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THE SYNTHESIS OF DIPHENYLTRIDECA-, -PENTADECA-, -HEPTADECA-, AND -NONADECAFULVENE DERIVATIVES1)

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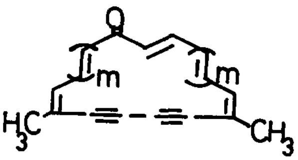
Summary: Title fulvenes were synthesized through the reaction of the large-membered annulenones with diphenylketene, and examination of ^{1}H-NMR spectra suggests that the fulvenes are atropic.

In recent year, we have rather extensively investigated experimental studies on the diatropic (4n+3)-membered- (type 1) and paratropic (4n+1)-membered annulenones (type 2) as well as α-methyl- and α-ethyl-substituted derivatives.2) The convenient syntheses of annulenones of both type 1 and 2 made it desirable to utilize these compounds for syntheses of cross-conjugated π-electron systems. A synthesis of heptatrideca-, heptapentadeca-, and heptaheptadecafulvalene derivatives through the reaction of 8-oxoheptafulvene with various annulenones has been reported.3)

We were interested in studies on another cross-conjugated π-electron system (3 and 4), fulvene, which might be derived from some of these annulenones (1 and 2).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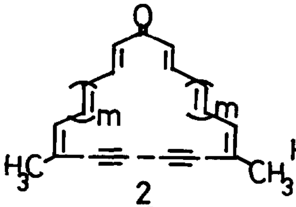
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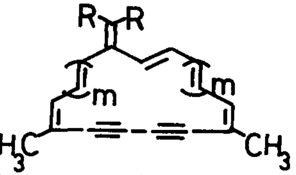
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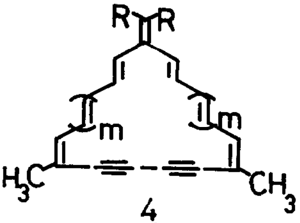
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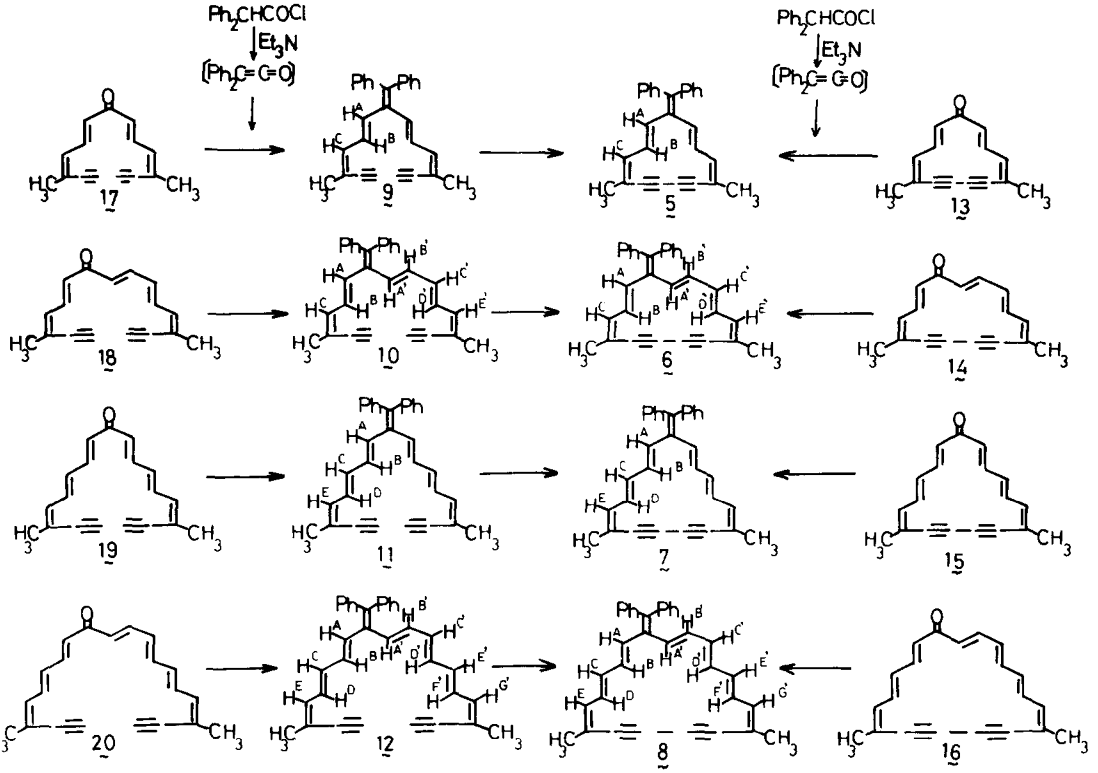
If polarization of the cross-conjugated double bond does not occur, the fulvene of type 3 is potentially paratropic and the fulvene of type 4 is potentially diatropic since the former contains (4n)π-electrons and the latter does (4n+2)π-electrons. We chose phenyl group (R=Ph: 3 and 4) as the substituent at ω,ω-positions of the fulvene from the following points of view. (1) Phenyl group is recognized to stabilize a large-membered conjugated π-electron system remarkably,4) and (2) diphenylketene which reacts with various annulenones (*vide infra*) is most easily obtainable.5)

In this paper, we describe a synthesis of the title fulvene derivatives, which are the largest ring monocyclic fulvene derivatives to be obtained.6)

The reaction of 5,10-dimethyl-6,8-bisdehydro[13]annulenone (13),2a) 5,10-dimethyl-6,8-bisdehydro[15]annulenone (14),2b) 7,12-dimethyl-8,10-bisdehydro[17]annulenone (15),2b) and 7,12-dimethyl-8,10-bisdehydro[19]annulenone (16),2b) with diphenylketene formed *in situ* from diphenylacetic acid chloride and triethylamine afforded diphenyltrideca- (5, orange crystals, mp 174–175°C, 32%),7) -pentadeca- (6, orange crystals, mp 160–161°C, 51%), -heptadeca- (7, orange crystals, mp 209–210°C, 62%), and -nonadecafulvene derivative (8, red crystals, mp 212–213°C, 35%),



respectively.

In order to examine the tropicities of these fulvenes, we prepared the corresponding acyclic compounds 9–12 for 5–8 by the same method as that used for the fulvenes. Thus, the reaction of 3,11-dimethyl-3,5,8,10-tridecatetraene-1,12-diyn-7-one (17),[2a] 3,13-dimethyl-3,5,8,10,12-pentadecapentaene-1,14-diyn-7-one (18),[2b] 3,15-dimethyl-3,5,7,10,12,14-heptadecahexaene-1,16-diyn-9-one (19),[2b] and 3,17-dimethyl-3,5,7,10,12,14,16-nonadecaheptaene-1,18-diyn-9-one (20),[2b] with diphenylketene afforded the corresponding acyclic compounds (9, yellow crystals, mp 141–143°C, 36%), (10, yellow crystals, mp 109–110°C, 35%), (11, yellow crystals, mp 151–152°C (dec), 22%), and (12, yellow oil,[8] 18%), respectively. Oxidative coupling of these acyclic compounds 9, 10, 11, and 12 with anhydrous copper(II) acetate in pyridine and ether at 50°C[9] furnished the corresponding monomeric cyclic compounds, which proved to be identical with above-described fulvenes (5, 62%), (6, 32%), (7, 72%), and (8, 30%), respectively.

The ^{1}H-NMR spectra of these fulvenes 5–8 as well as the acyclic model compounds 9–12 were taken at 200 MHz and the chemical shifts are tabulated in Table 1. Individual assignments were made on the basis of multiplicities and coupling constants, and were assisted by off-resonance technique where possible and necessary.

At first sight among these fulvenes 5–8, as can be seen from the Table 1, the ^{1}H-NMR data suggest that the [15]fulvene 6 is paratropic exhibiting the inner proton ($H^{A'}$, H^B, $H^{D'}$) signals at a relatively low field (τ 2.24–2.64) and, the outer (H^A, $H^{B'}$, H^C, $H^{C'}$, $H^{E'}$) and methyl

Table 1. The ^{1}H-NMR Chemical Shifts of the Compounds 5–12 in $CDCl_3$ at 200 MHz (τ-values)

Compd.	H^A	$H^{A'}$	H^B	$H^{B'}$	H^C	$H^{C'}$	H^D	$H^{D'}$	H^E	$H^{E'}$	$H^{F'}$	$H^{G'}$	CH_3	Ph H	-C≡CH
9	3.62		2.92		3.68								8.07	2.65–2.86	6.73
5	3.73		2.95		3.32								8.10	2.60–2.84	
10	3.65	3.63	3.03a)	3.31a)	3.67	3.68		3.33a)		3.67			8.07	2.69–2.88	6.68, 6.72
6	3.61	2.64	2.24	4.15	3.60	3.93		2.40		3.57			8.20	2.7–2.9	
Δ(6–10)	-0.04	-0.99	-0.79	+0.84	-0.07	+0.25		-0.93		-0.10			+0.13		
11	3.62		3.26		3.65		3.36		3.63				8.03	2.59–2.85	6.62
7	3.89		(3.37–3.60)		(3.37–3.60)		(3.37–3.60)		3.29				8.06	2.65–2.80	
12	(3.20–3.75)												8.06	2.6–2.9	6.66
8	(3.44–3.88)	3.30	2.62b)	(3.44–3.88)			2.89b)	3.12b)	(3.44–c)3.88)				8.13, 8.15	2.60–2.86	

a,b) Assignments may be reversed in each group. c) The $H^{F'}$ proton signal of 8 is submerged by those of phenyl group.

proton signals at a relatively high field (τ 3.57–4.15, 8.20). However, if we judge the tropicity of the [15]fulvene 6 from the differences in chemical shifts between the various protons for the cyclic compound (fulvene) and the corresponding acyclic model compound 10 (Table 1), the [15]fulvene 6 is seen to be atropic since no significant high field shift for the outer protons (H^A, H^C, $H^{E'}$) is observed, although the low field shift for the inner protons ($H^{A'}$, H^B, $H^{D'}$, Δ -0.79– -0.99) and the high field shift for the outer protons ($H^{B'}$, $H^{C'}$, Δ +0.25– +0.84) and methyl protons (Δ +0.13) are observed. Similar observation is made for the [19]fulvene 8. Therefore, it can be suggested that the fulvenes 6 and 8 are atropic, although further studies will be required to conclude the tropicities of 6 and 8.[10] Both the chemical shifts of the protons of the fulvenes 5 and 7, and comparison of the chemical shifts, as before, with those of the corresponding acyclic models 9 and 11, respectively, show that the fulvenes 5 and 7 are clearly atropic.

Also, the ^{1}H-NMR spectra of the fulvens 5–8 were found to be essentially temperature-independent over the range -60 to 60°C, revealing that the conformations indicated for 5–8 will remain unchanged over this temperature range.

The electronic absorption spectra (in dichloromethane) of the fulvenes 5–8 are illustrated in Figure 1. Although the main maxima of the fulvenes exhibit a bathochromic shift as the ring size increases, this shift is larger between the [13]fulvene (5, λ_{max}: 308 nm) and the [15]fulvene (6, 332 nm) and between the [17]fulvene (7, 343 nm) and the [19]fulvene (8, 363 nm) than that between the [15]fulvene 6 and the [17]fulvene 7. And it is apparent from Figure 1 that the electronic spectra of 5 and 7 ([4n+2]fulvenes, type 4) are similar, while those of 6 and 8 ([4n]fulvene, type 3) are similar except the bathochromic shift of each band. This might be considered to be due to the occurrence of the same sort of alternation between the maxima of [4n-2] and [4n] systems, as has been observed for annulenes and dehydroannulenes.11)

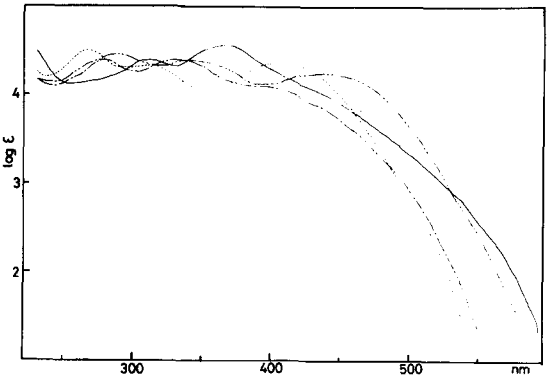


Fig. 1. UV spectra of the [13]- (5) (-------), [15]- (6) (-·-·-·-), [17]- (7) (--·--·-), and [19]fulvene (8) (————) in dichloromethane

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References and Notes

1) Dedicated to the memory of the late Professor Franz Sondheimer.

2) a) T. M. Cresp, J. Ojima, and F. Sondheimer, *J. Org. Chem.*, 42, 2130 (1977); b) J. Ojima, Y. Shiroishi, K. Wada, and F. Sondheimer, *ibid.*, 45, 3564 (1980); c) J. Ojima and M. Fujiyoshi, *J. Chem. Soc., Perkin Trans. I*, 1980, 466; d) J. Ojima, K. Kanazawa, K. Kusaki, and K. Wada, *ibid.*, 1980, 473; e) J. Ojima, K. Wada, K. Kanazawa, and Y. Nakagawa, *ibid.*, 1981, 947; f) J. Ojima, K. Wada, Y. Nakagawa, M. Terasaki, and Y. Juni, *ibid.*, 1982, 31; g) J. Ojima, Y. Nakagawa, K. Wada, and M. Terasaki, *ibid.*, 1982, 43; h) J. Ojima, K. Wada, and M. Terasaki, *ibid.*, 1982, 51; i) J. Ojima, Y. Juni, Y. Yoneyama, K. Wada, and Y. Murosawa, *Bull. Chem. Soc. Jpn.*, 54, 3466 (1981); j) J. Ojima and Y. Murosawa, *ibid.*, 54, 3473 (1981).

3) T. Asao, N. Morita, J. Ojima, and M. Fujiyoshi, *Tetrahedron Lett.*, 1978, 2795; N. Morita T. Asao, J. Ojima, and K. Wada, *Chem. Lett.*, 1981, 57.

4) T. Katakami, K. Fukui, T. Okamoto, and M. Nakagawa, *Bull. Chem. Soc. Jpn.*, 49, 297 (1976).

5) E. C. Taylor, A. McKillop, and G. H. Hawks, *Org. Syn.*, 52, 36 (1972).

6) a) For reviews, see E. D. Bergmann, *Chem. Rev.*, 68, 41 (1968) and F. Pietra, *ibid.*, 73, 293 (1973); b) For large-membered fulvenes containing bicyclic compound, see W. M. Jones, R. A. LaBar, and P. H. Gebert, *J. Am. Chem. Soc.*, 99, 6379 (1977) and H. Prinzbach, *Pure Appl. Chem.*, 28, 281 (1971).

7) All crystalline compounds described in this paper gave satisfactory spectral and analytical data.

8) Attempts to crystallize 12 from a variety of solvents were unsuccessful.

9) N. Darby, T. M. Cresp, and F. Sondheimer, *J. Org. Chem.*, 42, 1960 (1977).

10) The study on the benzannelated derivatives of 6 is now in progress.

11) P. J. Garratt and K. Grohmann, *Methoden Org. Chem. (houben-Weyl)*, 5, 533 (1972).

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