

gifts^{6,7} of synthetic isomers of sphingosine made it possible to settle this point in the experiments shown in Table II in which "active ceramide" is identified as N-acetyl-DL-threo-*trans*-sphingosine.

The possible biological significance of the fact that the enzymatically active form of sphingosine possesses the *threo* rather than the expected *erythro* configuration is currently being investigated.

(6) Gift of Dr. Paul O'Connell and the Upjohn Company.

(7) Gift of Prof. C. A. Grob and the Ciba Company.

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THE REACTION OF THIYL RADICALS WITH TRIALKYL PHOSPHITES¹

Sir:

Hoffmann and co-workers² recently have reported a remarkable reaction between mercaptans and trialkyl phosphites occurring at elevated tempera-



tures, or photochemically at room temperature. They make no suggestion as to reaction mechanism, but the light catalysis suggests a radical process. We find that the reaction is initiated by other free radical sources and evidently involves long radical chains. Thus, isobutyl mercaptan and a slight excess of triethyl phosphite show negligible reaction in 30 min. at 70°. In the presence of 2 mole % azobisisobutyronitrile reaction is complete in two minutes, from which we calculate a minimum chain length (from the known decomposition rate of the initiator) of 2700.

A quite analogous radical reaction between disulfides and trialkyl phosphites may be induced photochemically at 60° or by di-*t*-butyl peroxide at 120–125°, and follows the course



Equivalent quantities of isobutyl disulfide and triethyl phosphite react almost quantitatively in 3 hours at 60° on irradiation with a General Electric RS Sunlamp, the reaction being followed conveniently by gas chromatographic analysis of aliquots. The phosphorothionate was identified by fractional distillation and comparison of its infrared spectrum with an authentic sample. Similarly, equimolecular quantities of the same components show 60–70% reaction in 3 hours at 120–125° in the presence of 2 mole % of di-*t*-butyl peroxide, indicating a minimum kinetic chain of

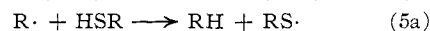
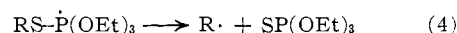
(1) Work supported by a Grant from the National Science Foundation.

(2) F. W. Hoffmann, R. J. Ess, T. C. Simmons and R. S. Hanzel, *THIS JOURNAL*, **78**, 6414 (1956).

400.³ Negligible reaction occurs at 140° in 3 hr. in the absence of peroxide, and azobisisobutyronitrile is ineffective as an initiator at 60–100°. This contrast with the mercaptan reaction suggests that chain initiation in both cases involves initiator radical attack upon the sulfur compound.

Jacobson, Harvey and Jensen⁴ have described the reaction of diethyl disulfide and triethyl phosphite on refluxing at a high temperature to give the phosphorothiolate, $\text{OP}(\text{SEt})(\text{OEt})_2$, which they consider to be an Arbuzov-type polar process. While our results do not rule out this alternative reaction, their reaction may well follow our path, since phosphorothionates readily undergo thermal isomerization to phosphorothiolates.⁵ We find that the original gas chromatographic peak of triethyl phosphorothionate almost disappears on heating for 23 hr. at 180°.

We propose these chain processes for the reactions, involving thiyl radical attack on phosphorus to yield a phosphorus radical with an expanded valence shell



(5a) and (5b) representing the usual chain transfer reactions of mercaptans and disulfides respectively. Certain limitations of the reaction are compatible with this formulation. Thus, judged by chain transfer experiments with styrene,⁶ benzyl-type radicals react only sluggishly with disulfides. Dibenzyl disulfide (0.04 mole) shows little reaction in 14 hr. on irradiation with triethyl phosphite (0.2 mole). In three weeks, at least 63% of the sulfur appears as crude phosphorothionate, while the benzyl radicals are converted to 19% toluene and 26% bibenzyl. Here there is evidently little chain reaction, but the latter products arise from benzyl radicals formed in (4).

It also is of interest that similar reaction intermediates involving an expanded valence shell of phosphorus appear to account for the products obtained in the reaction of *t*-phosphines with polyhalomethanes.⁷

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(3) Calculated from the peroxide decomposition rate in tributylamine, in which it is slightly faster than in other solvents, J. H. Raley, F. F. Rust and W. E. Vaughan, *ibid.*, **70**, 1336 (1948).

(4) H. I. Jacobson, R. G. Harvey and E. V. Jensen, *ibid.*, **77**, 6064 (1955).

(5) W. G. Emmett and H. O. Jones, *J. Chem. Soc.*, **99**, 713 (1911).

(6) R. M. Pierson, A. J. Costanza and A. H. Weinstein, *J. Polymer Sci.*, **17**, 221 (1955).

(7) F. Ramirez and N. McKelvie, *THIS JOURNAL*, in press.

(8) Columbia University Fellow, 1956–1957.