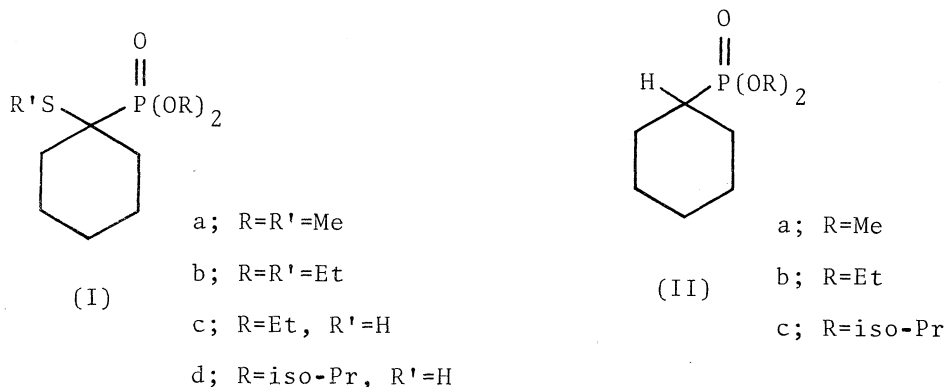


A NEW SYNTHESIS OF PHOSPHONIC ACID ESTERS

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It has been found that treatments of cyclohexanethione with trialkyl phosphites and subsequently with Raney nickel gave cyclohexanephosphonic acid esters in good yield.

We have recently reported<sup>1)</sup> that the reaction of cyclohexanethione with trialkyl phosphites gave new kinds of phosphonic acid esters (I) bearing alkylthio group in good yields.



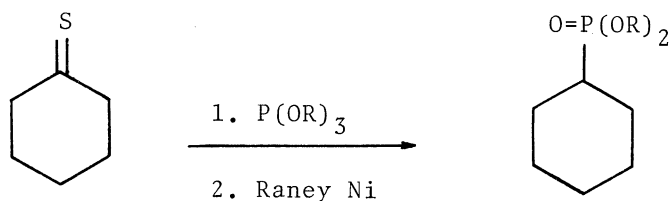
Primary alkyl halides are well known to react with trialkyl phosphites to yield phosphonic acid esters (Arbusov-Michaelis reaction<sup>2)</sup>), but in the case of secondary ones, the yields are very low because of side reactions (e.g. formation of alkenes). We report a new synthesis of phosphonic acid esters in high yields by desulfurization of I with Raney nickel. Reactions of I<sub>a~d</sub> with Raney nickel in ethanol under reflux for 10 ~ 20 hrs gave the corresponding phosphonic acid esters, II<sub>a</sub>, II<sub>b</sub> and II<sub>c</sub>, as viscous liquid in the yields shown in the Table. In the n.m.r. spectra of II<sub>a~c</sub>, the signals assigned to the alkylthio and mercapto groups of I<sub>a~d</sub> disappeared. The spectral data of II<sub>a</sub>, II<sub>b</sub> and II<sub>c</sub> clearly indi-

Table The yields of II<sub>a-c</sub>

Starting Material	Product	Yield (%)
I <sub>a</sub>	II <sub>a</sub>	78
I <sub>b</sub> + I <sub>c</sub>	II <sub>b</sub>	92
I <sub>d</sub>	II <sub>c</sub>	82

cated characteristic bands of the phosphonic acid ester: II<sub>a</sub>; i.r. (neat) 1240  $\text{cm}^{-1}$  (P=O), 1180 (P-O-Me), 1060 ~ 1020 (P-O-R); n.m.r. ( $\text{CDCl}_3$ )  $\delta$  3.68 (d,  $J_{\text{P-H}} = 10.1$  Hz, 6H, methyl): II<sub>b</sub>; i.r. (neat) 1240  $\text{cm}^{-1}$  (P=O), 1165 (P-O-Et), 1030 ~ 1020 (P-O-R); n.m.r. ( $\text{CDCl}_3$ )  $\delta$  4.01 (double quartet, 4H, methylene), 1.24 (t, 6H, methyl): II<sub>c</sub>; i.r. (neat) 1235  $\text{cm}^{-1}$  (P=O), 975 (P-O-R); n.m.r. ( $\text{CDCl}_3$ )  $\delta$  4.58 (double septet,  $J_{\text{P-H}} = 8.1$  Hz,  $J_{\text{H-H}} = 6.2$  Hz, 2H, methine), 1.25 (d,  $J_{\text{H-H}} = 6.2$  Hz, 12H, methyl).

The reaction mixtures of cyclohexanethione with trimethyl, triethyl and tri-iso-propyl phosphites were also converted by direct treatment with Raney nickel to II<sub>a</sub>, II<sub>b</sub> and II<sub>c</sub>, respectively, in good yields (60 ~ 80 %). Thus we can easily



synthesize cycloalkanephosphonic acid ester from the thione.

#### References

- 1) Z. Yoshida, T. Kawase, and S. Yoneda, *Tetrahedron Lett.*, No. 4, 235 (1975).
- 2) H. Krauch and W. Kunz, "Organic Name Reactions", John Wiley & Sons, Inc., New York, 1964, p. 17; G. M. Kosolapoff, *Org. Reactions* 6, 276 (1951).

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