

REACTIONS OF TRITHIOCYCLOPROPENYL CATION WITH SOME NUCLEOPHILES

Z. Yoshida, S. Yoneda, T. Miyamoto and S. Miki

Department of Synthetic Chemistry, Kyoto University

Yoshida, Kyoto, 606, Japan

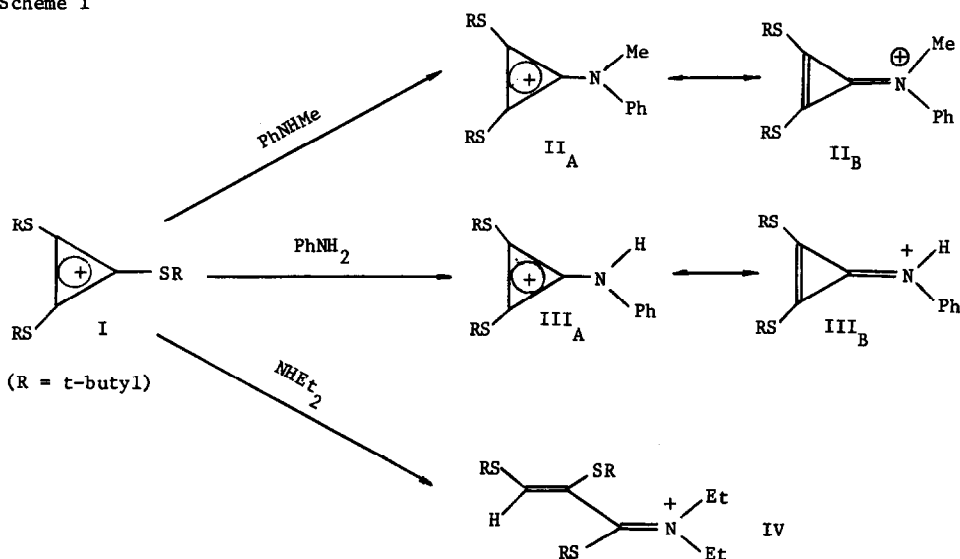
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We reported the synthesis of trithiocyclopropenyl cation as a new electron system.¹ In view of its intriguing structure, search on the reaction behaviors of the trithiocyclopropenyl cation is expected to be of interest. We wish to report, here, the reactions of tri-*t*-butylthiocyclopropenyl cation (I) with some nucleophiles.

The reactions of I with amines afforded a different type of products depending on amines used. Monoaminodithiocyclopropenyl cations were obtained with aromatic amines, and ring-opening products with aliphatic amines. To a solution of I ($X=BF_4^-$) in methylene chloride was added dropwise with stirring, equimolar *N*-methylaniline at room temperature. After stirring for 9 hr., the solvent was removed at reduced pressure from the reaction mixture and the residue was collected and repeatedly reprecipitated from chloroform-ether to give mono-*N*-methylanilino-di-*t*-butylthiocyclopropenium fluoroborate (II) in 52 % yield; mp 124.3° ~ 125.0°. In the infrared absorption spectrum of II, a characteristic absorption of cyclopropenium ring was observed at 1837 cm^{-1} . The ultraviolet absorption spectrum in methylene chloride exhibited absorption maxima at 246 nm (log ϵ 4.11) and 279 (4.10). The pmr spectrum in $CDCl_3$ showed broad singlets at δ 1.31 (9H, *t*-butyl) and 1.70 (9H, *t*-butyl), a sharp singlet at 3.83 (3H, *N*-methyl), and a multiplet at 7.47 (5H, phenyl). The appearance of two signals in the different fields (1.31 and 1.70 ppm) for the methyl protons of the *t*-butyl groups indicates the existence of the energy barrier for rotation about the C-N bond and, accordingly, the importance of the immonium structure (II_B) to the resonance hybrid of II as shown in Scheme 1. Similar treatment of I with aniline afforded monoanilino-di-*t*-butylthiocyclopropenium fluoroborate (III) in 68 % yield, mp 145.2 ~ 148.0° (dec.); ir (KBr) 1843 cm^{-1} ; uv (CH_2Cl_2) 259 nm (log ϵ 4.29) and 286 (3.8); nmr ($CDCl_3$) δ 1.64 (s, 9H, *t*-butyl), 1.70 (s, 9H, *t*-butyl), 7.36 (m, 5H, phenyl) and 10.73 (s, 1H, NH). When equimolar diethylamine

was added to a solution of I in chloroform at -20° to -10° , the solution was immediately colored to yellow. Work-up of the reaction mixture gave the ring-opening product (IV) in 62 % yield; dec. 105° ; uv (acetonitrile) 223 nm ($\log \epsilon$ 3.84), 275 (3.81) and 367 (3.78). The ir spectrum (KBr) did not show a characteristic absorption of $1800 \sim 1900 \text{ cm}^{-1}$ due to the cyclopropenium ring. The pmr spectrum revealed singlets at δ 1.37 (9H, t-butyl), at 1.50 (9H, t-butyl) and at 1.55 (9H, t-butyl), a triplet overlapping with t-butyl signals centered at 1.50 (methyl), two quartets at 4.21 (2H, methylene) and at 4.27 (2H, methylene), and a singlet at 8.23 (1H, vinyl).

Scheme 1

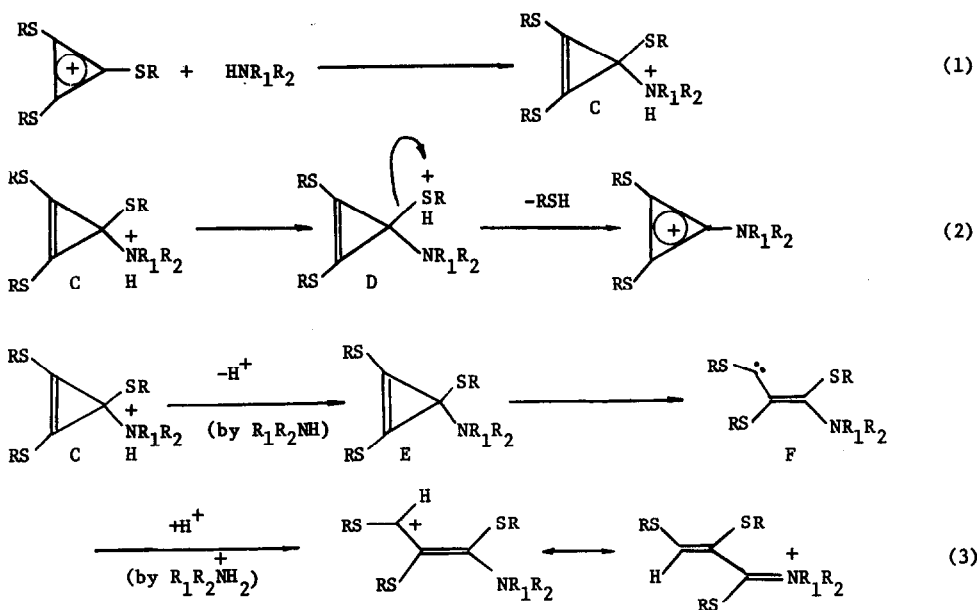


The difference of reaction behavior of I, depending on the type of amine, might be explained as shown in Scheme 2. In the reaction with aromatic amine, firstly, the 1,3-shift of proton in the intermediate C might occur because of its weaker basicity of the nitrogen atom and, then RSH group of D might be eliminated (eq. 2). On the other hand, the reaction with aliphatic secondary amine is considered to proceed as shown in eq. 3 to give the ring-opened product in view of its higher basicity and the reaction feature of tetra-heteroatom-substituted cyclopropene (E).²

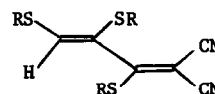
The reaction of I with equimolar malonitrile in the presence of base afforded the ring-opened product (V): A solution of malonitrile and potassium-t-butoxide in acetonitrile was added dropwise to a solution of I in the same solvent at -50° to -40° and the reaction

mixture was stirred at this temperature for 30 min. After filtration of potassium fluoro-borate, the solvent was removed at reduced pressure, the residue was chromatographed on silica gel, and purified by recrystallization from methanol to give orange-yellow crystallines (V). The isolated yield, 28 %; mp 148.3 ~ 149.1°. The structure of V was determined by its

Scheme 2



spectral data; ir (KBr) 3020 cm^{-1} ($\nu_{\text{-CH-}}$), 2210 cm^{-1} ($\nu_{\text{C=N}}$); uv (n-hexane) 256 nm ($\log \epsilon$ 4.05) and 386 nm (4.02); pmr (CDCl_3) δ 1.37 (s, 9H, t-butyl), 1.40 (s, 9H, t-butyl), 1.48 (s, 9H, t-butyl) and 7.87 (s, 1H, vinyl); mass spectrum (parent peak) m/e 368.



R = t-butyl
(V)

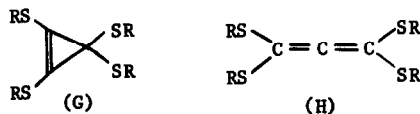
Reaction of I with alkali have been carried out as follows: 0.1 N aq. potassium hydroxide solution was poured to a solution of I in chloroform at room temperature. After the reaction mixture was stirred for 15 min., the organic layer was separated, washed with water, dried over anhydrous sodium sulfate and the solvent was removed at reduced pressure. The residue was purified by silica gel chromatography and by recrystallization to give the products (VI) and (VII). The white solid (VI) was readily identified as di-t-butylthiocyclopropenone from the spectral

data of the authentic sample.³ The other product (VII) is stable white crystallines, easily soluble in nonpolar solvents, but partly soluble in polar solvents such as methanol and acetonitrile; mp 138.8 ~ 139.5°; ir (KBr) 1908 cm⁻¹; uv (n-hexane) 219 nm (log ε 4.28) and 268 (4.21). The elemental analysis and the mass spectrum (M⁺ 392) indicated VII to be either cyclopropene (G) or allene (H). The pmr spectrum

of VII in deuteriochloroform showed a sharp singlet at δ 1.44, suggesting the structure (H).

The structure of VII was determined by means of the cmr spectrum of VII. As seen in Fig. 1, the

signals at 31.2, 49.1, 92.5 and 215.6 ppm corresponded to C₄, C₃, C₂ and C₁ atoms, respectively. Especially, the observed low field chemical shift (215.6 ppm) is characteristic⁴ of allene compounds. The reaction of I with sodium t-butyl mercaptide in ethanol also yielded VII in quantitative yield. The mechanism for the allene formation is now under investigation.



R = t-butyl

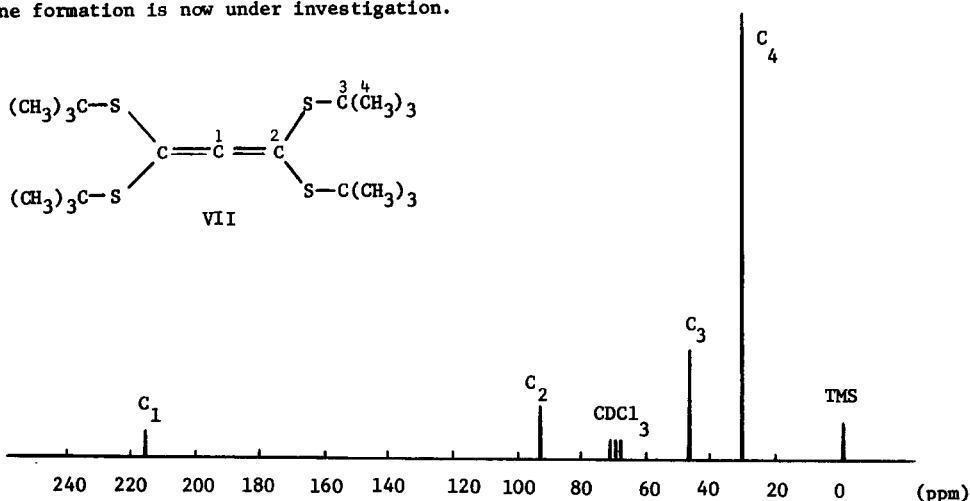


Fig. 1 The cmr spectrum of VII in deuteriochloroform

References

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