Tetrahedron Vol. 37, pp. 721 to 729
© Pergamon Press Ltd., 1981. Printed in Great Britain

0040-4020/81/0215-0721/$02.00/0

SYNTHESIS AND PROPERTIES OF TETRAPHENYLTRIAFULVENE

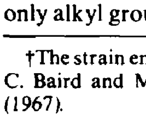
KOICHI KOMATSU, TAKAMASA MORIYAMA, TOMIHIRO NISHIYAMA and KUNIO OKAMOTO*

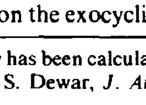
Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

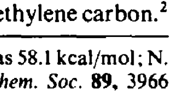
(*Received in Japan* 30 *May* 1980)

Abstract—The reaction of the 1,2-diphenylcyclo propenium ion (**5**) with benzhydrylmagnesium bromide exclusively affords 1,2-diphenyl-3-benzhydrylcyclo propene (**4**), though the reaction of **5** with benzhydryllithium in the presence of lithium chloride yields no cyclopropene **4** but 1,3-diphenyl-3-benzhydryl-cyclopropene (**6**) *via* the intermediate formation of 1,2-diphenyl-3-chlorocyclopropene (**7**). The hydride abstraction from the cyclopropene **4** followed by deprotonation gives tetraphenyltriafulvene (**2**) as dark red crystals. The ^{13}C NMR spectrum, as well as a bathochromic shift of the longest-wavelength absorption in the electronic spectrum with decrease in solvent polarity, indicates a considerable contribution of the dipolar structure at the ground state of **2**. The cyclic voltammetry on **2** reveals that **2** can be readily oxidized to a stable cation radical and a less stable dication. The cation radical was also generated by chemical oxidation with silver tetrafluoroborate or antimony pentafluoride, and was investigated by ESR spectroscopy.

The smallest ring homolog of cross-conjugated cyclic π-systems, triafulvene (methylenecyclopropene; **1**), has long been of particular interest to both theoretical and synthetic chemists, since it has been anticipated to possess special stability, in spite of its highly strained structure,† due to the contribution of a dipolar structure (**1a**) associated with Hückel aromaticity. Although various derivatives of triafulvenes have already been reported,[1,2] most of them bear electron-withdrawing substituents on the exocyclic methylene carbon[1] to reinforce the molecular polarization in favor of the form **1a**, and therefore do not seem quite partinent as models for investigating the intrinsic electronic property of the triafulvene π-system itself.


(1)


(1a)


(2)

While an attempt to prepare the parent compound **1** was reported to be unsuccessful,[3] there have so far been two reports on the syntheses of triafulvene carrying only alkyl groups on the exocyclic methylene carbon.[2] However, these are unfortunately too unstable to be isolated, and allowed only spectroscopic observation in solution at low temperatures. On the other hand, the phenyl group, unlike the alkyl, can conjugatively stabilize the unsaturated system, and yet exerts only little inductive perturbation. Thus, the triafulvene having the phenyl substituents both at the exocyclic methylene and at the three-membered ring, i.e. tetraphenyltriafulvene (**2**), is expected to be a suitable model with enough stability for detailed investigation on the inherent property and chemistry of the triafulvene π-system. In the literature, there appeared at least two attempts[4] for the synthesis of **2**,† but they were unsuccessful resulting in unexpected rearrangements. In connection with our previous study on another phenyl-substituted cross-conjugated system, phenylheptafulvenes,[5] we have synthesized and examined some properties of the triafulvene **2**, the results of which will be described in this paper.

Synthesis

As an unambiguous synthetic route to the triafulvene **2**, abstraction of the α-proton from 1,2-diphenyl-3-benzhydrylcyclopropenium ion (**3**) appeared promising based on our previous success in the synthesis of phenyl-substituted heptafulvenes[5] and on the reported synthesis of 1,2-diphenyl-4-carboethoxytriafulvene.[1f] As the precursor for the cation **3**, 1,2-diphenyl-3-benzhydrylcyclopropene (**4**) was expected to be readily obtainable by the cation-anion combination reaction of the 1,2-diphenylcyclopropenium ion (**5**) and the benzhydryl anion. According to the observation of Breslow *et al.* that nucleophilic attack occurs preferentially on the carbon atom of the cyclopropenium ion which is best able to localize the positive charge,[6] the reaction of **5**† with carbanionic reagents should afford 1,2-diphenyl-3-substituted cyclopropenes as the major product; this has been verified experimentally by Padwa *et al.* for the reaction with some Grignard reagents.[7]

Since the Grignard reagent cannot be prepared

---

†The strain energy has been calculated as 58.1 kcal/mol; N. C. Baird and M. J. S. Dewar, *J. Am. Chem. Soc.* **89**, 3966 (1967).

†It has also been reported that the triafulvene **2** is formed in *situ* by the reaction of 2,3-diphenylcycloprop-2-enyl-(triphenyl)phosphonium bromide with benzophenone in the presence of t-BuOK and is converted to the cyclopropenium ion **3** upon acidification; S. V. Krivun, N. S. Semenov, S. N. Baranov, and V. I. Dulenko, *Zh. Obschch. Khim.* **40**, 1904 (1970). However, no property of **2** has been described, and our reexamination on the reported reaction did not give any indication for the formation of **2**.

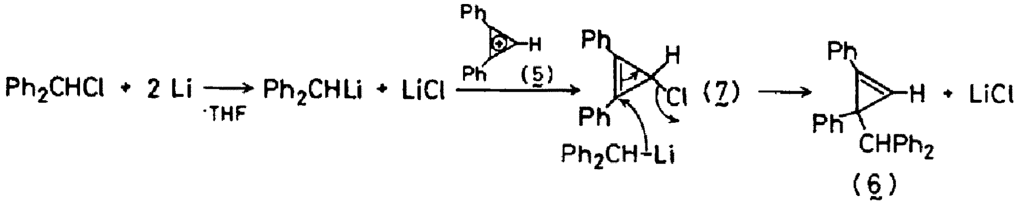
†The simple HMO calculation on the 1,2-diphenylcyclopropenium ion (**5**) indicated the following charge distribution: C-1,2, +0.2611; C-3, +0.2941; *ipso*-C, −0.0210; *ortho*-C, +0.0408; *meta*-C, −0.0014; *para*-C, +0.0342.

directly from benzhydryl halides, the reaction with benzhydryllithium was examined first. When the cation **5** was allowed to react at −60° with benzhydryllithium prepared from benzhydryl chloride and lithium metal in THF, the only hydrocarbon product containing the cyclopropene structure was, unexpectedly, 1,3-diphenyl-3-benzhydrylcyclopropene (**6**) (47% yield), and even a trace amount of **4** was not obtained. At first sight, this highly regiospecific addition of the benzhydryl anion to the rather sterically hindered C atom appeared quite unusual. However, since the chloride anion formed during the preparation of benzhydryllithium was inevitably present in the system, the formation of **6** could be interpreted as the nucleophilic substitution of an S_N2' type on the cyclopropenyl chloride **7**, first formed from **5** and the chloride anion, as is shown in Scheme 1. Actually, a control experiment indicated the smooth formation of the covalent chloride **7** from **5** and lithium chloride in THF. Melloni and Ciabattoni have reported a similar type of reaction between 1,2-diphenyl-3,3-dichlorocyclopropene and benzhydryllithium, but the supposed product, the chlorocyclopropene, has not been isolated due to the subsequent rearrangement.[4b]

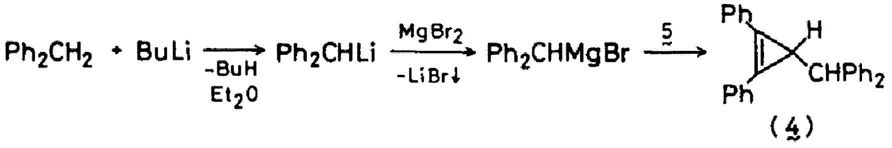
In contrast to this result, when benzhydrylmagnesium bromide was prepared from halide-free benzhydryllithium, which had been obtained from diphenylmethane and butyllithium,[8] and was allowed to react with the cation **5** in ethyl ether, the cyclopropene **4** was isolated in 6% yield with no detectable amount of **6** (Scheme 2). Although the yield was poor, no other hydrocarbon compounds were obtained except diphenylmethane from the unchanged benzhydryl anion and 1,1,2,2-tetraphenylethane which had already been present as an impurity in the benzhydryl anion reagent.

The structures of cyclopropenes **4** and **6** were assigned based on the spectral data given in Table 1. Both **4** and **6** were catalytically hydrogenated to give the corresponding cyclopropane derivatives in a quantitative yield. For the definitive confirmation of their structures, the compounds **4** and **6** were also prepared by the independent synthetic routes involving carbene addition to olefins and subsequent dehydrochlorination, as shown in Scheme 3. Especially for the preparative purpose of **4**, this route was found to be more practical than the aforementioned cation–anion reaction.

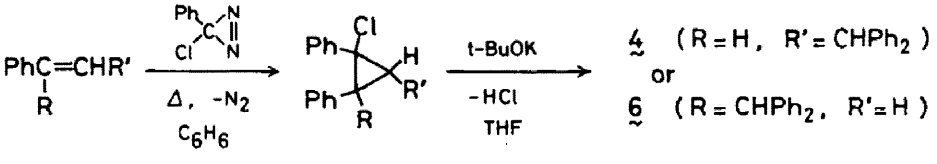
The cyclopropene **4** was readily transformed to the cation **3** in 95% yield by hydride abstraction with the triphenylmethyl cation in dichloromethane. The tetrafluoroborate salt $\mathbf{3}\cdot BF_4^-$ is an air stable white powder, and is characterized by strong IR absorptions at 1420 and 1060 cm^{-1} due to the cyclopropenium ring vibration and BF_4^- anion, respectively. Other spectral properties shown in Table 1 also support its structure. The salt $\mathbf{3}\cdot BF_4^-$ is soluble only in polar solvents such as acetonitrile and dichloromethane, and exhibits considerable acidity in aqueous acetonitrile or ethanol. The spectrophotometric titration of **3** in 50% aqueous acetonitrile exhibited its pK_a to be 1.6 ± 0.1 at 25°, and demonstrated that **3** can be reversibly transformed to a neutral species having a long-wavelength absorption at 450 nm, as shown in Fig. 1. This observation suggests that the α-proton of the benzhydryl group in **3** is readily removed upon basification to give the expected triafulvene **2** in solution. This supposition was further substantiated



Scheme 1



Scheme 2



Scheme 3

Table 1. Spectral data of the cyclopropenes **4** and **6**, the cyclopropenium ion **3**, and the triafulvene **2**.

Comp'd	IR ν (KBr), cm^{-1}	UV-Vis λ_{max}^{EtOH} nm (log ε)	^1H NMR δ ($CDCl_3$), ppm
4	3030 w, 2940 w, 1810 m, 1600 m	222 (4.45)	7.36-7.20 (m, 20H, Ph)
	1495 s, 1450 m, 1445 s, 1085 w	239sh(4.32)	3.64 (d, J=8Hz, 1H, C<u>H</u>Ph$_2$)
	1070 w, 1025 m, 920 w, 760 s	321 (4.31)	2.98 (d, 1H, -C<u>H</u>(CHPh$_2$))
	740 m, 700 s, 690 s	338 (4.17)	
6	3030 w, 2880 w, 1760 m, 1600 m	263 (4.03)	7.25-6.90 (m, 21H,
	1495 s, 1440 s, 1080 m, 1030 m		Ph + -CH=)
	920 w, 770 s, 750 s, 735 s		5.34 (s, 1H, C<u>H</u>Ph$_2$)
	705 s, 695 s		
3·BF_4^-	3060 w, 2900 w, 1840 w, 1595 s	249 (4.30)	7.87-7.54 (m, 10H, Ph)
	1500 s, 1450 m, 1420 br vs,	295 (1.47)	7.42 (s, 10H, Ph)
	1180 m, 1060 br vs, 770 s,	309 (4.47)	6.25 (s, 1H, C<u>H</u>Ph$_2$)
	740 m, 700 s, 680 s	(in CH_3CN)	(in CD_3CN)
2	3060 w, 1855 m, 1820 m, 1600 w	271 (4.55)	7.56-7.21 (m, Ph)
	1580 s, 1560 s, 1495 s, 1410 s	330 (4.78)	
	1185 w, 1080 w, 1015 m, 1000 m	462 (3.69)	
	920 w, 770 s, 750 s, 700 s	(in CH_3CN)	
	690 s		

by the disappearance of the methine proton and a concomitant upfield shift of the phenyl protons observed in the ^1H NMR spectrum when an equivalent amount of triethylamine was added, as shown in Fig. 2.

In accord with these observations, the cation **3**, when treated with equimolar triethylamine in dichloromethane, gave a dark red solution, which afforded a quantitative yield of the triafulvene **2** as dark red crystals after the usual work-up. The triafulvene **2** is unexpectedly stable in the air, though gradual decomposition was observed in a few hours for a highly diluted solution ($<10^{-4}$ M).

Properties

The triafulvene **2** exhibited the spectral properties shown in Table 1. While the ^1H NMR spectrum showed only the phenyl proton signals, the more positive proof for the structure was given by the IR spectrum, which exhibited both the absorptions due to

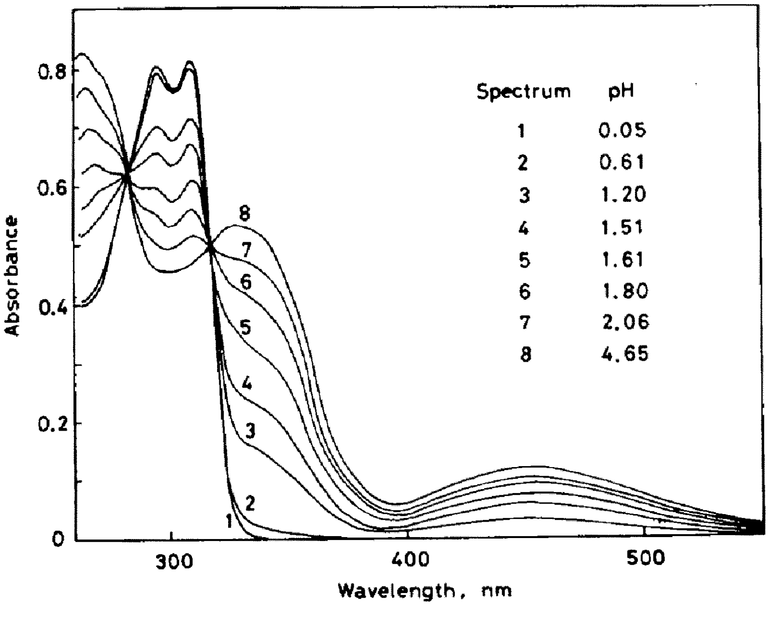


Fig. 1. The spectrophotometric titration of the cation **3** (2.8×10^{-5} M) in 50% aq. CH_3CN.

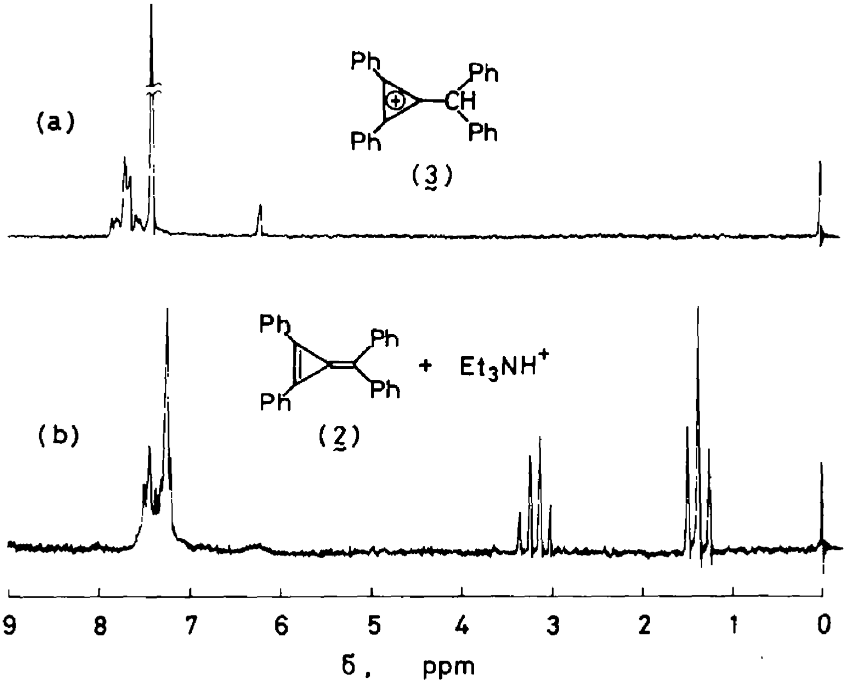
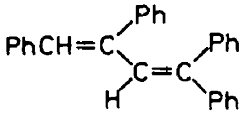


Fig. 2. The ^{1}H NMR spectra of (a) the cyclopropenium ion **3** in CDCl$_3$, and (b) the triafulvene **2** and Et$_3$NH$^+$ obtained by addition of one molar equivalent of Et$_3$N to the solution (a).

endocyclic (1850 and 1820 cm^{-1}†) and exocyclic double bonds (1560 cm^{-1}). In accord with this, the catalytic hydrogenation of **2** required two molar equivalents of hydrogen, and afforded the cyclopropane derivative identical to the sample similarly obtained from the cyclopropene **4**.

Another structural evidence was given by the mass spectrum, which exhibited the molecular ion peak at *m/e* 356 (M$^+$, 62%), together with the M + 1 and M + 2 ion peaks in intensities corresponding to the calculated values based on natural isotopic abundance for $C_{28}H_{20}$. Furthermore, the base peak at 178, which seemingly corresponds to M/2 (cleavage to diphenylacetylene moiety), is partly attributable to *m*/2*e* (the dipositive ion, M^{2+}) since the (M + 1)/2 ion peak is clearly observed at 178.5 (4.4%). This observation clearly indicates the formation of the dicationic species **2**$^{2+}$ in the gas phase, and is in qualitative accordance with the results of electrochemical oxidation (*vide infra*), which exhibited smooth formation of **2**$^{2+}$ in solution.

Compared with triafulvene derivatives reported so far, the triafulvene **2** has the absorption maximum in the electronic spectrum at a considerably longer wavelength, i.e. 462 nm in acetonitrile, as a result of electronic interaction of the cross-conjugated diene system with the four phenyl substituents. In contrast, a linearly conjugated diene system similarly substituted with four phenyl groups such as **8** absorbs only at 328 nm in cyclohexane.[9] The longest wavelength absorption of **2** exhibits a distinctive bathochromic shift upon decreasing the solvent polarity, as follows; 462 nm (log ε, 3.69) in acetonitrile, 467 nm (3.69) in acetone, 469 nm (3.65) in chloroform, 475 nm (3.58) in benzene, and 477 nm (3.59) in cyclohexane. This solvent effect serves as clear evidence for a larger contribution of the ionic dipolar structure such as **1a** at the ground state than at the excited state,[10] despite the absence of any polar substituent in **2**.



(8)

In order to obtain more precise information on the possible charge separation in **2**, the ^{13}C NMR spectrum was examined next. The observed spectrum of **2** consisting of 11 peaks is schematically shown in Fig. 3, together with those of the cyclopropene **4** and the cation **3** for comparison. The assignment of individual peaks was made on the basis of the peak intensity measured under the long enough pulse interval, the peak multiplicity observed in the fully and partially proton-coupled spectra, and the nuclear Overhauser effect, as follows. The two weakest signals with unit intensity (singlet in an off-resonance spectrum) at 120.4 and 96.9 ppm were obviously assigned to the carbons, C-2 and C-3, of the exocyclic double bond. Between these two, one at 120.4 ppm with the less nuclear Overhauser enhancement appears as a distinctively sharp singlet in a fully coupled spectrum, and thus was assigned to the inner carbon, C-2. Similarly, among three double-intensity signals

---

†It has been reported that the absorption due to the cyclopropene double bond splits into a doublet (1860 and 1828 cm^{-1}) also in 1,2,3,4-tetrachloro-5,6-diphenyltriapentafulvalene; M. Ueno, I. Murata, and Y. Kitahara, *Tetrahedron Letters* 2967 (1965); E. D. Bergmann and I. Agranat, *Tetrahedron* **22**, 1275 (1966).

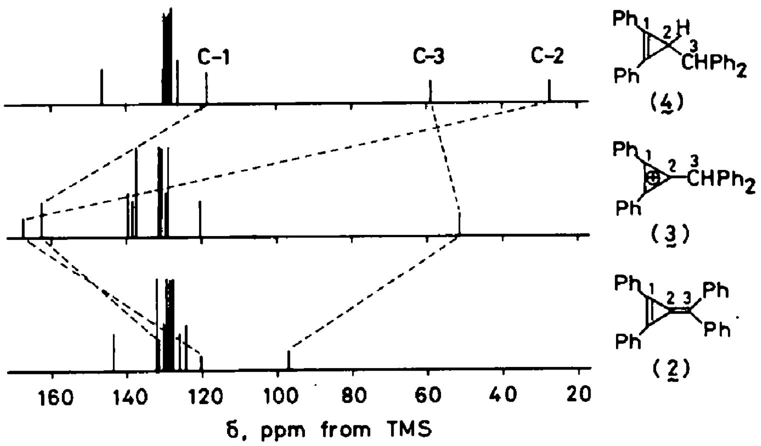


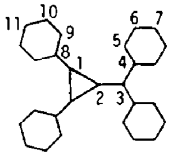
Fig. 3. Schematic presentation of the ^{13}C NMR spectra (proton-decoupled) of the cyclopropene **4** ($CDCl_3$), the cyclopropenium ion **3** (CD_3CN), and the triafulvene **2** ($CDCl_3$).

(singlet) at 143.8, 131.8, and 126.0 ppm, the one appearing at 131.8 ppm was tentatively assigned to the C-1 carbon, since it exhibited the least nuclear Overhauser enhancement. The assignment of the rest of signals to individual phenyl carbons was made based on similar consideration and on comparison with the charge densities obtained by simple HMO calculations. The results of the assignment are shown in Table 2, together with the calculated charge densities. It is noteworthy that the signals for carbons of triafulvene framework are distributed over a considerably wide chemical shift range (i.e. 131.8, 120.4, and 96.9 ppm) for sp^2 carbons in a neutral hydrocarbon π-system. A remarkable upfield shift (96.9 ppm) of the exocyclic methylene carbon, C-3, indicates the polarization with a negative end at the exocyclic methylene carbon, as has been suggested by the solvent effect on the electronic spectrum. This is in contrast to the case of 8,8-diphenylheptafulvene, in which only small charge separation was detected on the basis of both ^{13}C NMR and electronic spectral data.[5]

Table 2. The ^{13}C NMR chemical shifts and calculated charge densities for the triafulvene **2**.

Carbon [a]	δ ($CDCl_3$), ppm [b]	Charge density [c]
1	131.8 (s)	+0.1760
2	120.4 (s)	+0.1467
3	96.9 (s)	-0.2619
4	143.8 (s)	+0.0078
5	127.9 (d)	-0.0586
6	129.7 (d)	+0.0007
7	124.7 (d)	-0.0557
8	126.0 (s)	-0.0171
9	131.9 (d)	+0.0233
10	128.9 (d)	-0.0011
11	130.6 (d)	+0.0180

[a] Numbering:



[b] Peak multiplicity observed in the proton-coupled spectrum is shown in the parentheses.
[c] Calculated by the simple HMO method assuming the coplanarity of phenyl groups with the triafulvene framework.

One-electron oxidation

Another characteristic feature in the electronic state of the triafulvene **2** predicted by the HMO calculation is a very high energy level for the highest occupied MO ($\alpha + 0.1411\beta$ for a planar model), implying ready oxidation of **2** to its cation radical and dication by the sequential removal of a π-electron. To test this prediction, the behavior of **2** under electrochemical oxidation was examined by means of cyclic voltammetry in dichloromethane.

The voltammogram of **2** is shown in Fig. 4(a). Two anodic peaks at +0.74 and + 1.24 V vs SCE and the

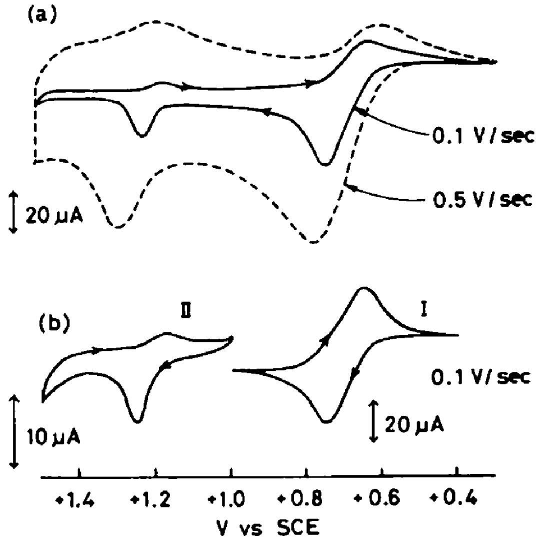
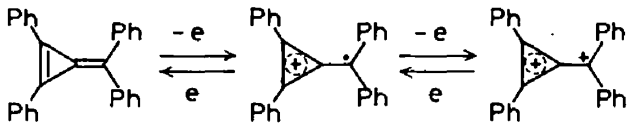


Fig. 4. Cyclic voltammograms of the triafulvene **2** (1 mM) with $Bu_4N\ ClO_4$ (0.1 M) as the supporting electrolyte in CH_2Cl_2.



(**2**) (**2**$^{+\cdot}$) (**2**$^{2+}$)

Scheme 4

corresponding two cathodic peaks at +0.64 and +1.16 V were observed at a scan rate of 0.1 v/sec. The first anodic wave was shown to correspond to the exchange of one electron per molecule by comparison of the peak current with that of ferrocene determined under the identical conditions.† By increasing the scan rate, the second anodic peak became larger approaching to the intensity comparable to the first one. These observations suggest that these two redox waves are due to two discrete one-electron transfer steps corresponding to the consecutive formation of the cation radical **2**$^{+\cdot}$ and the dication **2**$^{2+}$ (Scheme 4). When the whole voltammogram was separated into two individual redox waves (Fig. 4b), the first wave exhibited good reversibility as was shown by the peak current ratio of the cathodic and anodic peaks reaching unity at the scan rate greater than 0.25 V/sec, as well as by the difference in the peak potential between the cathodic and anodic peaks approaching to the theoretical value of 0.06 V[11] at slower scan rates. These data are shown in Table 3. Thus, the first formed cation radical **2**$^{+\cdot}$ is supposed to have enough stability to be reduced back to **2** at higher scan rates. In contrast, the second anodic peak exhibited very poor reversibility indicating that the secondly formed dication **2**$^{2+}$ is relatively much less stable, and is consumed by rapid follow-up reactions.

Based on these findings, it was examined next to oxidize the triafulvene **2** to its cation radical **2**$^{+\cdot}$ by chemical means. Various reagents ($SbCl_5$, $AgBF_4$, $AgClO_4/I_2$, $AlCl_3$, and $Pb(OAc)_4$ in CH_2Cl_2, CS_2, and CH_3NO_2), which are known to generate cation radicals,[12] all decolorized the deep red solution of **2** immediately after mixing, but only the following two reagents gave clear evidence for the formation of **2**$^{+\cdot}$. When antimony pentafluoride was added to **2** in dichloromethane or in carbon disulfide, the resultant yellow-brown solution exhibited a strong ESR signal of a broad single line. Evaporation of the solvent afforded a yellowish brown solid, which showed the IR spectrum quite similar to that for the cation salt **3**·BF_4^-, except that the absorptions due to the aliphatic C–H stretching and the tetrafluoroborate anion were absent. On the other hand, when silver tetrafluoroborate was added to a dilute solution of **2** in dichloromethane, there resulted a mixture of a pale green solution and gray powder. The solution showed an ESR signal consisting of a strong hyperfine structure with a g-value of 2.002616 typical for hydrocarbon cation radicals,[12a] as shown in Fig. 5. This signal persisted at room temperature for one day, demonstrating the stability of the radical species. The good symmetry of the signal indicates the presence of a single paramagnetic species. The observed spectral width and number of splitted peaks (*ca* 160 lines observable) suggest that this spectrum is due to the cation radical **2**$^{-}$ with the unpaired electron fully delocalized to all the four phenyl rings.†

Table 3. The peak potential (E_p) and peak current (i_p) data for the first and second redox waves observed separately by cyclic voltammetry of the triafulvene **2** in CH_2Cl_2.

Scan rate	The 1st wave (I)				The 2nd wave (II)			
	E_{pa}	E_{pc}	i_{pa}	i_{pc}	E_{pa}	E_{pc}	i_{pa}	i_{pc}
V/sec	V vs SCE		μA		V vs SCE		μA	
0.05	0.72	0.65	34	23	1.24	1.16	4	0.5
0.10	0.74	0.64	42	34	1.24	1.16	10	1
0.25	0.76	0.63	54	54	1.25	1.16	19	2
0.50	0.78	0.62	72	71	1.28	1.17	27	3
0.75	0.79	0.62	86	86	1.29	1.14	36	5

[a] Concentration: **2**, 1mM; supporting electrolyte (Bu_4NClO_4), 0.1M.

---

†The same method has been used to demonstrate the removal of one electron per molecule upon electrochemical oxidation of 4,4'-dimethoxystilbene; E. Steckhan, *J. Am. Chem. Soc.* **100**, 3526 (1978).

†Although a completely matching spectrum has not yet been obtained, the results of computer simulation experiments suggested that contribution of four sets of four equivalent protons (*ortho*- and *meta*-protons of two pairs of phenyl groups) and two sets of two equivalent protons (*para*-protons of two pairs of phenyl groups) must be taken into account to explain the observed spectrum.

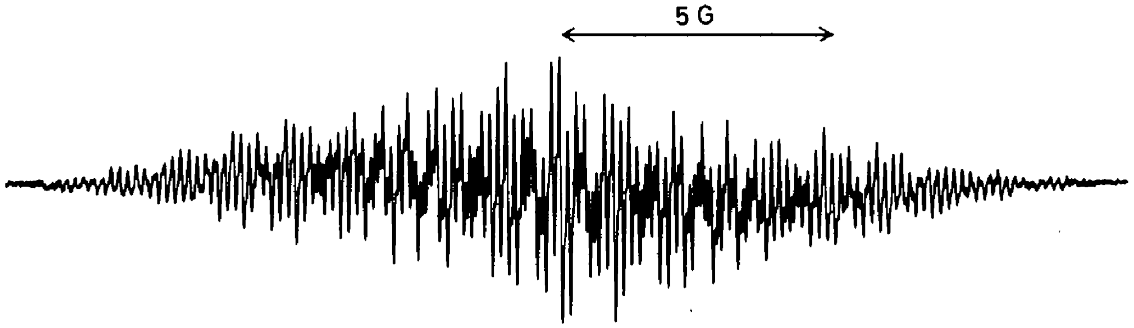


Fig. 5. The ESR spectrum of the cation radical 2^+ generated by oxidation of 2 with $AgBF_4$ in CH_2Cl_2.

Previously, the diphenylfulvene anion radical has been reported as a new "triarylmethyl" having a cyclopentadienide anion.[13] Analogously, the present cation radical $2^{\dot{+}}$ can be formally represented as a cationic homolog of the classical "triarylmethyl", in which one of the aryl group is replaced by the non-benzenoid aromatic three-membered ring, though unfortunately the exact data on spin delocalization is not available at present due to the difficulty in complete assignment of all the coupling constants arising from all the interacting protons of the two pairs of phenyl groups.

EXPERIMENTAL

General. M.ps are uncorrected. Elemental analyses were performed by Microanalytical Center, Kyoto University, Kyoto. IR and UV-Vis spectra were recorded with a Hitachi 215 and a Hitachi 200-10 spectrophotometers., respectively. ^1H NMR spectra (60 MHz) were taken on a Hitachi R-24 spectrometer with Me_4Si as an internal standard. ^{13}C NMR spectra (25 MHz) were obtained on a JEOL FX-100 spectrometer operated in the pulse Fourier transform mode. Mass spectra were recorded with a JEOL JMS-01SG spectrometer.

All reagents were of a reagent-grade quality unless otherwise noted. CH_3CN and CH_2Cl_2 were refluxed and distilled over P_2O_5, and THF was distilled over LAH, prior to use. Merck SiO_2 type GF_{254} and type PF_{254} were used for analytical and preparative tlc, respectively.

1,2-*Diphenylcyclopropenium tetrafluoroborate* ($5 \cdot BF_4^-$). A soln of triphenylmethyl tetrafluoroborate[14] (8.01 g, 24.3 mmol) in CH_3CN (45 ml) was added dropwise to a stirred suspension of 7[15] (5.58 g. 24.6 mmol) in CH_3CN (10 ml) at room temp. After stirring for 0.5 hr, dry ether (300 ml) was added with ice cooling to cause the formation of a white ppt, which was filtered off, washed with dry ether, and dried under reduced pressure to give $5 \cdot BF_4^-$ (6.18 g, 91.5%) as fluffy off-white needles; mp 160–161.3 (dec) (lit.[16] mp 158). (Found: C, 64.99; H, 4.25%. Calc. for $C_{15}H_{11}BF_4$: C, 64.79; H, 3.99%); ^{13}C NMR δ (CD_3CN) 163.8 (s, C-1, 2), 155.3 (d, C-3), 140.2 (d, *para*-C), 137.6 (d, *ortho*-C), 131.3 (d, *meta*-C), 120.0 (s, *ipso*-C). From the filtrate was obtained triphenylmethyl chloride (4.60 g, 68.0%) after recrystallization from benzene; mp 106–108° (lit.[17] 110.5°).

Reaction of $5 \cdot BF_4^-$ *with benzhydryllithium in the presence of* LiCl. A soln of benzhydryllithium in THF was prepared by adding a soln of benzhydryl chloride (1.70 g, 8.38 mmol) in THF (10 ml), dropwise, to a stirred suspension of Li chips (0.30 g, 43 mmol) in THF (16 ml) and stirring the mixture overnight. Then, the benzhydryllithium soln (24 ml) was added dropwise to a stirred suspension of $5 \cdot BF_4^-$ (1.24 g, 4.45 mmol) in THF (40 ml) cooled at -60°, by the use of a syringe over a period of 4 hr. The temp was slowly raised to 0 during 2 hr. The mixture was hydrolysed with 5% HCl (40 ml) and extracted with ether (60 ml × 3). The ethereal soln was washed with 10% NaCl (150 ml × 3), dried ($MgSO_4$), and evaporated *in vacuo* to give 2.31 g of the crude product, which exhibited four main spots at R_f 0.70, 0.40, 0.25, and 0.0 on an analytical tlc plate developed with benzene-hexane (1:9). By the use of preparative tlc developed under the same conditions, the fraction with R_f 0.40 afforded 6 (0.749 g, 47.0%) as white crystals, identified on the basis of spectral data shown in Table 1; m.p. 124–126° (hexane). (Found: C, 93.74; H, 6.42%. Calc. for $C_{28}H_{22}$: C, 93.81; H, 6.19%). Similarly, diphenylmethane and 1,1,2,2-tetraphenylethane were isolated from the fractions with R_f 0.70 and 0.25, respectively, and identified by comparison of their IR and NMR spectra with those of the authentic samples.

In a control experiment, LiCl (0.0886 g. 2.09 mmol) was added to a stirred suspension of $5 \cdot BF_4^-$ (0.478 g, 1.72 mmol) in THF (25 ml), causing immediate dissolution of 5. After stirring for 0.5 hr, the solvent was evaporated *in vacuo*, and the residue was extracted with dry benzene. Recrystallization of the crude extract from hexane-ether afforded white crystals (0.371 g, 95.2%), which were identified as 7 on the basis of following properties:† m.p. 79.5-81 , IR ν (KBr) 3060 w, 2920 w, 1820 w, 1570 m, 1495 m, 1480 m, 1440 s, 1330 m, 1240 m, 1140 m, 1105 m, 1090 m, 1020 s, 920 w, 760 s, 680 s cm^{-1}; ^1H NMR δ ($CDCl_3$) 7.90–7.42 (m, 10 H, Ph), 4.97 (s, 1 H, —CHCl—).

The chlorocyclopropene 7 thus obtained was allowed to react with benzhydryllithium exactly in the same way as described above. Recrystallization of the crude product from hexane afforded the cyclopropene 6 in 30% yield.

Reaction of $5 \cdot BF_4^-$ *with benzhydrylmagnesium bromide.* A soln of benzhydryllithium was prepared by addition of 1.6 N n-BuLi in hexane (2.0 ml, 3.2 mmol) to a soln of freshly distilled diphenylmethane (0.51 g, 3.0 mmol) in dry ether (6 ml) and refluxing overnight under N_2.[8] In order to prepare the Grignard reagent, this soln was added, by the use of a syringe, to a stirred soln of anhyd $MgBr_2$, which had been freshly prepared from Mg (0.080 g, 3.3 mmol) and Br_2 (0.48 g, 3.0 mmol) in dry ether (8 ml), under N_2. To the stirred soln of benzhydrylmagnesium bromide thus prepared and cooled at -20°, there was added $5 \cdot BF_4^-$ (0.557 g, 2.00 mmol) in one portion. After stirring at -20° for 1 hr and at room temp for 1 hr, the mixture was hydrolysed and worked up to give 1.04 g of the crude product, which showed four main spots at R_f 0.75, 0.50, 0.28, and 0.0 on an analytical tlc plate developed with benzene-hexane (1:4). Separation of the products by the use of preparative tlc afforded diphenylmethane (R_f 0.75), 1,1,2,2-tetraphenylethane (R_f 0.28), and 4 (0.0416 g, 5.8%) (R_f 0.50) as white crystals, identified on the basis of the spectral data shown in Table 1; m.p. 183–184°

---

†These properties were in complete agreement with those of the chlorocyclopropene 7 obtained by the method of Padwa and Eastman: Ref. 15.

(hexane–benzene); ^{13}C NMR[†] δ ($CDCl_3$) 118.2 (s, C-1), 27.3 (d, C-2), 58.9 (d, C-3), 146.5 (s, C-4), 130.0 (s, C-8), 130.0 and 126.0 (d, *para*-C), 129.9, 128.7, 128.6 and 128.3 (d, *ortho*- and *meta*-C). (Found: C, 93.62; H, 6.11%. Calc. for $C_{28}H_{22}$: C, 93.81; H, 6.19%).

Alternative synthesis of 1,3-diphenyl-3-benzhydrylcyclopropene (**6**). A soln of 2,3,3-triphenylpropene (0.0555 g, 0.205 mmol), which was prepared by the method of Russell and Becker,[18] and phenylchlorodiazirine[15] (0.231 g, 1.51 mmol) in dry benzene (4 ml) was heated to reflux for 4 hr. Evaporation of the solvent *in vacuo* afforded 0.261 g of the crude product, which exhibited five main spots at R_f 0.64, 0.48, 0.33, 0.25, and 0.09 on an analytical tlc plate developed with benzene hexane (1:4). By the use of preparative tlc, the unchanged 2,3,3-triphenylpropene (0.0265 g) was recovered from the fraction with R_f 0.48, while the fraction with R_f 0.25 afforded crude 1,2-diphenyl-1-chloro-2-benzhydrylcyclopropane (0.0218 g), which was used in the following reaction without further purification. t-BuOK (Merck) (0.080 g, 0.71 mmol) was added to a stirred soln of the crude chlorocyclopropane in THF (2 ml) under N_2. After stirring for 24 hr, the mixture was hydrolysed and worked up to give 0.0191 g of the crude product, which showed three main spots at R_f 0.77, 0.31, and 0.08 on an analytical tlc plate developed with benzene–hexane (1:4). From the fraction with R_f 0.31 was obtained, by the use of preparative tlc, white crystals (0.0059 g, 15% based on the consumed triphenylpropene) identified as the cyclopropene **6** by comparison of the IR and NMR spectra with those of the sample obtained by the cation–anion reaction described above.

Alternative synthesis of 1,2-diphenyl-3-benzhydryl cyclopropene (**4**). A soln of 1,3,3-triphenylpropene (1.08 g, 4.00 mmol), which was prepared by dehydration of 1,3,3-triphenylpropan-1-ol according to the method of Burkhalter and Johnson,[19] and phenylchlorodiazirine (0.670 g, 4.39 mmol) in dry benzene (40 ml) was heated to reflux for 2 hr. After evaporation of the solvent *in vacuo*, the product mixture was separated by the use of preparative tlc developed with benzene–hexane (1:4). While the fraction with R_f 0.52 afforded 0.576 g of the unchanged 1,3,3-triphenylpropene, the fraction with R_f 0.28 gave 1,2-diphenyl-1-chloro-3-benzhydrylcyclopropane (0.529 g, 33.5%) as pale yellow viscous oil; ^{1}H NMR δ (CCl_4) 7.33–6.95 (m, 20 H, Ph), 4.49 (d, J = 9 Hz, 1 H, C$\underline{H}$Ph$_2$), 2.70 (d, J = 8.5 Hz, 1 H, –C$\underline{H}$Ph–), 2.47 (dd, 1 H, C$\underline{H}$(CHPh$_2$)–). To a stirred soln of the chlorocyclopropane (1.43 g, 3.61 mmol) in THF (50 ml) was added t-BuOK (Merck) (2.03 g, 18.1 mmol) in one portion. After stirring for 18 hr under N_2, the mixture was hydrolysed and worked up to give 1.289 g of the crude product, which was shown to contain *ca* 0.8 g of **4** besides the unchanged starting material, by the NMR analysis. Recrystallization of the crude product from hexane-CCl_4 (1:1) (30 ml) afforded white crystals (0.608 g, 47.0%), which was identical to the cyclopropene **4** in all the physical and spectral properties.

Catalytic hydrogenation of the cyclopropenes **6** *and* **4**. The cyclopropene **6** (0.118 g, 0.330 mmol) was dissolved in dry benzene-THF (1:1) (6 ml) and catalytically hydrogenated over 5% Pd-C (0.10 g). After 1 hr, when 7.5 ml (0.33 mmol) of H_2 had been absorbed, the catalyst was filtered off and the filtrate evaporated *in vacuo* to give 0.116 g of the crude product. Purification with preparative tlc developed with benzene-hexane (1:3) afforded 1,2-diphenyl-1-benzhydrylcyclopropane (0.0977 g, 82.2%) as colorless, viscous oil; ^{1}H NMR δ ($CDCl_3$) 7.30–6.85 (m, 20 H, Ph), 3.73 (s, 1 H, C$\underline{H}$Ph$_2$), 2.50 (dd, 1 H, –C$\underline{H}$Ph–), 1.52, 1.50 (d × 2, J = 7 and 9 Hz respectively, 2 H, –CH$_2$–).

In the same way, **4** was catalytically hydrogenated to give 1,2-diphenyl-3-benzhydrylcyclopropane as white crystals in 82.6% yield after absorption of one molar equivalent of hydrogen; ^{1}H NMR δ ($CDCl_3$) 7.30–6.81 (m, 20 H, Ph), 3.99 (d, J = 10 Hz, 1 H, C$\underline{H}$Ph$_2$), 2.9–2.0 (m, 3 H, –CHPh– + –C$\underline{H}$(CHPh$_2$)–).

1,2-Diphenyl-3-benzhydrylcyclopropenium tetrafluoroborate (**3** · BF_4^-). Triphenylmethyl tetrafluoroborate (1.35 g, 4.09 mmol) was added to a stirred soln of **4** (1.31 g, 3.66 mmol) in CH_2Cl_2 (30 ml), and the mixture heated to reflux for 5 hr. Addition of dry ether (110 ml) to the mixture with ice cooling caused the formation of a white ppt, which were filtered, washed with dry ether, and dried under reduced pressure to give **3** · BF_4^- (1.55 g, 95.4%) as white crystals with pink tinge; mp 248–249° (dec) (CH_3CN); ^{13}C NMR[†] δ (CD_3CN) 162.7 (s, C-1), 167.2 (s, C-2), 51.4 (d, C-3), 138.4 (s, C-4), 129.6 (d, C-5), 130.7 (d, C-6), 129.8 (d, C-7), 120.4 (s, C-8), 137.4 (d, C-9), 131.2 (d, C-10), 139.7 (d, C-11). (Found: C, 75.71; H, 4.88%. Calc. for $C_{28}H_{21}BF_4$: C, 75.70; H, 4.76%).

Determination of pK_a for the cation **3**. A stock soln was prepared by dissolving **3** · BF_4^- (0.0015 g, 0.0034 mmol) in CH_3CN (60 ml). Each 5-ml portion of the stock soln was pipetted out and made up to 10 ml by adding aqueous solns of slightly different acidities prepared from dil HCl (pH < 2) or from the citrate-phosphate buffer[20] (pH > 2). Immediately after recording the UV spectrum, pH of each sample soln was determined on a Horiba Model H pH meter, which had been calibrated with standard buffers before use. The observed absorbance at the maximum absorption wavelength (310 nm) of the cation was plotted against the pH to give a classical titration curve, whose midpoint (pH 1.6, uncertainty limit ±0.1) was taken as the pK_a.

Tetraphenyltriafulvene (**2**). Triethylamine (0.0640 ml, 0.0464 g, 0.459 mmol) was added, by the use of a microsyringe, to a stirred soln of **3** · BF_4^- (0.201 g, 0.452 mmol) in CH_2Cl_2 (8 ml). The resultant dark red soln was stirred for 2 min, and then briefly washed with H_2O (10 ml). After drying over $MgSO_4$ for 2 min, the solvent was removed *in vacuo* to give **2** (0.155 g, 96.2%) as a dark red solid, which was characterized by the spectral properties shown in Table 1. Recrystallization from CH_2Cl_2 at −78° gave dark red crystals; however, the correct analysis was not obtained probably due to some instability towards gradual air oxidation; mp 182 183.5°. (Found: C, 93.38; H, 5.96%. Calc. for $C_{28}H_{20}$: C, 94.34; H, 5.66%).

The triafulvene **2** (0.155 g, 0.435 mmol) was found to absorb 19.0 ml (0.848 mmol) of hydrogen over 5% Pd-C (0.20 g) in benzene (10 ml) in 2 hr to give 0.157 g of the crude product, from which was isolated, by recrystallization from pentane, white crystals with the same spectral properties as 1,2-diphenyl-3-benzhydrylcyclo propane similarly obtained from **4**.

Cyclic voltammetry. The measurements were carried out with a Hokuto-Denko Model HA 104 potentiostat equipped with a Hokuto-Denko Model HB 107A function generator. A three-electrode cell was used, consisting of Pt wire working and auxiliary electrodes and a saturated calomel reference electrode. The reference electrode was connected to the bulk of the sample soln by a capillary salt bridge filled with the sample soln. The soln was 1 mM in **2** and 0.1 M in Bu_4NClO_4 as a supporting electrolyte in CH_2Cl_2. The voltammograms were recorded on a Hitachi Model 057 X-Y recorder.

One-electron oxidation of the triafulvene 2

(a) *With* $SbCl_5$. By the use of a syringe, a soln of $SbCl_5$ in dry CS_2 (0.187 M) was added dropwise to a stirred soln of **2** (0.0293 g, 0.0823 mmol) in CS_2 (1 ml) under N_2. When 0.47 ml (0.088 mmol) of the $SbCl_5$ soln was added, the color of the mixture changed from dark red to yellow brown. Evaporation of the solvent *in vacuo* afforded a dark green-brown solid (0.0553 g); IR ν (KBr) 3060 w, 1840 w, 1595 s, 1500 s, 1450 m, 1420 br vs, 1350 w, 1180 m, 1080 w, 1035 w, 1000 w, 970 w, 765 s, 730 m, 705 s, 680 s cm^{-1}.

In a repeated run carried out in the same way, a part of the mixture was transfered to an ESR sample tube. After dry N_2 was bubbled in for a few min through a fine capillary, the tube was sealed and the ESR spectrum recorded at room temp to exhibit a broad single line with a peak-to-peak width 5G.

[†] The numbering system is same as that shown in the footnote a in Table 2.

(b) *With* $AgBF_4$. In an ESR sample tube with a side arm, a soln of **2** (0.001 g, 0.003 mmol) in CH_2Cl_2 (1 ml) and $AgBF_4$ (0.003 g, 0.015 mmol) were charged separately. After the soln was degassed with the freeze-and-thaw technique, the whole system was sealed under vacuum. Then, $AgBF_4$ was mixed with the soln of **2** by shaking the tube at room temp, resulting in the color change of the soln to greenish yellow. The supernatent soln exhibited the ESR spectrum shown in Fig. 5 at room temp.

REFERENCES

[1a] M. A. Battiste, *J. Am. Chem. Soc.* **86**, 942 (1964); [b] W. M. Jones and J. M. Denham, *Ibid.* **86**, 944 (1964); [c] E. D. Bergmann and I. Agranat, *Ibid.* **86**, 3587 (1964); [d] A. S. Kende and P. T. Izzo, *Ibid.* **86**, 3587 (1964); [e] S. Andreades, *Ibid.* **87**, 3941 (1965); [f] W. M. Jones and R. S. Pyron, *Tetrahedron Letters* 479 (1965); [g] T. Eicher and A. Löschner, *Z. Naturforschg.* **21b**, 899 (1966); [h] W. M. Jones, M. E. Stowe, E. E. Wells, Jr. and E. W. Lester, *J. Am. Chem. Soc.* **90**, 1849 (1968); [i] P. Anderson, P. Crabbé, A. D. Cross, J. H. Fried, L. H. Knox, J. Murphy and E. Velarde, *Ibid.* **90**, 3888 (1968); [j] S. S. Hecht, *Tetrahedron Letters* 4385 (1970); [k] E. D. Bergmann and I. Agranat, *J. Chem. Soc.* (C), 1541 (1971); [l] Z. Yoshida and Y. Tawara, *Tetrahedron Letters* 3603 (1971); [m] I. Agranat and M. R. Pick, *Ibid.* 4079 (1973); [n] I. Agranat, S. Cohen, E. Aharon-Shalom and E. D. Bergmann, *Tetrahedron* **31**, 1163 (1975).

[2a] P. J. Stang and M. G. Mangum, *J. Am. Chem. Soc.* **97**, 3854 (1975); [b] W. E. Billups and A. J. Blakeney, *Ibid.* **98**, 7817 (1976).

[3] I. S. Krull, P. F. D'Angelo, D. R. Arnold, E. Hedaya and P. O. Schissel, *Tetrahedron Letters* 771 (1971).

[4a] R. Breslow and M. Battiste, *J. Am. Chem. Soc.* **82**, 3626 (1960); [b] G. Melloni and J. Ciabattoni, *Chem. Commun.*, 1505 (1968).

[5] K. Komatsu, M. Fujimori and K. Okamoto, *Tetrahedron* **33**, 2791 (1977).

[6] R. W. Johnson, T. Widlanski and R. Breslow, *Tetrahedron Letters* 4685 (1976).

[7] A. Padwa, T. J. Blacklock, D. Getman, N. Hatanaka and R. Loza, *J. Org. Chem.* **43**, 1481 (1978).

[8] L. H. Sommer and W. D. Korte, *Ibid.* **35**, 22 (1970).

[9] G. Köbrich and H. Fröhlich, *Chem. Ber.* **98**, 3637 (1965).

[10a] N. S. Bayliss and E. G. McRae, *J. Phys. Chem.* **58**, 1002 (1954); [b] E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

[11] R. N. Adams, *Electrochemistry at Solid Electrodes.* Chap. 5. Marcel Dekker, New York (1969).

[12a] G. Vincow, *Radical Ions*, (Edited by E. T. Kaiser and L. Kevan), Chap. 4. Wiley, New York (1968); [b] A. J. Bard, A. Ledwith and H. J. Shine, *Adv. Phys. Org. Chem.* **13**, 155 (1976).

[13] C. M. Camaggi, M. J. Perkins and P. Ward, *J. Chem. Soc.* (B), 2416 (1971).

[14] H. J. Dauben, Jr., L. R. Honnen and K. M. Harmon, *J. Org. Chem.* **25**, 1442 (1960).

[15] A. Padwa and D. Eastman, *Ibid.* **34**, 2728 (1969). It was found that the product from the reported reaction of phenylacetylene with phenylchlorodiazirine was not 1,3-diphenyl-3-chlorocyclopropene, as reported, but 1,2-diphenyl-3-chlorocyclopropene formed presumably *via* ionization and migration of the chloride ion.

[16] Th. Danzel and H. J. Bestmann, *Tetrahedron Letters* 3817 (1969).

[17] W. E. Bachmann, *Org. Synth.* Coll. Vol. III, 841 (1955).

[18] G. A. Russel and H.-D. Becker, *J. Am. Chem. Soc.* **85**, 3406 (1963).

[19] J. H. Burckhalter and S. H. Johnson, Jr., *Ibid.* **73**, 4830 (1951).

[20] G. Gomori, *Methods in Enzymology* (Edited by S. P. Colowick and N. O. Kaplan) Vol. I, p. 141. Academic Press, New York (1955).