopropenes and has been assigned to a molecular vibration involving stretching of the cyclopropene double bond; the absorption in the 6.5–6.9-μ region has been attributed to the intercyclic double bond. However, as Lord and Andreades have recently pointed out, these vibrations are probably heavily mixed so that neither observed absorption can be given an exclusive assignment.[12] Carbonyl groups attached to the five-membered ring show C–O stretching maxima at long wavelengths because of strong electron release from the pentatriafulvalene nucleus. Maxima in the 5–7-μ region for typical pentatriafulvalenes are specified in the Experimental Section.

Ultraviolet spectra of simple pentatriafulvalenes are also quite characteristic, and those of the acyl derivatives appear to vary with substitution in a simple way. Data for the diesters VI, VII, VIII, and X (Table I) show a bathochromic progression of the longest wavelength peak on going from β to α substitution. A similar trend is suggested by the dibenzoyl derivatives XIV and XV, and the aldehyde XVI likewise falls into line. The spectrum of the tetrachloro compound XVII suggests that the absorption maximum of the parent pentatriafulvalene system should lie very close to 300 mμ; this value is supported by the 310-mμ absorption maximum of the unstable dithioketal XXI prepared from the aldehyde XVI by the action of ethanedithiol and boron trifluoride etherate. If this estimate is

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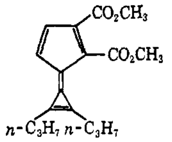
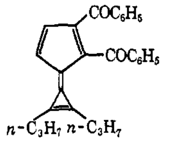
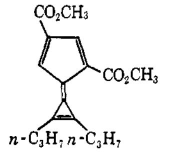
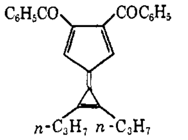
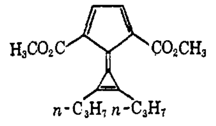
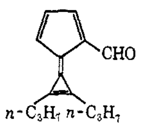
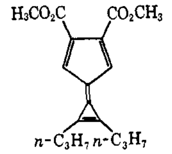
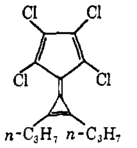
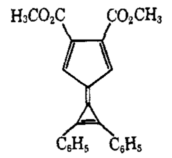
[10] The analogous 5,6-diphenyl derivative has been prepared directly from diphenylcyclopropenone and tetrachlorocyclopentadiene by M. Ueno, I. Murata, and Y. Kitahara, *Tetrahedron Letters*, **34**, 2967 (1965).

[11] (a) H. Riemschneider, A. Reich, and H. Horak, *Monatsh.*, **91**, 805 (1960); (b) see however a related synthesis of the stable and remarkably polar hexaphenylpentatriafulvalene, recently described by E. D. Bergmann and I. Agranat, *Chem. Commun.*, 512 (1965)

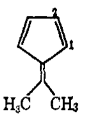
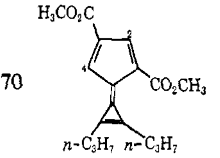
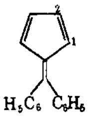
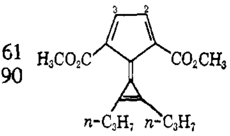
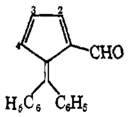
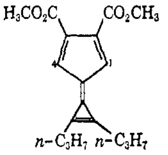
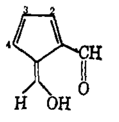
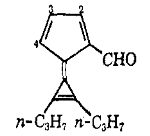
[12] S. Andreades, *J. Am. Chem. Soc.*, **87**, 3941 (1965).

Table I. Ultraviolet Spectra of Pentatriafulvalenes in CH_3OH

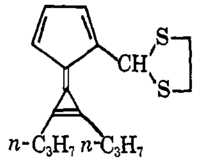
	330 mμ (4.53)[a] 223 mμ (4.24)		361 mμ (4.35) 260 mμ (4.32)
	336 mμ (4.42) 265 mμ (4.54)		331 mμ (4.50) 310 mμ (4.48) 252 mμ (4.32)
	364 mμ (4.12) sh 330 mμ (3.83)		373 mμ (3.91) 319 mμ (3.98) 237 mμ (4.12)
	319 mμ (4.62) 267 mμ (4.39)		314 mμ (4.64)
	351 mμ (4.85) 269 mμ (4.68)		

[a] Log ε values are in parentheses.

Table II. Chemical Shifts of Ring Protons in Fulvenes and Pentatriafulvalenes

Fulvenes			Pentatriafulvalenes		
	H (1) H (2)	τ 3.70		H (2) H (4)	τ 2.54
	H (1) H (2)	τ 3.61 τ 3.90		H (2)	τ 2.99
	H (2) H (3) H (4)	τ 2.37 τ 3.35 τ 3.46		H (1)	τ 2.92
	H (2) H (3) H (4)	τ 2.55 τ 3.38 τ 2.55		H (2) H (3) H (4)	τ 2.89 τ 3.59 τ 3.04

correct, the transition energy, 4.1 ev, is significantly higher for pentatriafulvalene than for the lowest energy

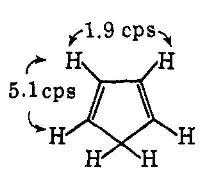


XXI

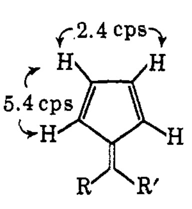
singlet transition of fulvene, 3.4 ev. It is of interest that this is the order of transition energies predicted by Pariser–Parr–Pople SCF calculations using conventional core parameters.[13]

Nuclear Magnetic Resonance Spectra. Chemical shifts of pentatriafulvalene ring protons do not differ significantly from those of typical fulvene derivatives (Table II). Because of the presence of polar, anisotropic substituents, it is not possible to ascertain the presence of a small ring current in the pentatriafulvalene system. There are, however, two accessible indices of aromatic character which permit instructive comparison between the pentatriafulvalenes and the conventional fulvenes. One of these is the relative magnitude of vicinal coupling constants on the five-membered ring. The second is the relative chemical shift of the α and β methylenes in the propyl side chain.

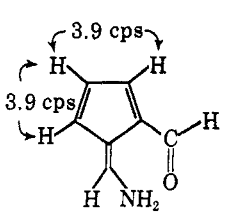
In cyclopentadiene itself the A_2B_2 olefinic proton pattern was analyzed by Manatt and Elleman,[14a] giving the parameters designated in formula XXII. Similar vicinal coupling constants have been deduced for simple dialkylfulvenes, as indicated in formula XXIII.[6,7] The large difference between $|J_{12}|$ and $|J_{23}|$ reflects the difference in bond order between the essentially double 1,2 bond and the essentially single 2,3 bond in these compounds.[14b] In contrast, the vicinal couplings in the more delocalized cyclopentadiene systems of the aminoaldehyde XXIV[15] and the diazocyclopentadiene derivative XXV[16] are more nearly equivalent. In the fully delocalized cyclopentadienide salt XXVI, the value of $|J|$ is 3.5 cps, roughly midway between the extremes represented in formulas XXII and XXIII. In the light of this qualitative correlation, the comparison between the vicinal couplings of the pentatriafulvalene aldehyde XVI and Hafner's fulvene aldehyde[17] XXVII is particularly revealing. Careful proton de-



XXII



XXIII



XXIV

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(13) Calculations were executed on an IBM 7094 using a program in Fortran IV written by Dr. J. Schachtschneider (Shell Development, Emeryville, Calif). We are indebted to Dr. E. M. Evleth (IBM Research Division, San Jose, Calif.) and Dr. J. H. van den Hende (Lederle) for valuable assistance in these computations, the details of which will be published elsewhere.

(14) (a) S. L. Manatt and D. D. Elleman, cited in J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 3896 (1965); (b) compare the reported variation of J_{vic} with bond order in aromatic systems, cited by N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, **36**, 2443 (1962).

(15) K. Hafner, H. E. A. Kramer, H. Musso, G. Ploss, and G. Schulz, *Ber.*, **97**, 2066 (1964).

(16) D. J. Cram and R. D. Partos, *J. Am. Chem. Soc.*, **85**, 1273 (1963).

(17) K. Hafner, *Angew Chem.*, **75**, 35 (1963).

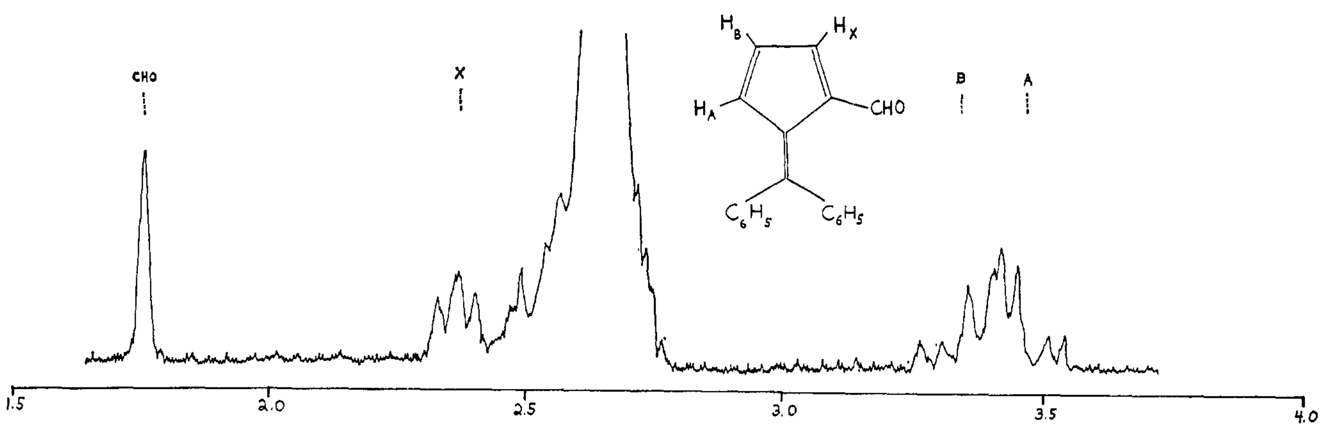


Figure 3. Low-field region showing ABX pattern of the cyclopentadiene ring protons of 1-formyl-6,6-diphenylfulvene, measured in $CDCl_3$ solution at 60 Mc; abscissa in τ units.

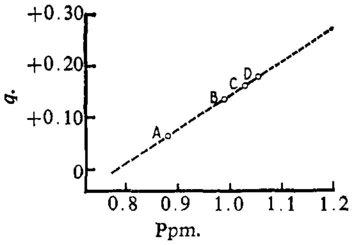
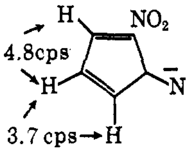
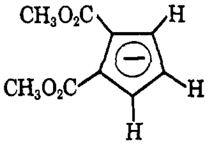


Figure 4. Ppm difference in chemical shift between α and β methylenes, plotted against excess positive charge per propyl-bearing carbon on a correlation line derived from literature data.[18] Points given are: A, 2-carbomethoxy-5,6-dipropyl-3,4-benzo[*a*]-pentatriafulvalene; B, VI; C, XVI; D, XV.

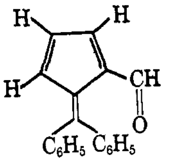
coupling studies of the spectrum of Figure 1 have confirmed the values $|J_{23}| = 3.25$ cps and $|J_{34}| = 4.21$ cps cited for couplings in XVI. By the same technique the fulvene XXVII reveals a spectrum (Figure 3) having the parameters $|J_{23}| = 2.51$ cps and $|J_{34}| = 5.05$ cps. Clearly the latter compound exhibits couplings typical of simple fulvenes whereas the couplings of the pentatriafulvalene derivative XVI indicate a major contribution of the dipolar form XXVIII to the ground state.



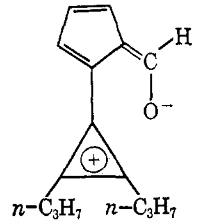
XXV



XXVI



XXVII



XXVIII

The relative chemical shift of the α *vs.* β methylenes in the pentatriafulvalenes is a measure of the positive charge on the propyl-bearing cyclopropene carbon atoms and hence of the extent to which a dipolar form such as XXVIII contributes to the molecule. Figure 4 locates some typical pentatriafulvalenes on a correlation line which has been calibrated by the parameters cited in a previous communication.[18] The ordinate measures charge on cyclopropene carbon, and it is seen that, in general, our pentatriafulvalenes lie roughly 30–50% of the way to full cyclopropenium character.

In conclusion, those pentatriafulvalenes which are readily accessible by the alkoxycyclopropenium route, namely derivatives having one or more electron-withdrawing substituents on the five-membered ring, show a considerable degree of cyclopropenium–cyclopentadienide aromatic character on the basis of these limited nmr studies. Our conclusion, however, does not invalidate the recent prediction by Dewar and Gleicher[19] that pentatriafulvalene itself will show negligible resonance stabilization, since the hydrocarbon should have much less electron transfer from the three- to the five-membered ring than the highly polar compounds described in the present paper.

Experimental Section[20]

Condensation of Sodium Dicarbomethoxycyclopentadienide with Dipropylcyclopropenone in Acetic Anhydride. To a solution of 1.9 g (0.014 mole) of dipropylcyclopropenone in 10 ml of freshly distilled acetic anhydride, stirred under a nitrogen atmosphere and heated in an oil bath at 120°, was added in portions in the course of 1.25 hr, 1.4 g (0.007 mole) of sodium dicarbomethoxycyclopentadienide.[5] The reaction mixture was stirred for 15 min longer, and the acetic anhydride was removed by distillation at reduced pressure at a temperature not exceeding 100°. The last traces of the acetic anhydride were removed by codistillation with benzene. The dark, tarry residue was chromatographed through a column, 1.5 in. in diameter, and filled with silica gel to a height of 20 in. The sample was put on in a benzene solution and was followed by 1 l. of benzene, 4 l. of a 9:1 mixture of benzene and ethyl acetate, and 2 l. of a 8.5:1.5 mixture of the same solvents. The front of the 9:1 solvent mixture eluted a dark material which crystallized in part on standing. Further purification of this fraction was effected by dissolving it in a very small volume of benzene, filtering through magnesium silicate, and eluting with methylene chloride. Evaporation of this solvent gave a crystalline product which was recrystallized from methanol to give 3.8 mg of **1,4-dicarbomethoxy-5,6-dipropylpentatriafulvalene** (X) as ochre-colored needles, mp 130–131°.

In the infrared spectrum, this compound showed bands at 5.93, 5.85, 6.55, 6.66, and 6.96 μ. The ultraviolet spectrum showed a

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[18] A. S. Kende and P. T. Izzo, *J. Am. Chem. Soc.*, **86**, 3587 (1964).

[19] M. J. S. Dewar and G. Gleicher, *Tetrahedron*, **21**, 3423 (1965).

[20] Melting points are uncorrected. Ultraviolet spectra were measured in pure methanol unless otherwise specified. Petroleum ether refers to the fraction with bp 30–60°. The authors wish to thank W. Fulmor, L. M. Brancone, Dr. P. Kohlbrenner, C. Pidacks, and their associates for the spectroscopic, analytical, preparative, and chromatographic services utilized in this investigation.

single peak at 364 mμ (log ϵ 4.12) with a shoulder at 330 mμ. The nmr spectrum exhibited the characteristic signals of equivalent propyl groups centered at τ 8.94 (CH_3), 8.14 (β-CH_2), and 6.80 (α-CH_2), a methoxyl singlet at 6.17 and a two-proton singlet at 2.99. A microanalysis could not be obtained because of insufficient material; however, the mass spectrum gave a parent peak at m/e 302 confirming the $C_{18}H_{22}O_4$ empirical formula.

The 8.5:1.5 benzene–ethyl acetate mixture eluted a brown material which also crystallized on standing. Partition chromatography using diatomaceous earth as support and methanol-heptane as the solvent system resolved this material into two compounds. Both products were obtained as colorless needles by recrystallization from methanol to constant melting points. The chromatographically slower component, **1,3-dicarbomethoxy-5,6-dipropylpentatriafulvalene** (VIII), mp 142–143°, weighed 22 mg.

Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.20; H, 7.34.

The infrared spectrum of this compound showed bands at 5.37, 5.89, 6.55, and 6.90 μ, and the ultraviolet spectrum showed peaks at 336 mμ (log ϵ 4.42) and at 265 mμ (log ϵ 4.54). In the nmr spectrum two magnetically dissimilar propyl groups were indicated by a methyl triplet at τ 8.93 and two ill-defined methylene multiplets at 8.17 and 6.95. The methoxyls signal occurred at τ 6.17, and the two ring protons showed up as a pair of doublets centered at 2.55 (J = ~2 cps). When the nmr spectrum was taken in a $CDCl_3$ solution containing 20% by volume of CF_3COOH, the chemical shifts remained essentially unchanged, but the propyl groups became equivalent.

The second and the more rapidly eluted compound in the partition chromatogram had a melting point of 127–128° which was depressed by mixing with either of the above two pentatriafulvalenes. The infrared spectrum exhibited, in addition to the characteristic pentatriafulvalene maxima at 5.38, 5.90, 6.62, and 6.94 μ, a band at 5.83 μ indicating another C=O group beside the ester carbonyls. The ultraviolet spectrum showed bands at 343 mμ (log ϵ 4.35), 265 (4.34), and 250 (4.36). In the nmr spectrum the equivalence of the propyl groups was indicated by a methyl triplet at τ 8.87, a β-methylene quartet at 8.20, and an α-methylene triplet at 6.94. In addition to a six-proton methoxyl singlet at τ 6.14 and a one-proton singlet at 2.59, there was a three-proton singlet at 7.73 indicating a $CH_3C{=}O$ group. This data, then, provided strong evidence that the compound was a pentatriafulvalene derivative in which the five-membered ring was substituted by an acetyl group in addition to the two ester groups. Further support was provided by the analytical data.

Anal. Calcd for $C_{20}H_{24}O_5$: C, 69.75; H, 7.02. Found: C, 69.69; H, 7.08.

The orientation of the substituents was not determined. The total pentatriafulvalene yield from the above experiment was 0.73%.

Preparation of Triethyloxonium Fluoroborate.[21] Experience showed that this product is sensitive to even traces of water, and the following complex assembly was developed to keep a nitrogen atmosphere on reactants, solvent, and product throughout the preparation. A three-necked, 500-ml, round-bottomed flask was equipped with a glass stirrer with ground-glass bearing, sealed and lubricated with paraffin oil. One side neck was equipped with an adapter having a hose connection (attached to a nitrogen line) and a 14/20 joint outer member. In the 14/20 joint was placed a plastic adapter with rubber ring seal, through which was passed an inverted 2-ml pipet. The pipet was connected by rubber hose to a 1-l. flask connected in turn to a vacuum line. In the third neck of the flask was placed a reflux condenser topped by a U-shaped connecting tube with two vertical 24/40 outer joints at the top. In one of these was placed a 50-ml graduated addition funnel with a pressure-equalizing bypass, and a 14/20 outer joint at the top. One side of a two-receiver fraction cutter was connected to the 14/20 joint. The other receiver was a small round-bottom flask. The cutter was connected to the condenser of a still for boron trifluoride etherate. The second joint of the U connecter was attached to a standard vacuum distillation adapter which was attached to the delivery arm of a distilling head which could be adjusted to total reflux or total distillation. The top of the distilling head condenser and the hose nipple of the vacuum distillation adapter were connected by rubber hoses and a T tube to the same nitrogen line. The still pot was a 2-l., round-bottom flask with a stirring magnet.

The entire apparatus was purged with prepurified nitrogen. Throughout the process a slight positive nitrogen pressure was maintained by the use of paraffin oil which filled escape valves in the nitrogen lines. Epichlorohydrin was distilled separately under nitrogen before use. Butylmagnesium bromide was prepared from 4.0 g of magnesium and 17.6 ml of n-butyl bromide in 1200 ml of ether in the large distilling apparatus set for total reflux. After the reaction subsided, the mixture was stirred and refluxed for 2 hr. About 90 ml of boron trifluoride etherate was placed in the small distilling apparatus, and a forerun was distilled into the small receiver. The main fraction of 50 ml (0.40 mole) was distilled into the addition funnel at 125.5–127°. The main fraction was added to the reaction flask, and the addition funnel and distilling apparatus were removed (nitrogen was blown through the apparatus to exclude moisture) and replaced by a freshly purged, 50-ml addition funnel containing 32.4 ml (0.41 mole) of epichlorohydrin. The apparatus was again closed, and about 200 ml of ether was distilled from the Grignard into the reaction flask. The rubber hoses connected to the pipet and the flask neck were closed by screw clamps. The reaction mixture was stirred rapidly, and the epichlorohydrin was added dropwise over 1 hr, thus maintaining a steady reflux. The two-phase mixture was then heated at reflux for 2.5 hr. by a heating mantle. The mixture was cooled and allowed to settle. The pipet was pushed down into the mixture, and the clamps were removed from the hose. The vacuum line was opened, and as much clear solvent as possible was removed. The pipet was raised, and about 200 ml of ether was distilled into the reaction flask. The mixture was stirred and then allowed to settle. The solvent was again removed by suction, and the washing process was repeated three more times. With nitrogen streaming into the reaction flask from the lower tube, the stirrer and the reflux condenser and other equipment were removed, and the necks were stoppered. The third connecter was then replaced by one attached to a two-way stopcock connected on one side to a nitrogen line and the other to a cold trap and mechanical vacuum pump. The reaction flask was evacuated and kept on the pump overnight. It was then refilled with nitrogen and placed in a nitrogen filled glove bag. The crystalline product was transferred to tared screw-cap vials, weighed, and stored over anhydrous calcium sulfate in the refrigerator. The yield of white crystalline powder was 25 g (45%).

Pentatriafulvalenes from 1,2-Dipropyl-3-ethoxycyclopropenium Fluoroborate and Sodium Dicarbomethoxycyclopentadienide. A solution of 1,2-dipropyl-3-ethoxycyclopropenium fluoroborate was prepared by mixing a solution 1.06 g (5.6 mmoles) of triethyloxonium fluoroborate in 5 ml of methylene chloride and a solution of 0.93 g (6.7 mmoles) of dipropylcyclopropenone in 5 ml of the same solvent. The colorless solution was allowed to stand at room temperature for 1 hr and then was added dropwise to a stirred suspension of 1.0 g (5.0 mmoles) of sodium dicarbomethoxycyclopentadienide. The addition was carried out over a period of 1.5 hr at room temperature and under a nitrogen atmosphere. After the addition of the cation, stirring was continued for another hour, and the mixture was filtered. The filtrate was evaporated to a crystalline mass which on recrystallization from methanol gave 618 mg (41%) of colorless needles, mp 131–133°. A second recrystallization from ethyl acetate–hexane gave 594 mg of pure **2,3-dicarbomethoxy-5,6-dipropylpentatriafulvalene** (VI), mp 134–135°.

Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.97; H, 7.76.

The infrared spectrum showed bands at 5.38, 5.90, 6.55, and 6.71 μ. The nmr spectrum indicated equivalent propyls by the signals at τ 8.92, 8.10, and 7.10, a methoxyl singlet at 6.17, and a two-proton singlet at 2.92.

The methanol and the ethyl acetate–hexane filtrates, resulting from the removal of VI above, were combined and evaporated to a dark, crystalline mush. Partition chromatography, using heptane–ethyl acetate–methanol–water as the solvent system and acid-washed diatomaceous earth as the support, resolved this material into two compounds. One, in trace amounts, after recrystallization from ethyl acetate–hexane, had mp 142–143° and was identified as the pentatriafulvalene VIII, described earlier. The main component was recrystallized twice from ethyl acetate–hexane to give 145 mg (10%) of **1,2-dicarbomethoxy-5,6-dipropylpentatriafulvalene** (VII), mp 103–104°.

Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.56; H, 7.34.

The characteristic infrared bands were exhibited at 5.36, 5.92, 6.55, 6.72, and 6.96 μ. The nmr spectrum showed nonequivalent propyl groups with signals at τ 8.95, 8.13, and 7.08, nonequivalent methoxyls by two singlets at 6.17, and a two-proton quartet at 3.43. When the nmr spectrum was taken in a solution of $CDCl_3$–CF_3-

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(21) H. Meerwein, *et al.*, *J. Prakt. Chem.*, **154**, 83 (1939).

COOH, the propyl groups became equivalent with signal at τ 8.87, 8.00, and 6.84. Two nonequivalent methoxyls were indicated by two signals at τ 5.75, and the two-proton quartet shifted downfield to 2.80.

2,3-Dicarbomethoxy-5,6-diphenylpentatriafulvalene (XII). To a suspension of 551 mg (2.7 mmoles) of sodium dicarbomethoxycyclopentadienide in 10 ml of methylene chloride, stirred under nitrogen at room temperature, was added in portions during 45 min 868 mg (2.7 mmoles) of crystalline 1,2-diphenyl-3-ethoxycyclopropenium fluoroborate (prepared from 2.0 g of triethyloxonium fluoroborate and 1.0 g of 2,3-diphenylcyclopropenone according to the procedure described by Breslow, *et al.*[8]). The reaction mixture was stirred for 2 hr longer and filtered. The filtrate was evaporated and the residue was slurried with hot ethyl acetate to give 241 mg (24%) of intensely yellow needles. Recrystallization from methanol gave the pure, crystalline product, mp 211–213° dec.

Anal. Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90. Found: C, 78.04; H, 5.30.

The infrared spectrum showed bands at 5.43, 5.83, 5.93, 6.25, 6.52, 6.75, and 6.98 μ. The nmr spectrum showed a six-proton methoxyl singlet at τ 6.10, a two-proton singlet at 2.64, and two five-proton aromatic multiplets at 2.20 and 1.90.

1,2-Dibenzoyl-5,6-dipropylpentatriafulvalene (XIV). A small flask containing dipropylcyclopropenone (0.85 ml), 1-benzoyl-6-hydroxy-6-phenylfulvene (0.85 g), sodium acetate (0.01 g), and reagent acetic anhydride (3.0 ml) was equipped with reflux condenser and magnetic stirrer, and the stirred contents was heated at 115° for 3 hr in a nitrogen atmosphere. After the flask had cooled, dry methanol was added, and the dark brown mixture was allowed to stand at room temperature overnight. The contents of the flask was taken up in warm toluene, and all solvents were removed under vacuum at 40–50°. The residual dark brown gum was taken up in a minimum amount of benzene and chromatographed over 200 g of silica gel. Elution with 3 l. of benzene recovered considerable unreacted fulvene; successive elution with 4% ethyl acetate in benzene and 15% ethyl acetate in benzene removed first some mixed fractions and then several cuts of the impure 1,2-dibenzoyl derivative, identified by the characteristic infrared maxima at 5.40, 6.14, 6.57, and 6.75 μ.

Slow crystallization of the latter cuts from ether–petroleum ether gave 57 mg (4.7%) of crystalline product, mp 109–111°; the analytical sample was recrystallized from the same solvent and then from aqueous methanol to nearly colorless flakes, mp 113–114°, dried at 80° and under oil-pump vacuum for 2 hr before analysis.

Anal. Calcd for $C_{28}H_{26}O_2$: C, 85.24; H, 6.64; mol wt, 394.2. Found: C, 85.58; H, 6.81; mol wt, 420 (thermistor).

2,3-Dibenzoyl-5,6-dipropylpentatriafulvalene (XV). To 58 mg of a 55% suspension of sodium hydride in oil were added 5 ml of anhydrous benzene and 1.0 ml of diglyme (distilled from sodium). The resulting suspension was stirred under nitrogen, and to it was added, in portions, 280 mg of 6-hydroxy-6-phenyl-1-benzoylfulvene. The sodium enolate solution was cooled to 10°, and to it was added slowly a solution of dipropylethoxycyclopropenium fluoroborate (prepared separately *in situ* by mixing 0.21 ml of dipropylcyclopropenone and 0.30 g of triethyloxonium fluoroborate in 4 ml of methylene chloride and allowing this solution to stand for 90 min). After the addition of the fluoroborate to the enolate, the reaction mixture was stirred for another 30 min at 10°, diluted with 30 ml of methylene chloride, washed twice with aqueous sodium bicarbonate, then water, and dried over magnesium sulfate.

Removal of solvent and crystallization of the brown mass first from hexane–ether and then from hexane–ethyl acetate gave 97 mg (25% yield) of the 2,3-dibenzoyl compound, mp 142–144° dec. The analytical sample was obtained by one further crystallization from hexane–ethyl acetate as tan needles, mp 146–147° dec, with infrared maxima (KBr) at 5.39, 6.12, 6.60, and 6.80 μ.

Anal. Calcd for $C_{28}H_{26}O_2$: C, 85.24; H, 6.66. Found: C, 85.25; H, 6.97.

Concentration of the mother liquors from the first hexane–ethyl acetate recrystallization above and cooling gave a second crop of tan crystals, mp 109–112°, which could be shown by ultraviolet spectroscopy to be the nearly pure 1,2-dibenzoyl isomer; yield, 26 mg (7%). This material was not further examined.

1-Formyl-5,6-dipropylpentatriafulvalene (XVI). A mixture of 0.867 g (7.34 mmoles) of sodium formylcyclopentadienide and 10 ml of dry dichloromethane was prepared under a prepurified nitrogen atmosphere in a 25-ml, round-bottom flask equipped with a magnetic stirrer and a closed addition funnel and cooled by an ice–water bath. A solution of 10 ml of dry dichloromethane, 1.03 g (8.15 mmoles) of dipropylcyclopropenone, and 1.62 g (8.52 mmoles) of triethyloxonium fluoroborate, prepared in the addition funnel and allowed to stand for 2 hr, was added to the flask over a 0.5-hr period. The stirred mixture was allowed to warm to 20°, poured into 100 ml of 30–60°, petroleum ether, and evaporated to a gummy residue. The residue was triturated with several portions of boiling petroleum ether. The extracts were decanted, filtered, and evaporated at reduced pressure to a volume of 5 ml. The residue was chromatographed on an 18 × 1 in. silica gel (100–200 mesh) column eluted with 25% ethyl acetate in benzene.

Fractions of 50 ml were taken and numbers 9 to 13 were combined and evaporated to 0.352 g of product melting 63–65°. The aldehyde was recrystallized from petroleum ether to give 0.280 g (17.0%) of amber needles, mp 64–65°, with infrared maxima (KBr) at 5.42, 6.10, and 6.51 μ.

Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.73; H, 8.54.

1,2,3,4-Tetrachloro-5,6-dipropylpentatriafulvalene (XVII). To a solvent mixture of 3 ml of anhydrous benzene and 0.3 ml of diglyme under a nitrogen atmosphere were added 60 mg of sodium hydride in oil (54% NaH). This suspension was stirred below −10° under nitrogen and 250 mg of tetrachlorocyclopentadiene was added, resulting in a deep violet suspension. After 2 min of stirring, there was introduced a solution of the ethoxycyclopropenium salt (from 0.27 ml of dipropylcyclopropenone and 0.36 g of triethyloxonium fluoroborate) in 4 ml of dichloromethane. After a reaction time of 15 min at −10°, the mixture was diluted with 15 ml of dichloromethane, washed with 0.01 *M* hydrochloric acid, then with water, dried over magnesium sulfate, and evaporated. Trituration of the residue with methanol gave 151 mg of the crystalline pentatriafulvalene, mp 176–178° (38% yield).

The analytical sample was prepared by a single recrystallization from ethyl acetate and obtained as colorless needles, mp 178–179°, with strong peaks in the infrared (KBr) at 5.37, 6.53, sh 6.64, and 6.90 μ.

Anal. Calcd for $C_{14}H_{14}Cl_4$: C, 51.90; H, 4.35; Cl, 43.72; mol wt, 324.1. Found: C, 52.26; H, 4.64; Cl, 43.58; mol wt, 319 (thermistor).

2-Aza-3,4-benzo-5,6-dipropylpentatriafulvalene Hydriodide (XX). To an ether solution of methylmagnesium iodide prepared from 0.68 g (0.028 g-atom) of magnesium turnings and 1.5 g (0.011 mole) of methyl iodide in 50 ml of ether was added a solution of 1.17 g (0.01 mole) of indole in 10 ml of ether. The mixture was refluxed for 30 min and cooled to about 5° with an ice bath. To this mixture, well stirred and under nitrogen, was slowly added approximately 2.5 g (0.01 mole) of 1,2-dipropyl-3-ethoxycyclopropenium fluoroborate, which was prepared by mixing 1.7 g (0.012 mole) of 2,3-dipropylcyclopropenone and 1.93 g (0.01 mole) of triethyloxonium fluoroborate in 10 ml of methylene chloride, allowing to stand for 1 hr and carefully removing the solvent at reduced pressure to give the colorless, oily cyclopropenium cation. The ice bath was removed, and the reaction was allowed to warm up to room temperature. After a few hours, the ether was decanted from the yellowish, insoluble solid which had formed. The solid was triturated with more ether. The ether solution and the washings were discarded, and the solid was crystallized by dissolving in methylene chloride and adding petroleum ether (bp 30–60°). A pale yellow crystalline product weighing 760 mg (21%) and melting at 173–175° dec was obtained. Further recrystallizations from other solvents, including water, did not alter this melting point.

Anal. Calcd for $C_{17}H_{19}N \cdot HI$: C, 55.90; H, 5.52; N, 3.84; I, 34.77. Found: C, 55.75; H, 5.67; N, 4.25; I, 34.22.

The infrared spectrum showed bands at 5.40, 6.61, 6.70, 6.85, and 7.02 μ. The ultraviolet spectrum exhibited peaks at $\lambda\lambda_{max}$ 319 mμ (log ϵ 4.27), 265 (3.98), 245 (4.12), and 222 (4.34).

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