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THE TRICYCLOPROPYLCYCLOPROPENIUM ION

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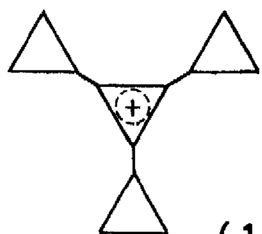
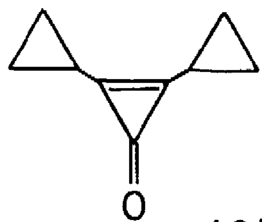
Summary: A novel non-benzenoid aromatic cation, tricyclopropylcyclopropenium ion, was synthesized by smooth addition of photochemically generated cyclopropylchlorocarbene to dicyclopropylacetylene, and was shown to have remarkable stability.

It has been well established that the cyclopropyl group conjugatively stabilizes an electron-deficient carbon by adopting the bisected conformation.[1] On the other hand, the cyclopropenium ion is reported to be less susceptible to conjugative stabilization by phenyl groups than to inductive stabilization by alkyl groups.[2] Based on these facts, it is of particular interest to examine the substituent effect of the cyclopropyl group upon stability of the cyclopropenium ion.[3] In this paper, we wish to report on the facile synthesis and some properties of tricyclopropylcyclopropenium ion (1), which is a novel non-benzenoid aromatic cation made up only with carbonaceous three-membered rings and is characterized by its remarkable stability.

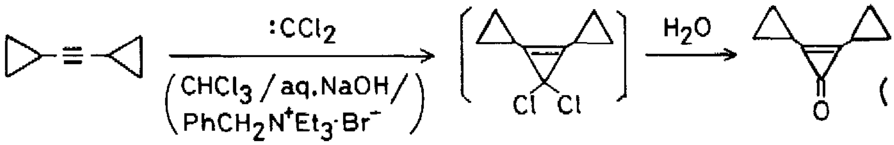

(1)


(2)

In the attempted synthesis of cation 1, Kerber and Hsu first prepared dicyclopropylcyclopropenone (2) by using a modified Favorskii reaction of 1,3-dibromo-1,3-dicyclopropylpropanone in a low yield (6%), and carried out its reaction with cyclopropylmagnesium bromide, but obtained no indication for the formation of 1 after acid treatment.[4]

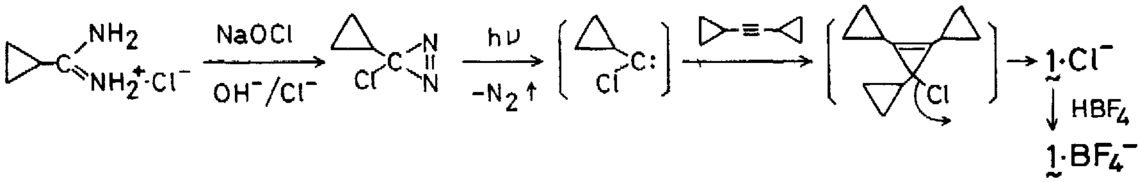
In contrast, we found that the addition of dichlorocarbene, generated under the phase-transfer-catalysis condition ($CHCl_3$ (15 ml) / 50% aq. NaOH (15 ml) / $PhCH_2N^+Et_3 \cdot Br^-$ (0.80 mmol)), to dicyclopropylacetylene[5] (5.7 mmol) gives the dichlorocyclopropene, which is spontaneously hydrolyzed to afford the cyclopropenone 2 in a higher yield (0.286 g; 38%) as colorless oil (bulb-to-bulb distillation, bp 60-70°C/0.5 mmHg) (Scheme 1); spectral properties of 2 are shown in Table 1. Although our several attempts to convert cyclopropenone 2 to cation 1 also failed,[6] the observed smooth addition of dichlorocarbene to dicyclopropylacetylene, together with a recent report on unexpectedly efficient capture of cyclopropylchlorocarbene by various olefins,[7] prompted us to explore the carbene addition route to reach the cation 1.

Scheme 1:



(2)

Scheme 2:



Thus, as shown in Scheme 2, cyclopropylchlorodiazirine was generated from cyclopropanecarboxamidine hydrochloride (35 mmol) and 0.7M aq. NaOCl (440 ml) / NaCl (84 g) / LiCl (14 g) in DMSO (210 ml) at 0-30°C under reduced pressure (10 mmHg),[8] and condensed into dicyclopropylacetylene (8 ml) at -78°C; irradiation of the acetylenic solution of the diazirine in a Pyrex vessel with a high-pressure mercury lamp at 0°C caused evolution of nitrogen (12.3 mmol) with concomitant formation of white precipitates during 6 hrs. The precipitates were identified as the ionic salt of 1·Cl⁻, which was apparently formed by the first addition of cyclopropylchlorocarbene to the acetylene followed by rapid ionic dissociation; mp 79-81°C (dec). The chloride was further converted to tetrafluoroborate salt $1\cdot BF_4^-$ by treating the aqueous solution with 42% HBF_4 (0.7 ml). Reprecipitation of $1\cdot BF_4^-$ from the CH_2Cl_2 solution by adding Et_2O afforded air-stable white crystals (0.839 g) in 27.7% yield based on the diazirine; mp 141-142°C (Found: C, 58.69; H, 6.36%. Calcd for $C_{12}H_{15}BF_4$: C, 58.58; H, 6.14%). The salt $1\cdot BF_4^-$ exhibits high solubility (>25 wt%) in polar solvents such as H_2O, MeCN, CH_2Cl_2, and $CHCl_3$, and is characterized by remarkable thermal stability as shown by its recovery without any decomposition after being kept molten at 150°C for 1 hr in a vacuum-sealed tube.

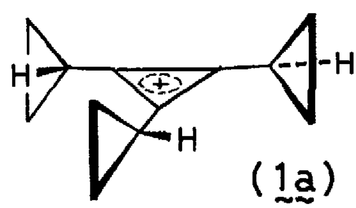
Structural assignment was made based on the spectral data given in Table 1. The IR spectrum of $1\cdot BF_4^-$ exhibits strong bands at 1440 (cyclopropenium ring vibration) and 1070 cm^{-1} (BF_4^-), the latter being absent in the spectrum of $1\cdot Cl^-$. In the ^1H NMR spectrum, both the α- and β-protons of the cyclopropyl group are shifted downfield compared with *cis*-1,2-dicyclopropylethylene (δ 1.65 (α-H), 0.50 (β-H)[9]). The larger shift of the β-protons ($\Delta\delta_{average}$ 1.01) than the α-proton (Δδ 0.74) is indicative of conjugative interaction of the cyclopropyl group with the cationic center. In accord with this result, the β-carbon is shown to be more deshielded than the α-carbon in the ^{13}C NMR spectrum. In contrast to tri-n-propylcyclopropenium ion, which has no UV absorption, cation 1 exhibits a strong UV absorption at 213 nm, reflecting conjugation of the cyclopropyl group with the cyclopropenium ring. This absorption is comparable in its intensity to that of tricyclopropylmethyl cation, though the latter cation absorbs at longer wavelength ($\lambda_{max}^{H_2SO_4}$ 270 nm (log ε, 4.34)[10]).

Table 1. Spectral Data for the Cyclopropenone 2 and the Cyclopropenium Salt $1 \cdot BF_4^-$

Compd	IR ν, cm^{-1}	^1H NMR (220MHz) δ, ppm from TMS	^{13}C NMR δ, ppm from TMS	UV λ_{max}^{MeCN} nm (log ε)
2 [a]	3090 w, 3010 m, 1860 vs, 1610 vs, 1430 m, 1395 m, 1320 m, 1295 w, 1190 m, 1080 m, 1060 m, 1040 m, 915 s, 890 m, 820 m, 730 m (neat)	1.83 (m, 2H, α-H) 1.13 (m, 8H, β-H) (in CCl_4)	200.1 (s, C=O) 157.0 (s, C=C) 10.0 (t, β-C) 7.4 (d, α-C) (in $CDCl_3$)	217 (3.77) 256 (2.96)
$1 \cdot BF_4^-$	3090 w, 3015 m, 1440 br vs, 1400 m, 1340 m, 1300 w, 1185 w, 1070 br vs, 910 s, 815 m, 765 m, 755 m, 745 m (KBr)	2.39 (m, 3H, α-H) 1.66 (m, 6H, β-H(*E*))[b] 1.36 (m, 6H, β-H(*Z*))[b] (in CD_3CN)	169.7 (s, $>C^+-$) 16.0 (t, β-C) 9.0 (d, α-C) (in CD_3CN)	213 (4.36)

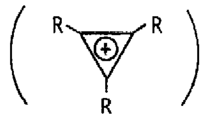
a) The IR, ^1H NMR, and UV spectral data were essentially in accord with those reported in Ref 4.
b) The assignment for the *E* and *Z* protons was made based on the coupling pattern and from the analogy with the previously studied systems of cyclopropyltropylium and *p*-cyclopropylphenyltropylium ions (K. Okamoto *et al.*, *JCS-Perkin II*, 262, 1005 (1979)).

The stability of cation 1, with reference to the corresponding covalent alcohol, was demonstrated by its remarkably high pK_R+ value, 10.0 ± 0.3, determined by potentiometric titration in 50% aq. MeCN.[11] Thus, in spite of its simple structure, the cation 1 is comparable in stability with recently reported triguaiazulenylcyclopropenium ion,[12] and is regarded as one of the most stable hydrocarbon cations known at present. Presumably the three cyclopropyl groups exert their maximal stabilizing effect by adopting the bisected conformation symmetrically as in 1a. As is apparent from the comparison of pK_R^+ data in Table 2, σ-conjugation with cyclopropyl groups was shown to be more effective than π-conjugation with phenyl groups, or than the inductive effect of n-alkyl groups, in stabilizing the cyclopropenium ion. As was expected, this stabilizing effect of cyclopropyl groups is much larger when directly attached to the cyclopropenium ring than when attached to the *para*-position of the triphenyl derivative.[13]


(1a)

Cation 1 reacts with a rather strong nucleophile, CN^- (pK_a for the conjugate acid, 9.14), to give the corresponding cyclopropenyl cyanide[14] quantitatively. However, towards less nucleophilic reagents, such as $PhCO_2^-$ (pK_a for the conjugate acid, 4.20), N_3^- (4.59), $MeCO_2^-$ (4.75), and $p\text{-}NO_2\text{-}C_6H_4\text{-}O^-$ (7.2), the cation 1 is unreactive and is recovered unchanged, in accord with its large pK_R+ value.

Table 2. The pK_{R^+} Values for the Cyclopropenium Ions Symmetrically Substituted with Hydrocarbon Substituents



R	H [a]	Ph	*p*-c-Pr-Ph [b]	t-Bu [c]	n-Pr [d]	c-Pr	GAz [e]
pK_{R^+}	-7.4	2.60 [b] (2.8 [d])	3.23	6.5	7.2	10.0	>10
Solvent	H_2SO_4-EtOH	23% aq. EtOH		50% aq. MeCN			

a) R. Breslow and J. T. Groves, *J. Am. Chem. Soc.*, 92, 984 (1970).
b) Ref 13 (c-Pr = cyclopropyl).
c) J. Ciabattoni and E. C. Nathan, III, *J. Am. Chem. Soc.*, 91, 4766 (1969).
d) Ref 2.
e) Ref 12 (GAz = guaiazulenyl).

References:

1) For review, see H. G. Richey, Jr., in "*Carbonium Ions*," G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York (1972), Chapter 25.
2) R. Breslow, H. Höver, and H. W. Chang, *J. Am. Chem. Soc.*, 84, 3168 (1962).
3) The substituent effect of the cyclopropyl group in 1,2-diphenyl-3-cyclopropyl- (Ref 4) and 1,2-dimethyl-3-cyclopropyl-cyclopropenium ions (Z. Yoshida, S. Hirota, and H. Ogoshi, *Abst. 6th Symposium on Nonbenzenoid Aromatic Compounds*, Fukuoka, Japan, p.76 (1973)) has already been reported. We are indebted to Professors Yoshida and Ogoshi for informing us of their unpublished results.
4) R. C. Kerber and C.-M. Hsu, *J. Am. Chem. Soc.*, 95, 3239 (1973).
5) G. Köbrich, D. Merkel, and K.-W. Thiem, *Chem. Ber.*, 105, 1683 (1972).
6) Either the Wittig reaction of **2** with cyclopropylidenetriphenylphosphorane or the reaction of **2** with $Et_3O^+BF_4^-$, or with $SOCl_2$, followed by addition of cyclopropyllithium did not afford cation **1** after acidification.
7) R. A. Moss and M. E. Fantina, *J. Am. Chem. Soc.*, 100, 6788 (1978).
8) W. H. Graham, *J. Am. Chem. Soc.*, 87, 4396 (1965).
9) T. Teraji, I. Moritani, E. Tsuda, and S. Nishida, *J. Chem. Soc. (C)*, 3252 (1971).
10) N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *J. Am. Chem. Soc.*, 87, 4533 (1965).
11) The spectrophotometric titration method indicated the cation's pK_{R^+} to be 10.5, which is, however, less reliable due to irreversible decomposition of the neutralized cation observed during the measurement.
12) I. Agranat and E. Aharon-Shalom, *J. Org. Chem.*, 41, 2379 (1976).
13) K. Komatsu, I. Tomioka, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, 52, 856 (1979).
14) Colorless oil (Found: C, 84.15; H, 8.25; N, 7.41%. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56%); IR ν (neat) 2220 (CN), 1890 cm^{-1} (cyclopropene); ^1H NMR δ (CCl_4) 1.67 (m, 2H), 1.0-0.2 (m, 13H); ^{13}C NMR δ ($CDCl_3$) 123.3 (s, CN), 110.6 (s, >C=), 18.8 (s, $\geq$C-), 14.9, 5.4 (d, α-CH), 7.5, 6.3, 4.0 (t, β-CH_2).

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