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Desulfurization of Thiiranes with Triethyl Phosphite

ROBERT D. SCHUETZ AND RICHARD L. JACOBS[1]

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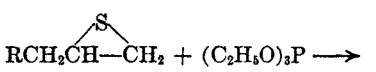
Recently Scott has reported[2] that the reaction of ethylene oxides with triethyl phosphite, results in the reduction of the epoxide to the corresponding olefin and oxidation of the phosphite to phosphate. For example, when equivalent amounts of triethyl phosphite and either ethylene or propylene oxide were heated in a stainless steel bomb at 150–175° for several hours, high yields of the corresponding olefin and triethyl phosphate were obtained.

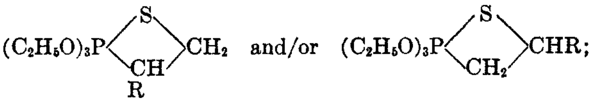
In the course of recent investigations in these laboratories concerned with the synthesis and ring opening reactions of unsymmetrically substituted thiacycloalkanes, it was observed that heating an equimolar mixture of triethyl phosphite and a thiirane at its reflux temperature for a short period of time resulted in the formation of triethyl thionophosphate with the simultaneous conversion of the thiirane to its corresponding unsaturated compound.



R = H, Cl, CH_3O

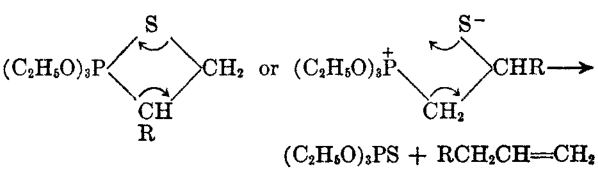
Preliminary results indicate that a wide variety of thiiranes are susceptible to this desulfurization process. In each instance, the reaction yields, within experimental limits, quantitative amounts of triethyl thionophosphate and the unsaturate under much milder conditions than those employed with the oxygen analogs.

With regard to the reaction of thiiranes with triethyl phosphite, a mechanistic interpretation similar to that offered by Scott[2] may be applicable. Thus, a nucleophilic attack by phosphite on either ring carbon atom could produce intermediates such as the following

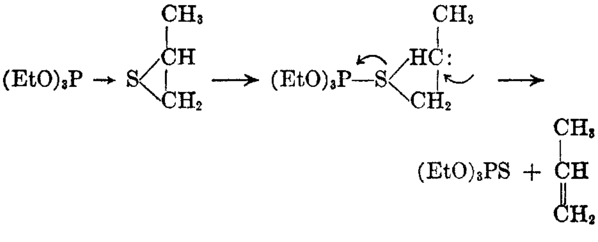


$(C_2H_5O)_3P^+CHRCH_2S^-$ and/or $(C_2H_5O)_3P^+CH_2CHRS^-$

A subsequent rearrangement of such intermediates could then account for the observed products



However, while the above mechanism would satisfactorily account for the observed products, the recent work of Bordwell[3] and collaborators on 1,2 elimination reactions of thiacyclopropanes with organolithium compounds, which give rise to olefins, would suggest an alternative mechanism in which direct attack by phosphite on sulfur occurs. This mechanism can be formulated as,



The first step in the reaction is facilitated by coordination of sulfur with phosphite and breaking of the carbon-sulfur bond. This yields a pair of electrons which could initiate a 1,2-elimination reaction resulting in the simultaneous formation of olefin and thionophosphite. It was found that the ethylene sulfides react readily under the mild conditions described in the experimental section while the corresponding ethylene oxides gave little or no reaction under the same experimental conditions.

The present work extends the list[4] of types of organosulfur compounds that are desulfurized by triethyl phosphite.

EXPERIMENTAL

Materials. Propylene oxide and epichlorohydrin were obtained from commercial sources and were used as received.

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[1] Abstracted in part from the doctoral thesis of R. L. Jacobs.

[2] C. B. Scott, *J. Org. Chem.*, **22**, 1118 (1957).

[3] F. G. Bordwell, H. M. Anderson, and B. M. Pitt, *J. Am. Chem. Soc.*, **76**, 1082 (1954).

[4] (a) H. I. Jacobsen, R. G. Harvey, and E. V. Jensen, *J. Am. Chem. Soc.*, **77**, 6064 (1955); (b) F. W. Hoffman, R. J. Ess, T. C. Simmons, and R. S. Hanzel, *J. Am. Chem. Soc.*, **78**, 6414 (1956); (c) C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **79**, 5326 (1957).

Methyl glycidyl ether was obtained by the method of Pollard.[5] The thiiranes were prepared from the corresponding epoxides following the procedure of Bordwell and Anderson.[6] Triethyl phosphite was obtained from the Virginia-Carolina Chemical Corporation and purified prior to use by distillation from metallic sodium.

Reaction of 2-chloromethylthiirane with triethyl phosphite. A mixture of 21.6 g. (0.20 mole) of 2-chloromethylthiirane and 33.2 g. (0.20 mole) of triethyl phosphite was distilled at atmospheric pressure employing a 30 cm. Fenske type column, removing distillate at such a rate that the distillate temperature remained in the range 45–46°. At the end of a 5 hr. period the temperature of the residual material remaining in the distillation flask had reached 180°. At this point 14.8 g. (0.195 mole) of allyl chloride had been obtained as distillate. Redistillation of the chloride gave 14.6 g. (0.190 mole), a 95% yield of allyl chloride, b.p. 44.8–45°/741.4 mm., n_D^{25} 1.4116. Literature values,[7] b.p. 44.7–44.8/760 mm., n_D^{25} 1.4116. Distillation of the liquid residue in the distillation flask under reduced pressure afforded 39.6 g. (0.20 mole) of triethyl thionophosphate distilling at 82–83°/5 mm., n_D^{25} 1.4460, n_D^{20} 1.4481. The reported[4,6] physical constants of thionophosphate are: b.p. 45°/0.5 mm., 105–106°/20 mm., n_D^{20} 1.4480, n_D^{25} 1.4461. Thus, a quantitative yield of triethyl thionophosphate was obtained. When the original distillation residue was heated above 180° or kept at about that temperature for long periods of time, the liquid became dark colored and subsequent distillation failed to give quantitative yields of triethyl thionophosphate. A possible explanation of this is found in the work of Emmett and Jones[8] who observed that thionophosphates readily undergo thermal isomerization to phosphorothiolates.

Reaction of 2-methylthiirane with triethyl phosphite. A mixture of 14.8 g. (0.20 mole) of 2-methylthiirane and 33.2 g. (0.20 mole) of triethyl phosphite was distilled employing the experimental procedure described above except that bromine-carbon tetrachloride traps were installed to collect any propylene liberated. At the end of 3 hr. of distillation the temperature of the residue had reached 180° at which point heating was discontinued. Vacuum distillation of the liquid residue gave 39.2 g. (0.199 mole) a 99% yield of triethyl thionophosphate. Treatment of the material in the bromine-carbon tetrachloride traps, following standard procedures, afforded a 97% yield of 1,2-dibromopropane, b.p. 137°/734.6 mm, n_D^{20} 1.5193. Literature[9] values for this dibromide are: b.p. 139°–142°, n_D^{20} 1.5194.

Reaction of 2-methoxymethyl thiirane[10] *with triethyl phosphite.* Distillation of a mixture containing 20.8 g. (0.20 mole) of 2-methoxythiirane and 33.2 g. (0.20 mole) of triethyl phosphite by experimental techniques already described gave a 94% yield of methyl allyl ether, b.p. 42°/746.5 mm, n_D^{20} 1.3786. The reported[11] physical constants for allyl ether are: b.p. 42.5–43°/757 mm, n_D^{25} 1.3778–1.3803. The other product in this reaction, triethyl thionophosphate, was obtained in a 96% yield.

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(5) H. Flores-Gallard and C. B. Pollard, *J. Org. Chem.*, **12**, 831 (1947).

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(9) M. S. Kharasch, J. C. McNab, and M. C. McNab, *J. Am. Chem. Soc.*, **57**, 2463 (1935).

(10) The preparation and properties of unsymmetrically substituted thiiranes will be reported in a forthcoming publication.

(11) S. C. Irvine, J. A. Macdonald, and C. W. Soutar, *J. Chem. Soc.*, **107**, 337 (1915).

Nitration Studies. X. Reaction of Dinitrogen Tetroxide with Hydrazides and Isocyanates[1]

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In its reactions with organic compounds, dinitrogen tetroxide sometimes behaves like a pseudo halogen and sometimes like a mixed anhydride of nitrous and nitric acids. Thus it reacts with aliphatic hydrocarbons to produce nitro alkanes in much the same way that chlorine produces chloro alkanes. However it reacts with aromatic amines to produce diazonium salts in much the same way that nitrous acid does. In continuing our efforts to clarify its chemical behavior we have investigated the reaction of dinitrogen tetroxide with acid hydrazides.

Carpino[3] has recently shown that acid hydrazide hydrochlorides react with chlorine to give acid chlorides. However, much earlier Curtius[4] showed that acid hydrazides react with nitrous acid to form acid azides, then isocyanates, and finally the solvolysis or solvation products of isocyanates. We have found that ethanoyl hydrazide reacts with dinitrogen tetroxide in a 1:1 mole ratio to give methyl amine nitrate, nitrogen, carbon dioxide, and acetic acid. The methyl amine nitrate was obtained in a 56% yield; the nitrogen and carbon dioxide evolved corresponded to 100% and 40% respectively of the expected amounts. The amount of acetic acid isolated was small, about 10% of theory, and probably arose from partial hydrolysis of the hydrazide or the azide. The methyl amine nitrate was identified by comparison with an authentic synthetic sample and by conversion to sodium nitrate and to the phenyl isothiocyanate derivative of methyl amine.

Butanoyl hydrazide reacts with dinitrogen tetroxide in an approximately 1:1 mole ratio to give propyl amine nitrate in 54% yield together with nitrogen, carbon dioxide, and some butyric acid.

The above reactions are assumed to proceed according to the following equations.

$$(1)\quad RCONHNH_2 + N_2O_4 \longrightarrow RCON_3 + HNO_3 + H_2O$$

$$(2)\quad RCON_3 \longrightarrow RNCO + N_2$$

$$(3)\quad RNCO + H_2O \longrightarrow RNH_2 + CO_2$$

$$(4)\quad RNH_2 + HNO_3 \longrightarrow RNH_3NO_3$$

$$(5)\quad RCONHNH_2 + N_2O_4 \longrightarrow RNH_3NO_3 + CO_2 + N_2$$

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(1) From the M. S. thesis of W. Michalowicz, Purdue University, January 1958.

(2) Present address: Koppers Company, Inc., Pittsburgh, Pa.

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(4) T. Curtius, *J. prakt. Chem.* **50**, 285 (1894).