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SYNTHESES AND PROPERTIES OF DITHIENYLCYCLOPROPENONE AND TRITHIENYLCYCLOPROPENIUM ION 1)

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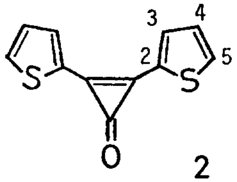
The smallest ring member of the Hückel aromatic system, the cyclopropenium ion, has been known for almost two decades since the first synthesis of the triphenylcyclopropenium ion (1).2) Among a variety of hydrocarbon substituents, the non-benzenoid aromatic rings such as ferrocene3) and azulene4) were recently reported to be particularly effective in stabilizing the cyclopropenium system. Thus, it seemed of interest to examine the cation-stabilizing effect of another type of aromatic substituent with electron-donating nature, i.e., the heteroaromatic ring. The cyclopropenium ions substituted with two phenyl and one indolyl groups have already been prepared5) and shown to be stabilized considerably,6) but the cation fully substituted with heteroaromatic rings is not known. In this paper we wish to report on the syntheses and properties of the cyclopropenone (2) and the cyclopropenium ion (3), fully substituted with thiophene rings.

Judging from fairly large reactivity of the α-carbon of the thiophene ring toward the electrophile (the estimated σ_{Ar}^{+} value, -0.84 7)), the use of an electrophilic substitution reaction of the trichlorocyclopropenium ion ($C_3Cl_3^{+}$), which was found and developed by West and coworkers,8) appeared most suitable for the present purpose.



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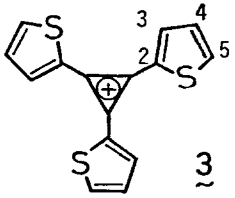

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Thus, a solution of thiophene (6.66 g, 79.2 mmol) in CH_2Cl_2 (40 ml) was added dropwise at -10°C to a stirred suspension of $C_3Cl_3^+AlCl_4^-$ prepared from C_3Cl_4 (6.40 g, 36.0 mmol) and $AlCl_3$ (5.30 g, 39.8 mmol) in CH_2Cl_2 (20 ml). After stirring at -15°C under nitrogen for 1 hr, the mixture was treated with water (100 ml) and worked up in the usual way. Preparative TLC (benzene-ether(3:2)/SiO_2) of the crude product afforded the cyclopropenone 2[9] (4.01 g, 51.1% yield) as a brownish white powder; mp 108.0-109.5°C (from benzene).

In a similar manner an excessive amount of thiophene (8.33g, 98.8 mmol) was allowed to react with $C_3Cl_3^+AlCl_4^-$ (20.1 mmol) in CH_2Cl_2 (35 ml) at -15°C for 1 hr, at 0-20°C for 3 hr, and at 40°C for 0.5 hr. After hydrolysis there was obtained a large amount of a dark brown solid containing mainly a polymeric compound. This solid was refluxed repeatedly with $CHCl_3$, and the concentrated $CHCl_3$ solution (ca. 5 ml) was treated with 42% HBF_4 (1 ml) to give the cyclopropenium salt $3 \cdot BF_4^-$ [9](0.499 g, 6.7% yield) as a yellowish white powder; mp 258-261°C (dec). The same cation salt $3 \cdot BF_4^-$, or the perchlorate $3 \cdot ClO_4^-$, was also obtained from the cyclopropenone 2 by the independent synthetic routes shown in Scheme 1.[10] The spectral properties of 2 and 3 are given in Table 1.

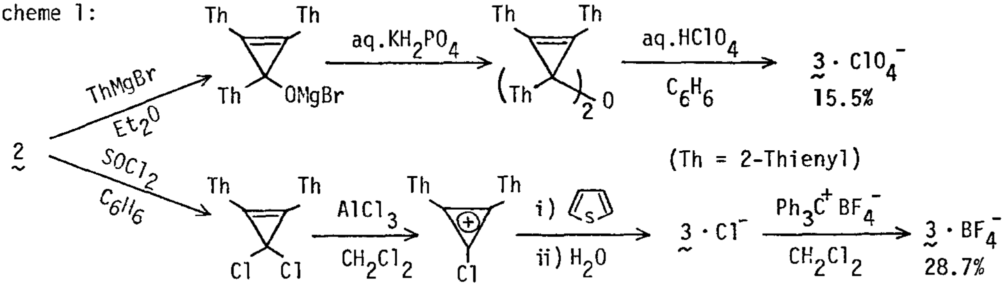
The cyclopropenone 2 and the cyclopropenium ion 3 are characterized by their diagnostic IR bands at 1840 and 1610 cm^{-1} and 1420 cm^{-1}, respectively, whereas the coupling patterns of their NMR spectra and the values of the coupling constants indicate that the thiophene rings are substituted at the 2-position. As shown in Fig. 1, the absorption bands in the electronic spectra of 2 and 3 are shifted to longer wavelengths compared with those of the phenyl

Table 1. Spectral Properties of the Cyclopropenone 2 and the Cyclopropenium Ion 3.

Comp'd	IR (KBr) ν, cm^{-1}	UV λ_{max} nm (log ε)	100MHz NMR δ, ppm from TMS
2 [a]	3100 w, 3060 w, 1840 br vs, 1610 br vs, 1415 sh, 1400 s, 1360 m, 1310 w, 1050 m, 850 s, 730 s, 720 s	252 (4.34), 271 (4.26), 325sh(4.44), 338 (4.58), 356 (4.51) (in EtOH)	7.79 (dd, H^3, $J_{3,4}$=3.8 Hz, $J_{3,5}$=1.1), 7.73 (dd, H^5, $J_{4,5}$=5.2), 7.23 (dd, H^4) (in $CDCl_3$)
3	3110 w, 3050 w, 1530 s, 1420 br vs, 1407 vs, 1120-1040 br s, 870 m, 770 sh, 760 s	271 (4.27), 296sh(4.09), 355 (4.65), 375 (4.65) (in MeCN)	8.51 (dd, H^3, $J_{3,4}$=4.2 Hz, $J_{3,5}$=1.2), 8.49 (dd, H^5, $J_{4,5}$=5.1), 7.69 (dd, H^4, (in CF_3COOH)

a) MS m/e 218 (M^+, 0.5%), 190 (M^+-CO, 100%).

Scheme 1:



derivatives, indicating the more effective charge delocalization attained in the thienyl-substituted compounds, 2 and 3.

Stabilization of the cation 3 is demonstrated by its pK_R+ value, 4.33, determined spectrophotometrically in 23% EtOH. A comparison with the reported pK_R+ value for the triphenyl derivative 1 in the same solvent, 2.80,[11)] clearly indicates the larger stabilizing effect of the thienyl group than the phenyl group upon the cyclopropenium ion.

In the earlier publications[12)] we have examined the rates of one-electron reduction of the substituted tropylium and cyclopropenium ions with the chromous ion, and shown that log k_2 for the reduction is linearly correlated with electron affinity, estimated from ν_{CT} and from half-wave reduction potentials, and also with pK_R+ of the cations. The second-order rate constants for the chromous-ion reduction of the cation 3 in 2.9N HCl were determined under the pseudo-first-order conditions by the method described previously[12b)] to give the results shown in Table 2.

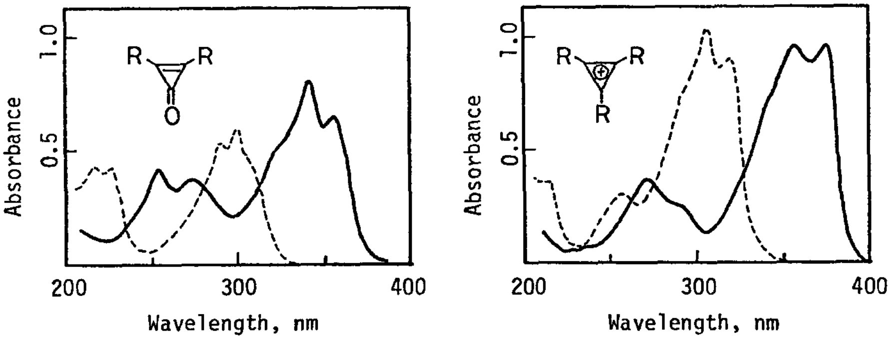


Fig. 1. UV spectra of cyclopropenones (—— 2, ----- diphenylcyclopropenone; 2.10x10^{-5}M in EtOH) and cyclopropenium ions (—— 3, ----- 1; 2.10x10^{-5}M in MeCN).

Table 2. Chromous-Ion Reduction Rates of Cations 1 and 3 in 2.9N HCl.

Cation	Temp	Initial conc'n Cation	 Cr(II)	Reduction rate, k_2 a)
	°C	10^{-4}M	10^{-2}M	$10^{-4}\cdot M^{-1}sec^{-1}$
1 b)	25	15.1	13.1	3.01 ± 0.20
3	75	1.31	5.55	52.6 ± 2.2
	50	1.52	8.23	8.56 ± 0.28
	25	—	—	1.01 c)

a) Averaged values from three runs. b) Data from Ref. 12b.

c) Extrapolated from data at higher temperatures.

The reduction rate of the cation 3 at 25°C is shown to be smaller than that of the triphenyl cyclopropenium ion (1) by the factor of three, indicating less electron affinity and greater stability of 3, which is in qualitative agreement with the result of pK_R+ measurement.

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9) Satisfactory elemental analyses were obtained.
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