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REACTION OF THIOCYCLOHEXANONE WITH TRIALKYL PHOSPHITE

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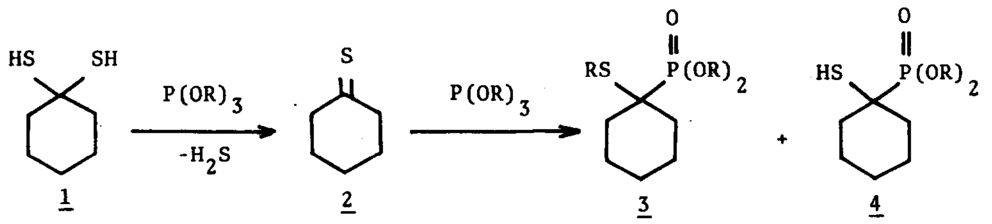
Although a considerable amount of studies on the reactions of thiocarbonyl compounds (RR'C=S) with nucleophiles have been reported,[1] the investigation of their reaction behaviors is still a fascinating problem, because they are sensitively affected by both the substituent groups (R, R') and the nature of nucleophiles. Especially, the reactions using trialkyl phosphite as a nucleophile have recently received much attention. For instance, Corey and Märkl[2] reported the reaction of 1,3-dithiacyclohexane-2-thione with trimethyl phosphite to afford 1,3-dithiacyclohexylidinephosphorane, which is converted to the phosphonate derivative by the rearrangement of the methyl group. Middleton and Sharkey[3] also reported the reactions of hexafluorothioacetone and thiofluorenone with trimethyl phosphite to give the corresponding phosphoranes.

We here report new type of reactions of thiocyclohexanone (2) with trialkyl phosphites to produce the phosphonic acid ester derivatives (3 and 4).



a	: R = Me	70 %	0 %
b	: R = Et	20	30
c	: R = i-Pr	0	81
d	: R = crotyl	65	0

The reaction mechanism for the formation of the thioether-type product

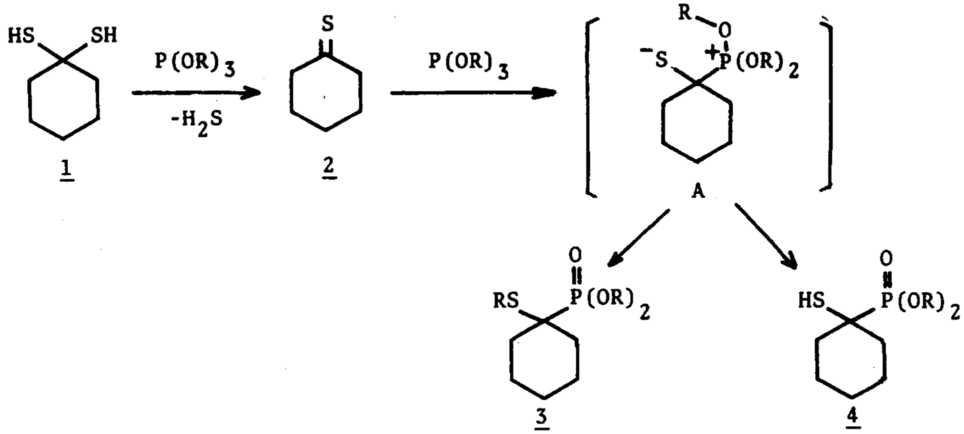
(3) and the thiol-type product (4) will be discussed later in this paper.

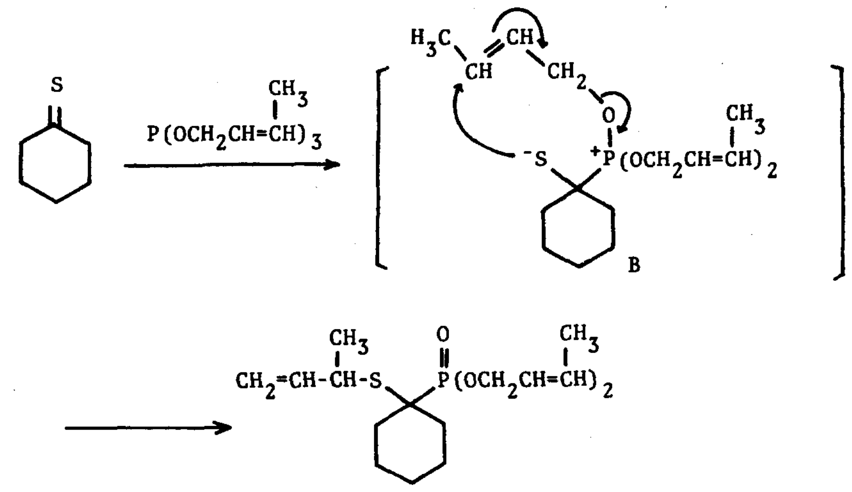
To a solution of 1,1-cyclohexanedithiol (1) in toluene was added dropwise excess trimethyl phosphite with stirring under nitrogen. As the reaction mixture was elevated to the reflux temperature, the evolution of hydrogen sulfide and the change of the color of the solution to pink were observed. After the pink color disappeared in several hours, excess trimethyl phosphite and toluene were evaporated. Distillation at reduced presure gave the product (3a) as a viscous liquid in 70 % yield; bp 112 ∿ 113°/2.5 mmHg. The structure of 3a was assigned unequivocally on the basis of the analytical and spectral data: ir (KBr) 1230 cm^{-1} (P=O stretching), 1180 (P-O-CH_3, CH_3 bending) and 1040 (P-O-R asymmetric stretch); pmr ($CDCl_3$) δ 1.45 ∿ 1.95 (m, 10H, methylene), 2.20 (s, 3H, S-CH_3), 3.79 ∿ 3.93 (d, J = 10.1 Hz, 6H, P-O-CH_3); mass m/e 238 (parent).

Reaction of 1 with triethyl phosphite was carried out in the same reaction condition gave liquid products, 3b and 4b in 20 % and 30 % yields, respectively, which were obtained as mixture by distillation (bp 114 ∿ 115°/2.5 mmHg) and separated by vpc. The structure of 4b was determined by its spectroscopic data: ir (KBr) 2500 cm^{-1} (SH stretching), 1245 (P=O stretching) and 1165 (P-O-Et, Et bending); pmr ($CDCl_3$) δ 1.29 ∿ 1.45 (t, J = 7.0 Hz, 6H, CH_3), 1.50 ∿ 1.93 (m, 10H, methylene) 1.93 (s, 1H, SH) and 4.07 ∿ 4.37 (p, J = 7.0 Hz, 4H, methylene); mass m/e 251 (parent). The structure of 3b was suggested by absence of a band due to SH stretching in the ir spectrum and confirmed by the pmr and mass spectra: pmr ($CDCl_3$) δ 2.65 ∿ 2.92 (q, J = 7.5 Hz, 2H, -SCH_2-), 1.15 ∿ 1.32 (t, J = 7.5 Hz, 3H, CH_3); mass m/e 280 (parent).

A similar reaction of 1 with tri-isopropyl phosphite gave only one product in 81 % yield; bp 114.0 ∿ 114.5°/2.5 mmHg. This product showed the SH absorption band in the ir spectrum and the peak at δ 1.91 (s, 1H, SH proton) in the pmr spectrum, which clearly supported the structure of 4c. The formation of the thioether-type product (3c) was not found. Triphenyl phosphite did not react with 2 in toluene at reflux temperature for 24 hr.

All the results mentioned above can be well accounted for by assuming the formation of the betaine intermediate (A). Firstly, dehydrogen sulfide of 1 might be caused by trialkyl phosphite to afford thiocyclohexanone. Then the phosphite might attack at the carbon atom of the thiocarbonyl group and the betaine intermediate should be formed. The alkyl group rearrangement in the intermediate A should yield the thioether-type product (3), on the one hand, and the proton transfer from alkyl group (R), the thiol-type product (4) on the other. The competing proton transfer seems to be governed by the stability of olefin formed from alkyl group (R). In order to examine whether the alkyl rearrangement occurs through concerted (intramolecular) or stepwise (intermolecular) mechanism, the reaction of 1 with tricrotyl phosphite was carried out. The product obtained in 65 % yield by the distillation (bp 149.0 ∿ 149.5/ 4 mmHg) was assigned to be the thioether-type (3d) on the basis of the analytical data. The ir spectrum showed an absorption at 910 cm^{-1} due to the terminal vinyl group, and the pmr spectrum exhibited a quintet at δ 4.33 (J = 7.5 Hz, 1H, methyne) and a doublet at 1.27 ∿ 1.47 (J = 7.5 Hz, 3H, methyl), which clearly indicates that the compound contains one methallyl group. The pmr signals due to two crotyl groups were also observed. Accordingly, it is clear that the alkyl rearrangment proceeds concertedly *via* the cyclic intermediate (B).





3d

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