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Reaction of Tris(alkylthio)cyclopropenyl Cation with Pyrrole and Indoles. A Novel Synthesis of Pyrrolizine and Fluorazene Derivatives

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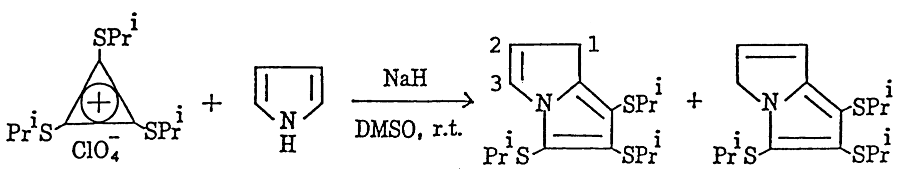
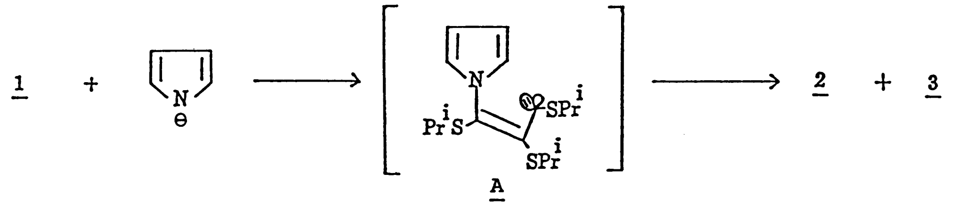
The treatment of tris(isopropylthio)cyclopropenylium perchlorate with pyrrole and indoles in the presence of a strong base afforded pyrrolizine and fluorazene derivatives, respectively.

Cyclopropenyl cations have attracted special attention because of their severe enforced bond angle deformation and aromatic character, and their physical and chemical properties have been widely investigated.1) Recently, interest in the chemistry of cyclopropenyl cations substituted by heteroatomic groups has been increasing. For example, the reactions of tris(alkylthio)cyclopropenyl cations with dialkylamines2) and sulfonium methylide3) and the reactions of 1-alkylthio- and 1-amino-2,3-diphenylcyclopropenyl cations with 1,3-dicarbonyl compounds4) and Grignard reagents5) have been reported. In relation to these studies, we have reported recently that the reaction of tris(isopropylthio)cyclopropenyl cation with m-substituted anilines affords 2,3-bis(isopropylthio)quinoline derivatives in good yields.6) To extend the reaction using trithiocyclopropenyl cation as a building block, we examined the reaction of tris(isopropylthio)cyclopropenylium perchlorate (1) with heterocyclic compounds containing nitrogen and now report our findings that the reaction of 1 with pyrrole and indoles affords pyrrolizine and fluorazene derivatives, respectively.

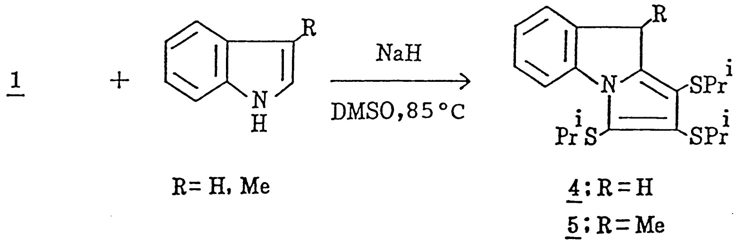


A typical procedure is as follows : Pyrrole (0.034 g, 0.5 mmol) was added to a suspension of sodium hydride (50% in mineral oil, 0.048 g, 1.0 mmol) in dry dimethyl sulfoxide (DMSO)(10 ml) and the mixture was stirred under nitrogen at room temperature for 2 h. Then a solution of 1 (0.361 g, 1.0 mmol) in dry DMSO (10 ml) was added in one portion. After stirring for 1 h, the mixture was poured into water (100 ml), extracted with ether (150 ml), dried over anhydrous sodium sulfate, and concentrated. The residue was chromatographed on silica gel by using hexane-dichloromethane (1 : 5) as the eluent. 1H- and 3H-pyrrolizine derivatives, 2 and 3, were obtained in 53 and 11% yields, respectively. In the absence of a base this reaction scarcely proceeded. Furthermore, we found that potassium hydroxide and potassium tert-butoxide can be used instead of sodium hydride (Yields of 2 and 3 : 41 and 18% and 49 and 9%, respectively).

This reaction would proceed via the formation of an electrophilic carbene-type intermediate A generated by the nucleophilic attack of the pyrrolyl N-anion$^{7)}$ to a cyclopropenyl cation, followed by an intramolecular reaction of the carbene with the pyrrole ring to yield 2 and 3.



The reactions of 1 with indole and 3-methylindole in the presence of sodium hydride in DMSO at 85 °C for 1 h afforded the corresponding fluorazene derivatives, 4 and 5, in 84 and 51% yields, respectively. The structures of 2—5 were determined by the IR, ^{1}H NMR,$^{8)}$ ^{13}C NMR, and mass spectra and the elemental analysis. Further studies on the reactivity of 1 are now in progress.



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6) S. Yoneda and H. Kojima, Bull. Chem. Soc. Jpn., 61, 1793 (1988).
7) Pyrrole is converted into pyrrolyl N-anion with sodium hydride, potassium hydroxide, and potassium tert-butoxide in DMSO: see A. R. Katritzky and C. W. Rees, "Comprehensive Heterocyclic Chemistry," ed by C. W. Bird and G. W. H. Cheeseman, Pergamon Press, London (1984), Vol. 4, pp. 235-240.
8) 2; ^{1}H NMR ($CDCl_3$) δ 7.17 (m, 1H), 5.89 (m, 1H), 3.49 (sep, 1H, J=6.7 Hz), 3.48 (d, 2H, J=2.4 Hz), 3.33 (sep, 1H, J=6.7 Hz), 3.20 (sep, 1H, J=6.7 Hz), 1.21 (d, 6H, J=6.7 Hz), 1.20 (d, 6H, J=6.7 Hz), and 1.18 (d, 6H, J=6.7 Hz).
3; ^{1}H NMR ($CDCl_3$) δ 6.71 (m, 1H), 6.37 (m, 1H), 4.52 (dd, 2H, J=2.1 Hz), 3.49 (sep, 1H, J=6.7 Hz), 3.37 (sep, 1H, J=6.7 Hz), 3.20 (sep, 1H, J=6.7 Hz), 1.22 (d, 12H, J=6.7 Hz), and 1.19 (d, 6H, J=6.7 Hz).

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