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TRIALKYLTHIO- AND TRIPHENYLTHIO-CYCLOPROPENYL CATIONS

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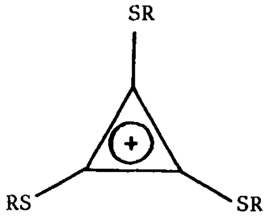
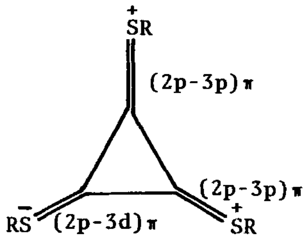
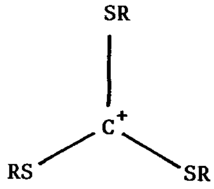
Recently increasing attention has been focussed to heteroatom-substituted cyclopropenyl cation system in order to elucidate the features of the electronic behavior of this highly strained three-membered carbonium ions purturbed with hetero-atoms.[1-3] Especially, trithiocyclopropenyl cations are of much interest, because hetero-[3]radialene structure (II) is expected to contribute to the ground state structure of I by the additional [2p-3d]π conjugation other than [2p-3p]π conjugation of the carbon-sulfur bond of I. It has been reported that such a [2p-3d]π conjugation was observed in a sulfur-containing carbonium ion, thiopyrylium ion.[4]



I

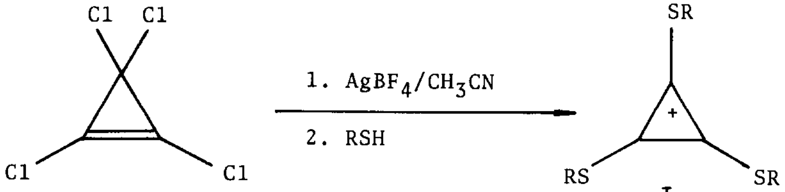


II



III

If we assume that the three-membered ring (C_3^+ core) of I corresponds to a sp^2 carbon atom as has been pointed out by us,[5] then we will get trithiocarbonium ion (III) which is already obtained by Tucker and Roof.[6] These consideration prompted us to synthesize trialkylthio- and triphenylthio-cyclopropenyl cations (I). The preparation of I also would arouse an attention from view point of preparative organic chemistry, because it could be a convenient synthetic intermediate as II is. We wish to report, in this communication, the successful synthesis[7,8] of I_a (R = Me), I_b (R = Et), I_c (R = i-Pr), I_d (R = t-Bu) and I_e (R = phenyl) by a method treating tetrachlorocyclopropene with silver fluoroborate followed by addition of thiols in acetonitrile. In this case, the reaction is considered to proceed by S_N1 mechanism. The general experimental procedure is as follows: Tetrachlorocyclopropene (1.78 g, 0.01 mole) in acetonitrile was added dropwise, with stirring, to a solution of silver fluoroborate (1.95 g, 0.01 mole) in the same solvent at -20° ∿ -15° under nitrogen. To this solution was added a solution of thiols (0.04 mole) and the reaction mixture was continued to stir at room temperature for 3 ∿ 16 hr. After filtration of silver chloride and removal of the solvent from the filtered solution, the residue was collected and recrystallized from chloroform-ether. The white crystalline products were confirmed to be trithiocyclopropenium fluoroborate by the spectral data and the elemental analyses.



I

The pmr spectra showed the signals due to the corresponding alkyl- and phenyl-groups in $I_{a\sim e}$ and the infrared spectra all exhibited characteristic bands between 1390 ∿ 1440 cm^{-1} due to ring vibration (E') of the cyclopropenium ring[9,10] and a broad fluoroborate absorption at 1020 ∿ 1100 cm^{-1}. These trithiocyclopropenium fluoroborate are all stable without moisture[11] and soluble in chloroform, acetonitrile, acetone and dimethylformamide. The isolated yield, melting points and analytical data of $I_{a\sim e}$ are summarized in Table I. $I_{a\sim e}$ (as perchlorate) was also prepared according to our method[1] which was used to prepare triaminocyclopropenium ion. In the pmr spectra of I_a, I_b and I_c, the methyl, the methylene and the methyne protons directly attached to the sulfur atom show substantial downfield shift (0.73 ∿ 0.90 ppm) in comparison with the corresponding thiols. The methyl and the phenyl proton signals intervening one carbon atom from the sulfur atom of I_b, I_c, I_d and I_e also appeared at lower field than those of the corresponding thiols, respectively. This remarkable low field shift indicates that the electron-donating π conjugative effect of the sulfur atom to the C_3^+ core is dominant. The chemical shifts of the system $I_{a\sim e}$, and those of the cooresponding thiols are

Table I

	Substituent	Yield (%)	Melting Point (°C)	Elemental Analysis	C	H	S
I_a	CH_3S	26	133 ∿ 134	Found	27.33	3.51	36.65
				Calcd.	27.28	3.43	36.42
I_b	CH_3CH_2S	29	107 ∿ 108	Found	35.34	5.24	31.43
				Calcd.	35.30	4.94	31.42
I_c	$(CH_3)_2CHS$	28	102 ∿ 105 (dec.)	Found	41.11	6.22	28.56
				Calcd.	41.38	6.08	27.62
I_d	$(CH_3)_3CS$	36	136 ∿ 138 (dec.)	Found	45.92	7.01	25.80
				Calcd.	46.15	6.97	24.64
I_e	C_6H_5S	38	124 ∿ 126 (dec.)	Found	55.75	3.04	22.23
				Calcd.	56.05	3.36	21.37

listed in Table II.

Table II Comparison of the Chemical Shifts of $I_{a\sim e}$ with the corresponding Thiols

		Chemical Shift (δ)		
		Cyclopropenyl cation	The corresponding thiol	Δ ppm
I_a	CH_3	2.93 (s)[a]	1.20 (d)[a,b]	0.73
I_b	CH_2	3.43 (q)[a]	2.53 (q)[a,b]	0.90
	CH_3	1.57 (t)[a]	1.30 (t)[a,b]	0.27
I_c	CH	3.93 (sep.)[a]	3.17 (sep.)[a]	0.76
	CH_3	1.53 (d)[a]	1.35 (d)[a]	0.18
I_d	CH_3	1.67 (s)[a]	1.47 (s)[a]	0.20
I_e	C_6H_5	7.82 ∿ 7.30 (m)[a]	7.21 (s)[a]	0.09 ∿ 0.61

a) The spectra was measured in deuterochloroform in the concentration of ca. 5 % of both $I_{a\sim e}$ and the corresponding thiols. b) S. Forsén, Acta Chem. Scand., 13, 1472 (1959).

Furthermore, since δ 2.93 of methyl proton signal for I_a is close to that (δ 3.09) of trimethylthiomethyl carbonium ion (R = CH_3 in III) in which [2p-3d]π interaction between carbon (sp^2)-sulfur bond can not take place, contribution of hetero-[3] radialene structure to I might be neglected. The high field shift of 0.16 ppm of I_a compared with III (R = CH_3) is attributed to the decrease of positive charge (1/3) of I relative to III (R = CH_3). The ultraviolet absorption at long-wave length of the cyclopropenyl cations, I_a (274 nm), I_b (274 nm), I_c (275 nm), I_d (276 nm) and I_e (277 nm), also supports the π-electron delocalization. The values of pK_{R^+} of $I_{a\sim d}$ estimated from the pK_{R^+} — ring vibration (E') relationship[12] were 2.3 ∿ 2.4 indicating that trithiocyclopropenyl cation has similar stability to triphenylcyclopropenyl cation (pK_{R^+}, 2.8). Various reactions of trithiocyclopropenyl cation are now under investigation in our laboratory which will be published soon.

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