

NOVEL CYCLOPROPENYL PHOSPHONIC ACID ESTERS AND NEW SYNTHESIS OF PYRROLE DERIVATIVE.  
REACTIONS OF TRIALKYLTHIOCYCLOPROPENIUM ION AND DIALKYLTHIOCYCLOPROPENETHIONE WITH  
TRIVALENT PHOSPHORUS COMPOUNDS

Shigeo YONEDA, Hideo HIRAI, and Zen-ichi YOSHIDA\*  
Department of Synthetic Chemistry, Kyoto University,  
Yoshida, Kyoto 606

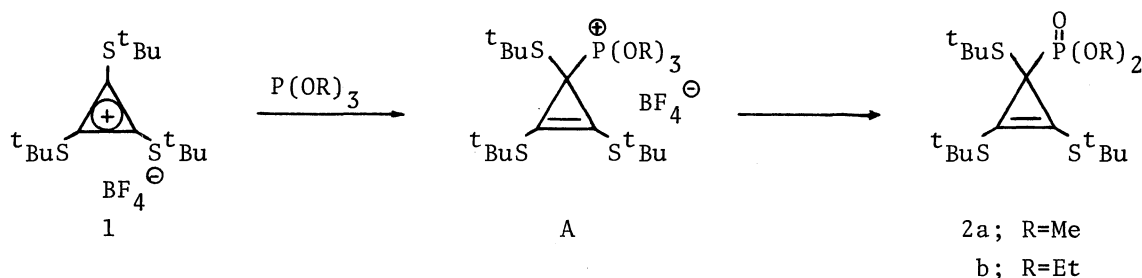
The reactions of trialkylthiocyclopropenium ion (1) and dialkylthiocyclopropenethione (6) with various trivalent phosphorus compounds were investigated. The reactions of 1 and 6 with trialkyl phosphite were found to give the cyclopropenyl phosphonic acid esters. The similar treatment of 1 with hexamethylphosphorous triamide led to the formation of the pyrrole derivative.

Recent interest in the cyclopropenium ion chemistry has been focused on the hetero-atom substituted ones. Since the physical and chemical properties of the aromatic but highly strained  $3C-2\pi$  ring system are sensitively affected by substituents at the  $C_3$  ring, the investigation of behavior of cyclopropenium ion substituted by a hetero-atom is a fascinating problem.<sup>1-8)</sup> The synthesis of trialkylthiocyclopropenium ion (1) and its reactions with several nucleophiles were previously reported.<sup>6,9)</sup> We wish to report here the reactions of 1 with trivalent phosphorus compounds. The novel phosphonic acid ester possessing highly strained cyclopropenyl group was exclusively formed from 1 or 6 and trialkyl phosphite, and the pyrrole derivative from 1 and hexamethylphosphorous triamide. The pyrrole formation is particularly noteworthy, because this is the first example of the pyrrole ring formation from the cyclopropenium compounds, although a few ring expansion reactions of cyclopropenium ions have been found so far.<sup>10)</sup>

In this study tri-*t*-butylthiocyclopropenium ion, 1, was chosen as the trialkylthiocyclopropenium ion, and trialkyl and triphenyl phosphites, triphenylphosphine, and hexamethylphosphorous triamide (HMPT) were used as trivalent phosphorus compounds.

Excess trimethyl phosphite was added dropwise to 1 in acetonitrile under  $N_2$  at room temperature. Color of the solution immediately changed to orange. After stirring under reflux for 1 hr, work-up of the reaction mixture gave the phosphonic acid ester (2a) in 73 % yield, mp  $41^\circ$ . The structure of 2a was determined by the spectral data; IR (KBr) 1915, 1369, 1055-1022  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.45 (s, 27H, *t*-butyl), 3.79 (d, 6H,  $J=12.4Hz$ , methyl). Similar reaction of 1 with triethyl phosphite gave the corresponding phosphonic acid ester (2b) as sirupy oil in 90 % yield; IR (neat) 1917, 1372, 1060-1022  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.27-1.41 (td, 6H,  $J_{H-H} = 7.5Hz$ ,  $J_{P-H} = 1.0Hz$ , methyl), 1.46 (s, 27H, *t*-butyl), 4.01-4.31 (qd, 4H,

$J_{H-H} = 7.5\text{Hz}$ ,  $J_{P-H} = 8.3\text{Hz}$ , methylene). The exclusive formation of novel phosphonic acid esters (2a and 2b) is explained by the following reaction scheme, where trialkyl phosphite initially attacks at the cyclopropenyl ring followed by the dealkylation. No ring-opened products were isolated.



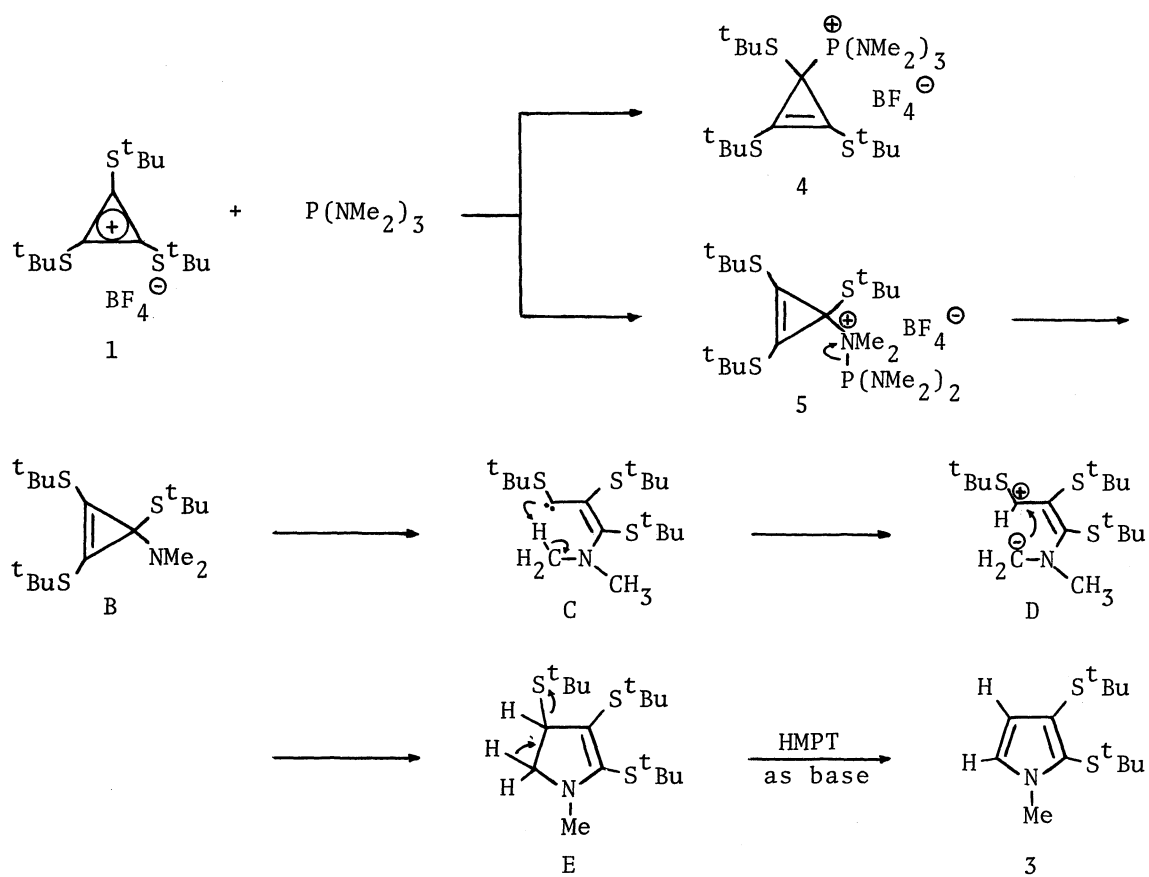
Triphenyl phosphite did not react with 1 in acetonitrile at reflux temperature even after 24 hrs. On the other hand the reaction of 1 with triphenylphosphine led to the quantitative formation of the phosphonium salt of type (A).

Treatment of 1 with HMPT in acetonitrile at room temperature for 1 hr and the subsequent column chromatography on Silica afforded an oily pyrrole derivative (3) in 26 % yield along with the phosphonium salt (4) in 69 % yield, mp  $106^\circ$ . The elemental analyses and the spectral data of 3 are all consistent with the formulation of 3. The mass spectrum revealed the parent ion peak at 257. The  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) showed two doublets at  $\delta$  6.34 (1H,  $J=3.9\text{Hz}$ ) and at 6.80 (1H,  $J=3.9\text{Hz}$ ) due to the pyrrole ring protons, an N-methyl singlet at  $\delta$  3.73 (3H) and two sharp singlets at 1.22 (9H) and 1.23 (9H). IR (neat)  $1365$ ,  $1166$ ,  $796\text{ cm}^{-1}$ ; UV (n-hexane)  $\lambda_{\text{max}}$  253 nm ( $\log \epsilon = 3.95$ ) with a shoulder at 235 nm. Desulfurization of 3 with Raney nickel in ethanol gave N-methyl pyrrole.

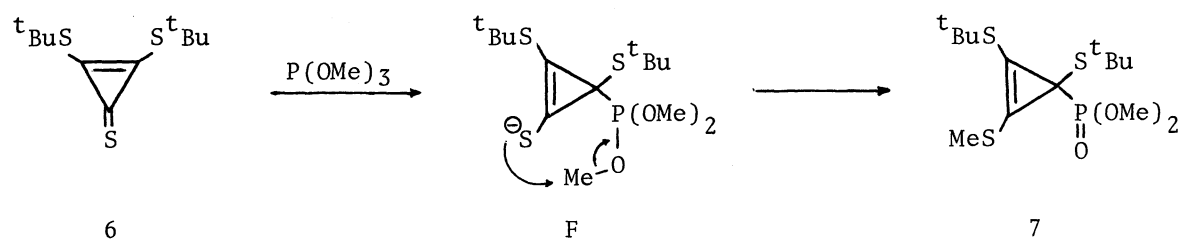
The ring expansion reaction of trialkylthiocyclopropenium ion in the presence of HMPT provides a new pyrrole synthesis. The reactions of 1 with HMPT might proceed as shown in the Scheme 1.

Since HMPT has ambident nucleophilic centers at P and N atoms, the attack of HMPT on 1 should form the phosphonium (4) and the ammonium (5) salts. In the former (4), the N-P bond is stabilized by (P-d) $\pi$  interaction. On the other hand, the N-P bond without such a stabilization in the latter (5) should be unstable to form a cyclopropene substituted with four electron-donating heteroatoms (B), which has a tendency to give the carbene (C).<sup>1)</sup> Subsequent intramolecular hydrogen shift to D, the cyclization to E, and the base (HMPT) catalyzed 1,2-elimination should form the pyrrole derivative (3).

The reaction of 6 (thiodeltic acid diester<sup>11)</sup>) with trimethyl phosphite at reflux temperature for 2 hrs in acetonitrile afforded the phosphonic acid ester (7)<sup>12)</sup> in 45 % yield, 7: mp  $46^\circ$ ; IR (KBr)  $1910$ ,  $1362$ ,  $1056$ - $1088\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.44 (s, 9H, t-butyl) 1.46 (s, 9H, t-butyl), 2.28 (s, 3H, -SMe), 3.80 (d, 6H,  $J=12.4\text{Hz}$ , -OMe). This reaction behavior of dialkylthiocyclopropenethione is similar to that of cycloalkanethione and not to that of trithiocarbonate suggesting that the generation of dithiocyclopropenylidene by the reaction with trialkyl phosphite should be difficult.<sup>13)</sup>



Scheme 1



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- (11) For synthesis of thiodeltic acid derivatives including the diester, see Z. Yoshida, S. Miki, and S. Yoneda, Abstracts of the 6th National Symposium on the Chemistry of Nonbenzenoid Aromatic Compounds, October 14-15 (1973), Fukuoka, and Abstracts of the 32nd National Meeting of Chemical Society, Japan, April 1-4 (1975), Tokyo.
- (12) All reaction products we reported here are novel, and gave the satisfactory elemental analyses.
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