alcohol, and (2) the reaction of the ketyls (**3**-*6*-d_2)$^-$·M$^+$ to give enolate and alcoholate, since both reactions resemble radical disproportionations. Mechanistically, the latter involve transfer of a hydrogen atom from one radical to another. In radical anion chemistry, the term usually denotes the transfer of an electron from one radical anion to another. Either type of process may be involved in both our reactions; see ref 6 and the mechanistic discussion.

(6) V. Rautenstrauch and M. Geoffroy, *J. Am. Chem. Soc.*, **98**, 5035 (1976).

(7) For clarity we initially leave open the degree of association of the ketyls and then write **1**$^-$·Li$^+$, (**3**-*6*-d_2)$^-$·Li$^+$. The association phenomena are introduced subsequently, and we then write [**1**$^-$·Li$^+$]$_1$, [(**3**-*6*-d_2)$^-$·Li$^+$]$_1$ for the ion pairs, and [**1**$^-$·Li$^+$]$_2$, [(**3**-*6*-d_2)$^-$·Li$^+$]$_2$ for the ion quadruplets.

(8) Analysis by low resolution mass spectrometry (see the Experimental Section). Estimated, absolute, analytical error: (a) 2–3%; (b) ca. 5%.

(9) The prefix *c*- is used to designate the conjugate base (enolate, alcoholate, dialcoholate) of a given substrate and the prefix *r*- is used to designate the radical derived from a given substrate by hydrogen or deuterium atom abstraction.

(10) In principle, it would be more correct to leave open the possible mechanisms [a deuterium atom abstraction and a reduction (as formulated, Scheme II), or the corresponding dedeuteronation (leading to *c*-(**3**-*6*-*d*)$^-$Li$^+$ and the O-deuterated ketyl radical corresponding to (**3**-*6*-d_2)$^-$·Li$^+$) and a reduction (of the ketyl radical)] at this stage, and to formulate instead a purely kinetic scheme (corresponding to Scheme I) which is essentially the same for both mechanisms. We nevertheless introduce the more likely mechanism[11] explicitly at this stage, for the following reasons (and for clarity and brevity): (1) the underlying kinetic scheme is subsequently excluded experimentally; the dedeuteronation mode is (2) unfavorable (estimated pK_a values) and is (3) subsequently excluded experimentally (independently from (1): disproportionation is found to occur without loss of the deuterium label to protic, acidic media).

(11) Analogy: J. E. Bennett, B. Mile, and A. Thomas, *J. Chem. Soc. A*, 298 (1968).

(12) Estimated, absolute, analytical error: (a) 0.2; (b) 0.1.

(13) Below ca. 0.038 M, the reaction does not start.

(14) Reference 6 and literature cited therein.

(15) Analogy: G. P. Laroff and H. Fischer, *Helv. Chim. Acta*, **56**, 2011 (1973).

(16) U. Schöllkopf, "Houben-Weyl", Vol. XIII/1, Georg Thieme Verlag, Stuttgart, 1970, Chapters 1 and 3.

(17) W. C. Meuly, West Germany Patent 1 244 784 (1968).

(18) A. F. Thomas, "Deuterium Labeling in Organic Chemistry", Appleton-Century-Crofts, New York, N.Y., 1971, p 168.

(19) Data not included in the table.

(20) As judged from visual examination.

Syntheses of Mono-, Bis-, and Tris(diisopropylamino)triphenylcyclopropenium Ions. Cyclopropenyl Analogues of Triphenylmethane Dyes

Koichi Komatsu, Robert West,* and David Stanislawski

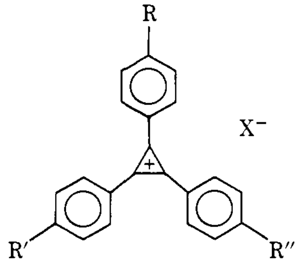
Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received April 14, 1976*

Abstract: Mono-, bis-, and tris(*p*-*N*,*N*-diisopropylamino)triphenylcyclopropenium ions have been synthesized as their perchlorate or tetrafluoroborate salts (**4–6**) by reacting *N*,*N*-diisopropylaniline with the appropriate chlorocyclopropenium ion, ($Ph_nC_3Cl_{3-n}^+$, n = 0–2). These substances are bright yellow dyes which absorb at much shorter wavelengths than the corresponding triphenylmethane dyes (λ_{max} **4**, 411 nm; **5**, 438; **6**, 447). Measurements of the pK_{R^+} values, ^{13}C chemical shifts, and reduction potentials reveal that these ions are much more stabilized than the triarylmethyl analogues, in agreement with results of Hückel MO calculations.

The triphenylmethane dyes, consisting of triphenylmethyl cations substituted with strongly electron-donating amino groups, are a well-known and important class of synthetic coloring matters.[1] Two of the most useful are malachite green (**1**) and crystal violet (**2**), in which triarylmethyl cations contain two and three *p*-dimethylamino groups, respectively. In an early theoretical paper Dewar used simple Hückel molecular orbital theory to calculate the wavelengths of the lowest energy electronic absorption band for these and other basic dyes, with remarkable success.[2]

The series of triarylcyclopropenium ions with *p*-dialkylamino substituents (**4–6**) can be considered as analogues of the triphenylmethane dyes, in which the central carbon atom is replaced by a three-membered ring, giving a larger and more nearly planar[3] conjugated system. Therefore it seemed quite interesting to prepare this series of compounds and compare their properties with those of the classical triphenylmethane dyes.

Syntheses of *p*-Amino-Substituted Triphenylcyclopropenium Ions (4–6). The syntheses of triphenylcyclopropenium ions with mono-[4a] and bis(dimethylamino)[4b] substituents have been reported previously. However, the methods used in these syntheses are not applicable for the entire series of cations with one to three *p*-dialkylamino substituents. We found that these species were prepared in a simple and straightforward manner starting from the trichlorocyclopropenium ion, $C_3Cl_3^+$.[5]



	R	R′	R″	X
3	H	H	H	ClO_4
4	*i*-Pr_2N	H	H	ClO_4
5	*i*-Pr_2N	*i*-Pr_2N	H	ClO_4
6	*i*-Pr_2N	*i*-Pr_2N	*i*-Pr_2N	BF_4

For the synthesis of the mono- or bisamino compounds, 1 or 2 molar equiv of *N*,*N*-diisopropylaniline was allowed to react with diphenylchlorocyclopropenium or phenyldichlorocyclopropenium ions which had been prepared in situ from $C_3Cl_3^+AlCl_4^-$ and 2 or 1 molar equiv of benzene in chloroform. After hydrolysis, the crude chloride salts of the corresponding triarylcyclopropenium ions were converted to and analyzed as the perchlorate salts (**4** and **5**).

The use of $AlCl_3$ for the generation of chlorocyclopropenium ions is known to have wide applicability.[6] However, we found

Table I. Longest Wavelength Absorptions of the Triarylcyclopropenium and Triarylmethyl Cations

		λ_{max}, nm (log ϵ)		
Substituent[a]		Triphenylcyclopropenium[b]		Triphenylmethyl[c]
None	**3**	320 (4.62)		431 (4.60)
4-Dialkylamino	**4**	411 (4.79)		490 (4.05)
4,4′-Bis(dialkylamino)	**5**	438 (5.11)	**1**	620 (5.00)
4,4′,4″-Tris(dialkylamino)	**6**	447 (5.18)	**2**	590 (4.95)

[a] For triarylcyclopropenium series, the dialkylamino group refers to diisopropylamino, whereas for triarylmethyl series, it refers to dimethylamino. [b] Measured in CH_3CN. [c] Reference 15.

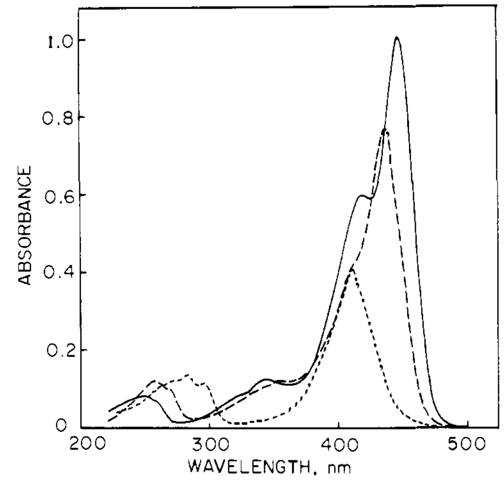


Figure 1. The UV-visible spectrum of the cyclopropenium ions, **4** (- - - -), **5** (– – –), **6** (—); 6.69 × 10^{-5} M in CH_3CN; cell length, 0.10 cm.

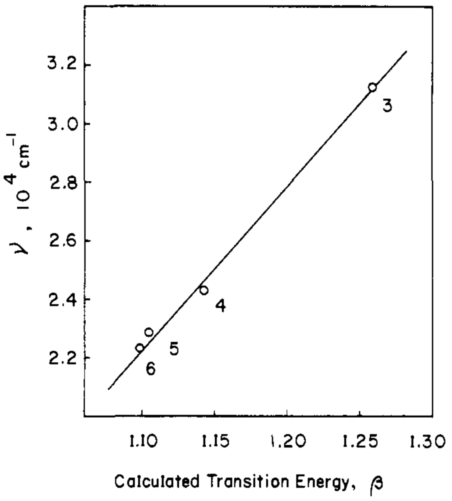


Figure 2. The correlation of the observed wavenumber (ν) of the longest wavelength absorption with the calculated transition energy for unsubstituted (**3**), mono- (**4**), bis- (**5**), and tris(p-diisopropylamino)triphenylcyclopropenium (**6**) ions.

that the direct reaction of $C_3Cl_3^+AlCl_4^-$ (which does not dissolve in chloroform) with diisopropylaniline was too vigorous for convenient control of the reaction. A homogeneous reaction mixture and milder reaction was obtained by using boron trifluoride etherate. Reaction of a mixture of BF_3·OEt_2 and C_3Cl_4 with 3 molar equiv of N,N-diisopropylaniline gave, after hydrolysis and proper workup, tris(p-diisopropylaminophenyl)cyclopropenium fluoroborate (**6**).

All of these cyclopropenium salts are brilliant yellow, crystalline compounds, having very strong infrared bands in the region 1400–1380 cm^{-1} characteristic of the cyclopropenium system[7] and at 1100–1000 cm^{-1} assigned to ClO_4^- and BF_4^-.[8] In the ^1H NMR spectra, aromatic protons of the aminophenyl groups appeared as two doublets (an A_2X_2 system) in all compounds, indicating that attack by the cyclopropenium ion on the aromatic ring all occurred para to the diisopropylamino group. This result is to be compared with the BF_3-catalyzed reaction of C_3Cl_4 with dimethylaniline, where partial ortho substitution occurred to give an inseparable mixture of ortho and para isomers. Apparently steric hindrance around the nitrogen atom by isopropyl groups prohibits the ortho attack.

Yields in these three reactions ranged from 32 to 40% based on C_3Cl_4. However, about half of the aniline is consumed in neutralizing the protonic acid evolved when the cyclopropenium ion attacks the aromatic ring, and this was recovered in 44–58% yield after hydrolysis. The yields based on unrecovered N,N-diisopropylaniline are therefore about double those reported. Complexing of the dialkylamino group to the Lewis acid, if it takes place, does not seem to hinder the reaction significantly.

Color and Visible Spectra. The very appearance of the brilliant yellow compounds **4–6** shows that the cyclopropenium cations have electronic absorption at shorter wavelength than the analogous triphenylmethane dyes. This result, although contrary to what might be expected from qualitative reasoning, is in good accord with simple MO theory.

Visible and UV spectra for **4–6** are shown in Figure 1, and the longest wavelength absorptions for these species and the corresponding triarylmethyl cations are listed in Table I. The trends in these two series are quite different. In the triphenylmethanes substantial bathochromic shifts are recorded upon introduction of the first two dialkylamino groups, followed by a slight hypsochromic shift going from the **1** to **2**. The latter change has been rationalized both qualitatively and theoretically.[2] In the triphenylcyclopropenium compounds the first dialkylamino group is associated with a large bathochromic shift. Introduction of the second and third amino groups leads to further bathochromic shifts, but these are quite small. The results are well matched by Hückel MO calculations, as shown by the correlation in Figure 2.[9]

The spectral differences between the triarylmethyl and triarylcyclopropenium compounds can be rationalized qualitatively in the following way. Amino-substituted triarylmethyl cations are stabilized by contribution of canonical forms of the immonium type (d). This resonance can be associated with the observed bathochromic shift in the absorption spectrum. The "aromatic" 2π-electron system in cyclopropenium compounds

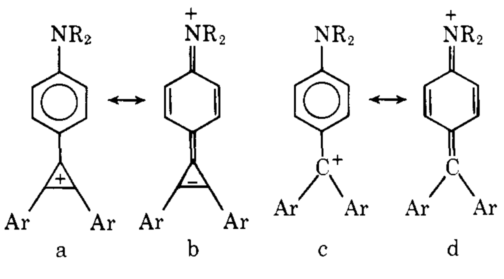


Table II. ^{13}C NMR Chemical Shifts for the Triphenyl- and the Tris(*p*-aminophenyl)carbinols, Carbenium Ions, and Cyclopropenium Ions[a]

Compd	Solvent[10]	C_1	C_2	C_3	C_4	C_5	Ref
Ph_3COH	THF	80.3	150.1	128.6	128.6	128.6	13
Ph_3C^+	$ClSO_3H$	211.8	140.8	144.2	131.2	144.0	13
$Ph_3C_3^+$	$ClSO_3H$	155.4	120.1	135.9	131.2	139.2	14
$(p\text{-}Me_2NPH)_3COH$	THF	80.5	138.2	129.1	111.7	149.7	13
$(p\text{-}Me_2NPh)_3C^+$	EtOH	176.9	126.4	139.7	112.8	156.1	13
$(p\text{-}iPr_2NPh)_3C_3^+$	$CDCl_3$	136.0	115.2	134.1	127.2	133.6	This work

[a] Shifts in parts per million from Me_4Si. A conversion factor of 193.7 ppm was used to convert shifts originally referenced to external CS_2.

Table III. Empirical Charge Densities for Compounds **3** and **6** and Their Carbenium Analogues[a]

Compd	q_1	Δq_2	Δq_3	Δq_4	Δq_5
Ph_3C^+	+0.267	−0.058	+0.098	+0.016	+0.096
$(p\text{-}NMe_2Ph)_3C^+$	+0.049	−0.074	+0.066	+0.007	+0.040
3	+0.330	−0.187	+0.046	+0.016	+0.066
6	+0.219	−0.144	+0.031	+0.097	−0.101

[a] Given as net positive charge at the carbon position.

gives cations which are decidedly more stable than triarylcarbenium ions, so that even in the amino-substituted species, much more of the positive charge remains in the three-membered ring. Contribution of immonium resonance form (b) is less important and the cyclopropenium absorption is correspondingly less shifted.

^{13}C NMR Spectra. The decreased importance of the immonium resonance form for the cyclopropenium ion can also be seen in the changes in charge densities determined empirically from ^{13}C NMR chemical shift data. The low-field chemical shifts for **6** are given in Table II along with the previously reported data for **3** as well as for the analogous triaryl carbenium ions and their parent triarylcarbinols.[10] The numbering system used in presenting this data designates the central carbon(s) as C_1 and the phenyl carbons are then numbered consecutively in the usual manner.

The charge densities for C_2 to C_5 are derived for the ions using the empirical relationship $\Delta\sigma = 160\Delta q$ where $\Delta\sigma$ is the difference in chemical shifts (in parts per million upfield) and Δq is the positive charge delocalized onto the carbon position.[11,12] The densities derived in this manner are recorded in Table III. However, because the hybridization at C_1 differs in the carbinol and the cations, the change in the charge density at C_1 cannot be determined in the same way. For Ph_3C^+ and $(p\text{-}Me_2NC_6H_4)_3C^+$ the charge densities at the central carbon atom were obtained from the relationship $1 - (\sigma + 135)/160$ of Ray et al.[13] The charge density on the cyclopropenium carbons in **3** was obtained by summing the charge densities on all other carbon atoms and subtracting from the net positive charge of one. The remaining positive charge is divided by three to give the charge density at each of the cyclopropenium carbons.[14] The charge density at the cyclopropenium carbons in **6** was then estimated using the value for **3** and the usual relationship $\Delta\sigma = 160\Delta q$.

The charge densities at C_1 provide a means of assessing how much charge is withdrawn from the central carbons upon substituting amino groups in the para positions of the phenyl rings. The difference in charge shows that while the carbenium ion loses better than 80% of the charge originally on C_1 the cyclopropenium ring loses only slightly more than 35%. Thus, the decreased importance of the immonium resonance form in the cyclopropenium case is also supported by the ^{13}C chemical shifts.

pK_R^+ and Reduction Potentials. To measure the effect of the dialkylamino groups on the stabilization of the cyclopropenium ions, we measured the pK_R^+ values and reduction potentials of the cations by spectrophotometry and cyclic voltammetry, respectively. The results of the measurements are listed in Table IV, together with some of the results of the Hückel molecular orbital calculations described above.

In Figure 3 the pK_R^+ values are plotted against the increasing number of the para substituents for both the cyclopropenium and triarylmethyl[15] cations to compare general tendencies in the two systems. Each additional dialkylamino group stabilizes the cation in both series, but the total change is much greater in the triarylmethyl cations. This is again consistent with decreased interaction of the amino nitrogen with the positive center in **4–6** compared to the triphenylmethyl analogues. In **3–6**, increased stabilization with increased numbers of amino groups is consistent with the values of the π-electron energy per π electron from the MO calculations shown in Table IV.

As has been reported for unsubstituted triphenylcyclopropenium ion (**3**),[16] the cyclic voltammetry of the cyclopropenium ions, **4–6**, did not give reversible waves even at high sweep rate (100 V/s), probably because of irreversible dimerization of the cyclopropenyl radical. Therefore the reduction potential was obtained from the values at 85% of the cathodic peak heights[16] while sweeping at 50 V/s. Even though the reduction wave is irreversible, there is a qualitative correlation between the observed reduction potential and the lowest unoccupied MO energy shown in Table IV.[17] The general trend in which each dialkylamino group makes the cation more resistant to one-electron reduction is the same as has been reported for the triarylmethyl cations.[16,18]

From its remarkably high pK_R^+ and reduction potential values, the triamino species (**6**) can be ranked as one of the most stable cyclopropenium ions reported so far. Chemically **6** is indeed difficult to reduce. Reduction of **6** with zinc powder in acetonitrile was attempted, but after 10 days of reaction 79% of the cation was recovered and only a small amount (6%) of product was obtained. By analogy with the formation of hexaphenylbenzene by zinc reduction of triphenylcyclopropenium ion[19] and from the simplicity of the NMR spectrum of this product, its structure is tentatively assigned as hexakis(*p*-diisopropylaminophenyl)benzene.

The trisaminocyclopropenium ion[20] has previously been reported to be resistant to reduction but readily oxidized to a stable radical dication.[21] In contrast to this, an attempt to oxidize the tris(*p*-aminophenyl)cyclopropenium analogue **6** was not successful,[22] indicating that the highest occupied MO in **6** is lower in energy.

Table IV. pK_R^+, Reduction Potentials, and Results of the Hückel Molecular Orbital Calculation on Triarylcyclopropenium Ions

Compd	pK_R^+ [a]	Redn potential,[b] V vs. SCE	$E_{\pi/n}$[c] β	E_{LUMO}[d] $(E - \alpha/\beta)$
3	2.80[e]	−0.94[f]	1.4594	−0.5043[g]
4	6.60	−1.28	1.4892	−0.5043
5	7.85	−1.54	1.5141	−0.5222
6	9.75	−1.80	1.5352	−0.5592[g]

[a] Measured in 23% aqueous EtOH at 25 °C. [b] Measured in CH_2Cl_2 with Bu_4NClO_4 as a supporting electrolyte; sweep rate, 50 V/s. [c] Total π-electron energy divided by the number of π electrons. [d] Energy level of the lowest unoccupied MO. [e] Value taken from ref 22. [f] Literature value measured in Me_2SO is −0.85 V vs. SCE (ref 16). [g] These MOs are double degenerate.

Experimental Section

General Procedures. Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared and ultraviolet spectra were recorded with Perkin-Elmer 237 and Cary 14 spectrometers, respectively. ^1H NMR spectra were taken with a JEOL MH 100 spectrometer. The ^{13}C NMR spectrum was taken on a JEOL FX-60 spectrometer. Diisopropylaniline was prepared according to the literature.[23] Tetrabutylammonium perchlorate used was the reagent supplied by Eastman Kodak. Triphenylcyclopropenium perchlorate was prepared according to the literature.[24]

***p*-Diisopropylaminophenyldiphenylcyclopropenium Perchlorate (4).** A solution of diphenylchlorocyclopropenium ion was prepared by the reaction of 1.76 g (22.5 mmol) of benzene with $C_3Cl_3^+AlCl_4^-$ in chloroform at 50 °C, which had been made from 1.87 g (10.5 mmol) of tetrachlorocyclopropene and 1.40 g (10.5 mmol) of $AlCl_3$. To this solution, there was added 2.14 g (12.1 mmol) of diisopropylaniline, dropwise with vigorous stirring. After the mixture was stirred at 60 °C for 20 min, it was cooled and poured into 50 mL of ice water. The dark brown organic layer was separated, washed repeatedly with water, and dried over $MgSO_4$. The dark brown oily solid, obtained after rotary evaporation, was reprecipitated from acetonitrile-ether and gave 1.34 g (31.8%) of *p*-diisopropylaminophenyldiphenylcyclopropenium chloride as a brownish-yellow solid. A chloroform solution of the chloride was treated with sodium methoxide in methanol. By the usual workup, the cyclopropenyl methyl ether was isolated, which was then redissolved in benzene and treated with 60% $HClO_4$ without further purification. The oily crude product was reprecipitated from acetonitrile-ether and recrystallized from methanol repeatedly to give a yellow powder: mp 210-211.5 °C dec; IR (KBr) 3020 (w), 2960-2860 (m), 1820 (w), 1590 (s), 1480 (w), 1460 (w), 1445 (sh), 1425 (sh), 1405 (s), 1380 (sh), 1335 (m), 1310 (w), 1210 (m), 1180 (w), 1155 (m), 1090 (s), 1015 (w), 830 (w), 770 (m), 680 (w), 620 cm^{-1} (w); UV-visible λ_{max} (CH_3CN) 272 nm (sh) (log ε 4.25), 282 (4.30), 296 (4.23), 411 (4.79); ^1H NMR (CD_3CN) δ 8.40 (m, 4 H), 8.22 (d, 2 H), 7.86 (m, 6 H), 7.18 (d, 2 H), 4.28 (septet, 2 H), 1.42 (d, 12 H). Anal. Calcd for $C_{27}H_{28}NClO_4$: C, 69.59; H, 6.06; N, 3.01. Found: C, 69.44; H, 6.11; N, 2.95.

All the aqueous layer and aqueous washings were combined, basicified with aqueous KOH, and extracted with ether. The ethereal solution, after drying and rotary evaporation, gave 1.12 g (52%) of *N,N*-diisopropylaniline by bulb-to-bulb distillation, 60 °C (0.2 Torr).

Bis(*p*-diisopropylaminophenyl)phenylcyclopropenium Perchlorate (5). In the same way as described above, 2.23 g (12.6 mmol) of diisopropylaniline was allowed to react with phenyldichlorocyclopropenium ion, which was prepared from 0.90 g (4.1 mmol) of 1-phenyl-2,3,3-trichlorocyclopropene[25] and 0.60 g (4.5 mmol) of $AlCl_3$ in 5 mL of chloroform. The same workup afforded 1.02 g of the crude chloride salt, which was then converted to 1.03 g (45.3%) of the perchlorate salt (**5**) by the procedures described above. Repeated recrystallization from methanol-acetonitrile gave yellow powder: mp 260-261 °C dec; IR (KBr) 2980-2880 (w-m), 1835 (w), 1600 (s), 1490 (sh), 1470 (w), 1430 (m), 1400 (s), 1335 (m), 1305 (m), 1200 (m), 1150 (m), 1120 (m), 1080 (s), 1010 (w), 830 (w), 800 (w), 780 (w), 770 (m), 695 (s), 620 cm^{-1} (w); ^1H NMR (CD_3CN-$CDCl_3$) δ 8.16 (m, 2 H), 8.02 (d, 4 H), 7.72 (m, 3 H), 7.02 (d, 4 H), 4.16 (septet, 4 H), 1.40 (d, 24 H); UV-visible λ_{max} (CH_3CN) 256 nm (log ε 4.33), 270 (sh) (4.19), 351 (4.28), 438 (5.11). Anal. Calcd for $C_{33}H_{41}N_2ClO_4$: C, 70.13; H, 7.31; N, 4.96. Found: C, 69.91; H, 7.26; N, 4.95.

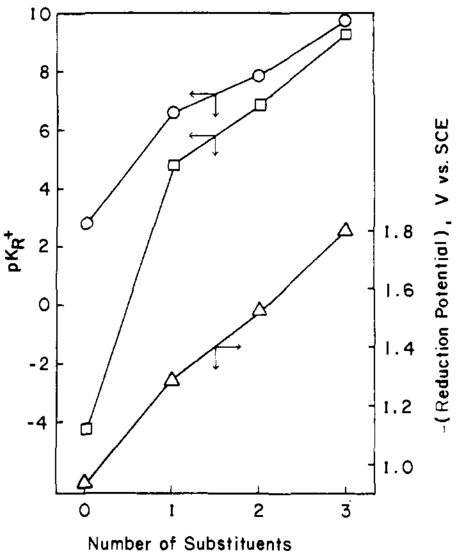


Figure 3. Plot of pK_R^+ (○, triarylcyclopropenium ions: □, triarylmethyl cations) and reduction potential (△, triarylcyclopropenium ions) vs. the number of substituents.

As described above, 1.40 g (58%) of *N,N*-diisopropylaniline was recovered.

Tris(*p*-diisopropylaminophenyl)cyclopropenium Fluoroborate (6). To a stirred solution of 0.89 g (5.0 mmol) of tetrachlorocyclopropene in 2.13 g (15.0 mmol) of boron trifluoride etherate, there was added 2.66 g (15.0 mmol) of diisopropylaniline, dropwise, at room temperature. The mixture was stirred at 60 °C for 1 h. Then it was cooled, poured into 10 mL of ice water, and extracted with chloroform. The organic layer, after washing with four 30-mL portions of water and drying, afforded 3.06 g of brown, oily solid. Crystallization from methanol gave 1.12 g (34.4%) of tris(*p*-diisopropylaminophenyl)cyclopropenium fluoroborate (**6**) as yellow leaves: mp 232-233 °C dec; IR (KBr) 2980-2860 (w-m), 1590 (s), 1470 (w), 1430 (m), 1400 (s), 1380 (sh), 1335 (m), 1330 (m), 1205 (s), 1160 (m), 1130 (m), 1090 (m), 1060 (s), 945 (w), 840 (w), 780 cm^{-1} (w); ^1H NMR (CD_3CN) δ 8.00 (d, 6 H), 7.08 (d, 6 H), 4.18 (septet, 6 H), 1.40 (d, 36 H); ^{13}C NMR ($CDCl_3$) δ (relative to internal Me_4Si) 136.0 (C_1), 134.1 (C_3), 133.6 (C_5), 127.2 (C_4), 115.2 (C_2), 48.4 ($-CH(CH_3)_2$), 20.7 ($-CH_3$); UV-visible λ_{max} (CH_3CN) 249 nm (log ε 4.10), 344 (4.28), 418 (4.95), 447 (5.18). Anal. Calcd for $C_{39}H_{54}N_3BF_4$: C, 71.88; H, 8.35; N, 6.45. Found: C, 71.51; H, 8.09; N, 6.16.

The workup on the basicified aqueous layers gave 1.40 g (45%) of *N,N*-diisopropylaniline.

Tris(dimethylaminophenyl)cyclopropenium Fluoroborate (Isomeric Mixture). The same procedures as above using dimethylaniline instead of diisopropylaniline gave a yellow, crystalline solid (36.3% yield), which was identified as a mixture of tris(*p*-dimethylaminophenyl)cyclopropenium (A, 40%) and bis(*p*-dimethylaminophenyl)-*o*-dimethylaminophenylcyclopropenium (B, 60%) fluoroborates on the basis of the following spectral and analytical data. The composition of the mixture was calculated from the integrated proton ratio of the NMR spectrum: mp 239-240 °C dec; IR (KBr) 2960-2840 (w), 1890 (w), 1595 (s), 1540 (w), 1490 (s), 1450 (m), 1435 (m), 1405 (s), 1365 (s), 1285 (w), 1230 (w), 1190 (s), 1185 (sh), 1140 (m), 1090 (m), 1050 (s), 940 (m), 810 (m), 795 (w), 780 (m), 745 (w), 700 cm^{-1} (w); ^1H NMR (CD_3CN) δ 7.8-6.6 (m, aryl H), 3.89 (s, *o*-NMe_2 for B), 3.07 (s, *p*-NMe_2 for B), 2.99 (s, *p*-NMe_2 for A). Anal. Calcd for $C_{27}H_{30}N_3BF_4$: C, 67.09; H, 6.26; N, 8.69. Found: C, 66.95; H, 6.02; N, 8.81.

Determination of pK_R^+s. The pK_R^+ measurements were carried out spectrophotometrically following the reported method[26] with 23% aqueous ethanol as the solvent. The buffer solutions were made up by mixing 0.1 M citric acid and 0.2 M Na_2HPO_4 (pH 2.6-7.0), 0.2 M Na_2HPO_4 and 0.2 M NaH_2PO_4 (7.4-8.0), and 0.2 M glycine and 0.2 M NaOH (>8.4).[27] The pH values were read on a Beckman Model G pH meter calibrated with standard buffers before use.

Cyclic Voltammetry. A Princeton Applied Research Model 170 electrochemistry system was used with a three-electrode cell, having platinum wire working and auxiliary electrodes and a saturated calomel reference electrode. Fast sweep voltammograms (>5 V/s) were recorded with a Tektronix Type RM503 oscilloscope equipped with a Polaroid camera. All solutions were 1 mM in the cyclopropenium salts and 0.1 M in tetrabutylammonium perchlorate in dichloromethane. Sweeps ranged from 0.1 to 50 V/s. The cathodic peak moved slightly toward a positive potential when the sweep rate was decreased. The potential at 85% of the peak height at 50 V/s sweep was read on an oscillograph scale and shown in Table IV.

Zinc Reduction of Tris(*p*-diisopropylaminophenyl)cyclopropenium Fluoroborate (6). To a solution of 0.196 g (0.300 mmol) of **6** in 12 mL of dry acetonitrile, there was added 1.00 g (15.3 mg-atoms) of zinc dust. The mixture was stirred at room temperature under nitrogen for 10 days. The mixture was filtered and washed well with acetonitrile and benzene. The filtrate was evaporated in vacuo to give 0.189 g of orange-brown solid. The acetonitrile extract of this solid gave 0.154 g (78.8% recovery) of unchanged **6**. The solid which did not dissolve in acetonitrile was separated by preparative TLC on silica gel (Merck PF_{254}) with benzene-ether (1:2) as a solvent. The ether extraction of the portion with R_f 0.5 gave 0.012 g of pale yellow solid, which structure was tentatively assigned as hexakis(*p*-diisopropylaminophenyl)benzene (0.010 mmol, 6.5% yield) from the following spectral data: mp >270 °C (no definite melting point observed); IR (KBr) 2980–2800 (m), 1600 (m), 1505 (s), 1460 (w), 1450 (w), 1410 (w), 1380 (m), 1355 (m), 1335 (sh), 1325 (w), 1280 (m), 1260 (m), 1235 (m), 1180 (m), 1150 (m), 1115 (m), 1100 (sh), 1020 (m), 950 (w), 930 (w), 860 (w), 830 (m), 780 (w), 750 (w), 685 cm^{-1} (w); ^1H NMR (CCl_4-$CDCl_3$) δ 6.59 (q, 4 H), 3.46 (septet, 2 H), 0.92 (d, 12 H).

Acknowledgment. This work was supported by Grant MPS74-01345 from the National Science Foundation.

References and Notes

(1) For a review, see K. Venkataraman, "The Chemistry of Synthetic Dyes", Vol. II, Academic Press, New York, N.Y., 1952, p 705.

(2) M. J. S. Dewar, *J. Chem. Soc.*, 2329 (1950).

(3) Compared with the propeller shaped structure reported for triphenylmethyl perchlorate [twisting angles between phenyl planes and sp^2 plane of central carbon, 31.8°: Gomes de Mesquita, C. H. MacGillevry, and K. Eriks, *Acta Crystallogr.*, **18**, 437 (1965)], the angles between the phenyl planes and the central three-membered ring in cation **3** are reported to be smaller [7.6, 12.1, and 21.2°: M. Sundaralingam and L. H. Jensen, *J. Am. Chem. Soc.*, **88**, 198 (1966)]. Among the triphenylmethane dyes, only one preliminary x-ray structure has been reported for tris-*p*-aminophenylmethyl cation which indicates twisting angles of 29, 34, and 34° (K. Eriks and L. L. Koh, Petroleum Research Fund Report No. 8, 1963, p 5). For the relationship between coplanarity and absorption spectra of triphenylmethane dye molecules, see N. R. Ayyanger and B. D. Tilak in "The Chemistry of Synthetic Dyes", Vol. IV, K. Venkataraman, Ed., Academic Press, New York, N.Y., 1971, p 140, and references cited therein.

(4) (a) B. Föhlisch and P. Bürgle, *Justus Liebigs Ann. Chem.*, **701**, 67 (1967); S. V. Krivun, V. I. Dulenko, S. V. Sayapina, N. S. Semenov, Yu. A. Nikolyukin, and S. N. Baranov, *Khim. Geterotsikl. Soedin.*, 1174 (1974); *Chem. Abstr.*, **82**, 72724e (1975); (b) W. Broser and M. Brockt, *Tetrahedron Lett.*, 3117 (1967).

(5) R. West, A. Sado, and S. W. Tobey, *J. Am. Chem. Soc.*, **88**, 2488 (1966).

(6) R. West, D. C. Zecher, and W. Goyert, *J. Am. Chem. Soc.*, **92**, 149 (1970).

(7) For example, see ref 5 and 6.

(8) H. Cohn, *J. Chem. Soc.*, 4282 (1952).

(9) The parameters used for the calculations are as follows: $\alpha_N = \alpha + 1.5\beta$, $\alpha_{C(\text{adjacent to N})} = \alpha + 0.2\beta$, $\beta_{CN} = \beta$.

(10) Various solvents were used in obtaining the NMR data because of greatly differing solubilities for the species studied and because the amine groups are readily protonated in acid solvents. No corrections were made for solvent effects since these have not been characterized for carbenium ions.

(11) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 469 (1961).

(12) P. C. Lauterbur, *Tetrahedron Lett.*, 274 (1961).

(13) G. J. Ray, R. J. Kurland, and A. K. Colter, *Tetrahedron*, **27**, 735 (1971).

(14) G. J. Ray, A. K. Colter, and R. J. Kurland, *Chem. Phys. Lett.*, **2**, 324 (1968).

(15) Measured in H_2SO_4: N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Org. Chem.*, **19**, 155 (1954).

(16) R. Breslow and W. Chu, *J. Am. Chem. Soc.*, **95**, 411 (1973).

(17) The LUMOs in **3** and **6** are doubly degenerate and so would be lowered in energy upon reduction to free radicals by a Jahn–Teller effect.

(18) H. Volz and W. Lotsch, *Tetrahedron Lett.*, 2275 (1969).

(19) R. Breslow, P. Gal, H. W. Chang, and L. J. Altman, *J. Am. Chem. Soc.*, **87**, 5139 (1965).

(20) Z. Yoshida and Y. Tawara, *J. Am. Chem. Soc.*, **93**, 2573 (1971); Z. Yoshida, *Top. Curr. Chem.*, **40**, 47 (1973).

(21) (a) F. Gerson, G. Plattner, and Z. Yoshida, *Mol. Phys.*, **21**, 1027 (1971); (b) R. Weiss and K. Schloter, *Tetrahedron Lett.*, 3491 (1975).

(22) Electrolytic oxidation in acetonitrile at room temperature and at −60 ° did not give any ESR signal for the radical dication. This is in accord with the results of HMO calculation which indicate the highest occupied MO energy of **6** ($\alpha + 0.5387\beta$) to be lower than that of trisaminocyclopropenium ion ($\alpha + 0.38\beta$).

(23) Th. Kauffmann, H. Fischer, R. Nürnberg, and R. Wirthwein, *Justus Liebigs Ann. Chem.*, **731**, 23 (1970).

(24) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Am. Chem. Soc.*, **87**, 1320 (1965).

(25) J. Chickos, E. Patton, and R. West, *J. Org. Chem.*, **39**, 1647 (1974).

(26) R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 2367 (1961).

(27) G. Gomori in S. P. Colowick and N. O. Kaplan, "Methods in Enzymology", Vol. 1, Academic Press, New York, N.Y., 1955.

Alkylidenediquinocyclopropanes. Synthesis and Properties

Koichi Komatsu, Robert West,* and Douglas Beyer

Contribution from the Department of Chemistry, University of Wisconsin,
Madison, Wisconsin 53706. Received April 14, 1976

Abstract: Reaction of bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)cyclopropenone (**4**) with active methylene compounds gives alkylidenecyclopropenes **6a–f** which undergo oxidation to alkylidenediquinocyclopropanes, **5a–f**. The latter are brilliantly colored, strongly dichroic solids, blue or blue-violet in solution but reflecting metallic gold or red. Cyclic voltammetric studies show that **5a–f** are powerful oxidizing agents. The ESR spectra of anion radicals of **5a–f** were studied and compared with the results of Hückel MO calculations.

The triquinocyclopropanes (**1**, R = alkyl), a new class of highly conjugated compounds, were reported several years ago.[1] The oxidation–reduction cycle of **1** with the corresponding quinodiarylcyclopropenes **2** and their anions has been investigated in some detail.[2] Also known is the diquinocyclopropanone **3**[3] in which a carbonyl group replaces one of the quinonoid groups in **1**. Compound **3** somewhat resembles **1** but is unstable, losing carbon monoxide rather rapidly in solution.[3] It is obtained by the oxidation of the diarylcyclopropenone **4**, which is easily available by the reaction of $C_3Cl_3^+$ with 2 equiv of 2,6-di-*tert*-butylphenol.

By the reaction of **4** with active methylene compounds, we have prepared a series of methylenecyclopropene derivatives (**6a–f**) which undergo oxidation to a new family of stable alkylidenediquinocyclopropanes, **5a–f**. The latter compounds are deeply colored, crystalline solids, royal blue or blue-purple