

elements of diethylamine and ring cleavage, respectively. Whether the reaction proceeds by a concerted cycloaddition or by a Michael-type addition followed by ring closure of the dipolar intermediate is open to question. Further investigations of these cycloaddition reactions will be reported at a later date.

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(9) Alfred P. Sloan Fellow

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The Phosphine Oxide Catalyzed Isomerization of Epoxides

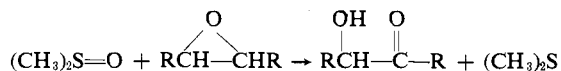
Sir:

During the course of our work on the opening of epoxides with tertiary phosphines in the presence of *m*-chlorobenzaldehyde¹ we have found that tertiary phosphine oxides catalyze the isomerization of *cis*- and *trans*-4-octene oxides to 4-octanone. We have also discovered that *trans*-stilbene oxide is similarly isomerized to a mixture of deoxybenzoin and diphenylacetaldehyde while *cis*-stilbene oxide undergoes prior or simultaneous isomerization to *trans*-stilbene oxide which is then converted to deoxybenzoin and diphenylacetaldehyde.

In a typical experiment, 0.61 g. (0.0047 mole) of *trans*-4-octene oxide, 1.03 g. (0.0047 mole) of tributylphosphine oxide, and 2.0 g. (0.0142 mole) of *m*-chlorobenzaldehyde were placed in a glass tube and the solution was thoroughly degassed with nitrogen. The tube was then sealed and heated at 160° for 10 days. Analysis (g.l.p.c.) of the reaction mixture showed that 85% of the 4-octene oxide had been isomerized to 4-octanone. Samples of the 4-octanone, collected from the analytical g.l.p.c., were identical in every respect with the authentic material. *cis*-4-Octene oxide was also isomerized under these conditions although at a somewhat slower rate. The conversion of either epoxide to ketone did not occur in the absence of *m*-chlorobenzaldehyde. This is thought to be a solvent effect because other epoxides do isomerize in the absence of this aldehyde. Triphenylphosphine oxide also catalyzes the isomerization of epoxides but the reaction is much slower. Most of our work has therefore been confined to tributylphosphine oxide.

There are at least two mechanisms which may be written for the isomerization of 4-octene oxide by phosphine oxide (eq. 1 and 2). These mechanisms differ in that the first involves hydride transfer with synchronous departure of phosphine oxide whereas the second utilizes phosphine oxide as both a nucleophile and a base and involves the intermediacy of the enolate ion.

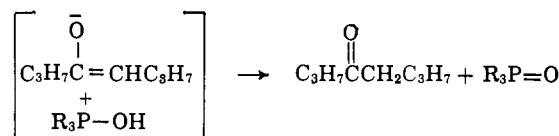
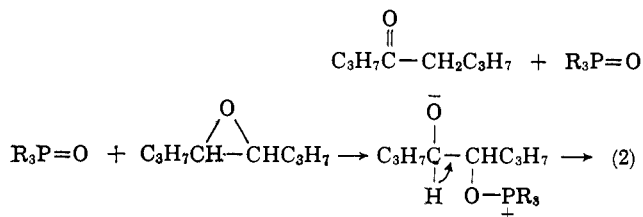
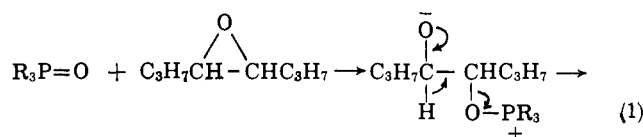
Dimethyl sulfoxide also reacts with epoxides to give α -hydroxy ketones.² The fact that the phosphine



(1) (a) A. J. Speziale and D. E. Bissing, *J. Am. Chem. Soc.*, **85**, 1888 (1963); (b) A. J. Speziale and D. E. Bissing, *ibid.*, **85**, 3878 (1963); (c) D. E. Bissing and A. J. Speziale, *ibid.*, in press.

(2) T. Cohen and T. Tsuji, *J. Org. Chem.*, **26**, 1681 (1961).

oxide reaction does not take the same course emphasizes the extreme affinity of phosphorus for oxygen. In addition, the dimethyl sulfoxide reaction requires equimolar quantities of the reactants while the phosphine oxide reaction is truly catalytic.



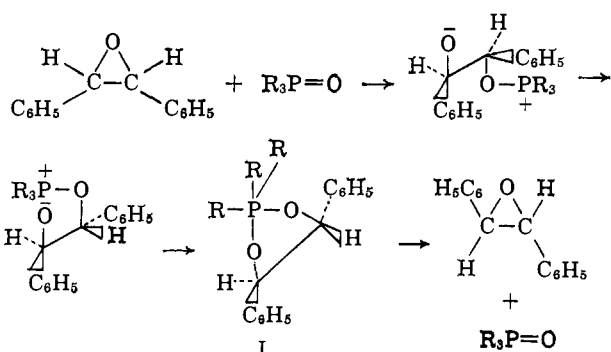
The reactions of *cis*- and *trans*-stilbene oxide with tributylphosphine oxide were also investigated. Tributylphosphine oxide and *trans*-stilbene oxide react to give deoxybenzoin and diphenylacetaldehyde in the ratio of 9:1 (by n.m.r.). Deoxybenzoin was isolated in a 67% yield while the presence of diphenylacetaldehyde was detected and confirmed only by n.m.r. Deoxybenzoin is presumably formed *via* a mechanism similar to that suggested for the formation of 4-octanone. Diphenylacetaldehyde probably arises *via* phenyl migration rather than hydride transfer. The same product ratio was also obtained in the presence of *m*-chlorobenzaldehyde. When an n.m.r. spectrum of the mixture was taken after 30% reaction, the only detectable products were deoxybenzoin and diphenylacetaldehyde in the reported ratio. On completion of the reaction the epoxide had disappeared and the ratio of the ketone to aldehyde had remained unchanged.

cis-Stilbene oxide, under the above conditions, gave the same products in exactly the same proportions. However, the n.m.r. spectrum of the partially completed reaction showed a new peak which was proved to be due to *trans*-stilbene oxide. Thus, *cis*-stilbene oxide undergoes isomerization to *trans*-stilbene oxide either prior to or concomitantly with formation of deoxybenzoin and diphenylacetaldehyde. It is not known whether the *cis*-epoxide gives ketone and aldehyde directly. Since the ratio of deoxybenzoin to diphenylacetaldehyde is independent of the stereochemistry of the starting epoxide, it is reasonable that the *cis*-epoxide is isomerized to *trans*-stilbene oxide more rapidly than to ketone and aldehyde.

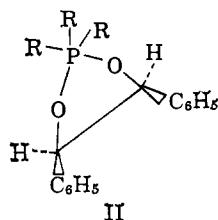
The isomerization of *cis*-stilbene oxide is interesting and quite possibly involves a reasonably stable pentacoordinate phosphorus intermediate.³

The stability of the pentacoordinate phosphorus intermediate I may be enhanced because the phenyl groups

(3) (a) F. Ramirez, S. B. Bhatia, R. B. Mitra, Z. Hamlet, and N. B. Desai, *J. Am. Chem. Soc.*, **86**, 4394 (1964); (b) F. Ramirez, R. B. Mitra, and N. B. Desai, *ibid.*, **82**, 2651 (1960); (c) F. Ramirez, A. V. Patwardhan, N. B. Desai, N. Ramanathan, and C. V. Greco, *ibid.*, **85**, 3056 (1963).



are *trans* while in the starting epoxide they are eclipsed. Conversely, the fact that *trans*-stilbene oxide is not isomerized to *cis*-stilbene oxide probably reflects the fact that the phenyl groups are eclipsed in the corresponding intermediate II.



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Hexamethylphosphoramide. An Aprotic Solvent for Active Metals

Sir:

Active metals of group I and II dissolve in liquid ammonia to yield blue solutions. Extensive investigations of the conductance,¹ e.s.r.,² n.m.r.,³ and ultraviolet absorption spectroscopy,⁴ respectively, of these solutions establish that they contain solvated electrons. Similar solutions have been prepared with other simple primary amines, diamines, and ethers, the latter being of low concentration.⁵ So far no tertiary amine or aprotic organic compound has been found to dissolve metals in the manner and concentrations obtained with liquid ammonia.

We have now found that sodium, potassium, and lithium dissolve in hexamethylphosphoramide to give blue solutions, up to 1 *M* and stable for several hours.^{6,7} The solvent peaks in the n.m.r. spectra of these solu-

tions are broadened with respect to those in the pure amide. On admission of oxygen to these solutions the blue color disappears and the solvent peaks (n.m.r.) become sharp again. The e.s.r. absorption consists of a single sharp line at $g = 2.00210$ (width 0.4 gauss),⁸ close to the value for the free electron, $g = 2.0022$.

After several hours storage at room temperature these solutions turned red and were no longer paramagnetic. The blue solutions reacted violently with water, alkyl halides, and olefins and took fire in air. On the basis of all this information and by analogy to the results for simple amines there is no doubt that the blue color comes from solvated electrons.⁹

Attempts to obtain similar solutions to those described above with tris(dimethylamino)phosphine so far have failed.

Hexamethylphosphoramide is an excellent solvent for organometallic compounds.¹⁰ We have found that both Grignard reagents and organolithium compounds form solid complexes with it. These complexes could be handled briefly in air but decomposed on standing.¹¹

Since hexamethylphosphoramide, HMPA, is a good solvent for active metals it might be expected to be a good medium for reduction reactions. Actually, both Grignard reagents and organolithium compounds may be prepared in it in good yields: (1) Simple aliphatic halides, methyl iodide, bromoethane, and 1-bromopropane were all converted with magnesium in HMPA at 80° to the corresponding Grignard reagents. (2) These latter reactions have been accomplished in 90% benzene-10% HMPA at 30°. (3) The corresponding organolithium compounds were made by adding the halides to lithium wire in HMPA at room temperature. Under all these circumstances blue color was not generated. (4) Addition of organic halides to solutions of sodium, potassium, and lithium in HMPA yielded only Wurtz coupling products. (5) Benzophenone treated with sublimed magnesium and traces of MgBr_2 in HMPA at room temperature gave both blue (monomeric) and red (dimeric) forms, respectively, of the ketyl radical ion.¹² The latter was recognized by the identity of its e.s.r. spectrum with that of benzophenone radical ion obtained by Hirota and Weissman.¹³ Approximately 10% of the benzophenone was converted to dibenzopinacol when these solutions were allowed to stand 24 hr. at room temperature.

The fact that solvated electrons have been detected in so many different basic solvents (ammonia,¹⁻⁴ aliphatic amines,¹⁻⁴ HMPA, certain polyethers,⁵ water,¹⁴

(7) The hexamethylphosphoramide was kindly donated by Tennessee Eastman Corporation, Kingston, Tenn. The material was distilled and carefully degassed before use.

(8) All e.s.r. spectra were determined with the Varian V4502 electron resonance spectrometer, at 3400 gauss and a frequency of 9.5 kMc., 100 kc. modulation. We are indebted to Dr. J. G. Calvert for letting us use this instrument.

(9) The possibility that phosphoryl radical ions $(\text{Me}_2\text{N})_3\text{PO}^\cdot$ or any other radicals exist in these solutions to any measurable extent is excluded by the absence of fine structure in the e.s.r. spectra. It is doubtful whether fast electron exchange between phosphoryl radicals and solvent molecules could be responsible for our results.

(10) V. R. Sandell and H. H. Friedman, *J. Am. Chem. Soc.*, **85**, 2328 (1963).

(11) The products of decomposition of these complexes appear to be phosphorylated derivatives of the organometallic compounds.

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(14) J. W. Boag and E. J. Hart, *Nature*, **197**, 45 (1963); E. J. Hart and J. W. Boag, *J. Am. Chem. Soc.*, **84**, 4090 (1962); L. M. Dorfman and I. A. Taub, *ibid.*, **86**, 4218 (1964).

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(5) J. L. Down, J. Lewis, B. Moore, and G. Wilkinson, *J. Chem. Soc.*, 3767 (1959); F. A. Cafasso and B. R. Sundheim, *J. Chem. Phys.*, **31**, 809 (1959); F. S. Dainton, D. M. Wiles, and H. N. Wright, *J. Chem. Soc.*, 4283 (1960).

(6) First observed by John P. Matanovich, N.S.F. Undergraduate Research Participant, Summer 1962.