

Stokes⁶ has suggested that we can use a radio-tracer method to measure salt-diffusion coefficients in the case where the ratios of isotopic concentrations are the same inside and outside the capillary. This would allow the continual monitoring apparatus with its high precision to be calibrated directly against other precise data. For instance, Harned and Hildreth's⁷ conductometric NaCl diffusion values, whose smoothed curves ought to be accurate to within ± 0.1 – 0.2% , could be used. In such a determination, we need to have a solution of the diffusion equation for the capillary conditions with a concentration-dependent D and this has been formulated recently by Mills and Blackwell.⁸ When our flow conditions have been confirmed by this new type of calibration, these investigations will be published in more detail.

(6) R. H. Stokes, private communication.

(7) H. S. Harned and C. L. Hildreth, *THIS JOURNAL*, **73**, 650 (1951).

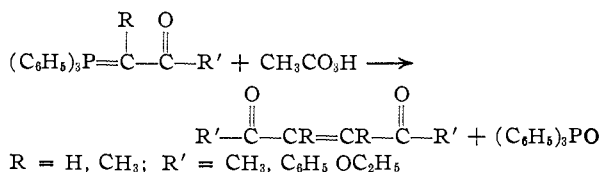
(8) R. Mills and J. W. Blackwell, in press.

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THE FORMATION OF OLEFINS FROM WEAKLY BASIC PHOSPHORANES AND PERACETIC ACID

Sir:

In recent years the reactions of phosphoranes have assumed considerable importance. In many cases they provide an easy route to otherwise difficultly obtainable substances.¹ It has now been found that weakly basic phosphoranes react with peracetic acid (40% in acetic acid) to give poor to good yields of the dimeric olefin and the phosphine oxide.



These reactions have been conducted by adding the peracetic acid (slightly more than 1 mole) to a solution of the phosphorane (1 mole) in benzene. The reactions are in general vigorously exothermic. The products have been isolated by basic extraction of the reaction mixture with subsequent removal of the solvent and extraction of the residue with hexane. The olefinic product in these cases is soluble in hexane while the triphenylphosphine oxide is not. Thus, (C₆H₅)₃P=CHCO₂C₆H₅ gave triphenylphosphine oxide (I) in 86% yield and *trans*-dibenzoyl ethylene (73%), m.p. 110–112° (lit.² 111°). The *trans*-dibenzoyl ethylene was converted to 3,6-diphenylpyridazine, m.p. 220–222° (lit.² 221–222°). Similarly, (C₆H₅)₃P=CHCOCH₃ gave I and *trans*-diacetyl ethylene (52%), m.p. 78–79.5° (lit.³ 78°), di-2,4-dinitrophenylhydrazone, m.p. 290–292° (lit.³ 291–292°). Reaction of (C₆H₅)₃P=CHCO₂C₂H₅ afforded I (96%) and diethyl fumarate (41%), b.p. 100° (block) at 10

(1) U. Schollkopf, *Angew. Chem.*, **71**, 260 (1959).

(2) C. Paal and H. Schulze, *Ber.*, **33**, 3798 (1900).

(3) K. F. Armstrong and R. Robinson, *J. Chem. Soc.*, 1650 (1934).

mm., infrared spectrum identical to that of a known sample. This material was further characterized by conversion to di-*p*-nitrobenzyl fumarate, m.p. 152–153° (lit.⁴ 151°). The phosphorane, (C₆H₅)₃P=C(CH₃)CO₂C₂H₅, gave I (89%) and diethyl dimethylfumarate, b.p. 105° at 9 mm. (lit.⁵ 111° at 12 mm.), yield 7%. Saponification yielded the acid, m.p. 247–248° (lit.⁶ 240°). The infrared spectra were in agreement with the assigned structures of all of the compounds listed above.

Treatment of phenylmethylenetriphenylphosphorane, (C₆H₅)₃P=CHC₆H₅, in ethanol with peracetic acid gave no stilbene. Triphenylphosphine oxide was formed in 66% yield. It is felt that the greater base strength of this phosphorane caused formation of the phosphonium salt which subsequently decomposed to triphenylphosphine oxide and presumably toluene. This reaction could also contribute to a lowering of the yields from the other phosphoranes.

Recently Bestmann⁷ has shown that oxygen sensitive phosphoranes can be converted to dimeric olefins and phosphine oxides by treatment with oxygen. His method and that now being reported complement each other and therefore provide routes to a wide variety of unsaturated materials. The mechanism of the peracetic acid reaction is under study as is its application to synthesis.

(4) J. A. Lyman and E. E. Reid, *THIS JOURNAL*, **39**, 708 (1917).

(5) K. v. Auwers and L. Harres, *Ber.*, **62**, 1685 (1929).

(6) C. K. Ingold, *J. Chem. Soc.*, 397 (1923).

(7) H. J. Bestmann, *Angew. Chem.*, **72**, 34 (1960).

(8) National Science Foundation Cooperative Graduate Fellow, 1959–1960.

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STEREOCHEMISTRY OF DISPLACEMENT REACTIONS AT AN ASYMMETRIC PHOSPHONIUM CATION

Sir:

Methylethylphenylbenzylphosphonium iodide (I), in which the phosphorus atom is the sole center of asymmetry, has been resolved recently.¹ Reaction of optically pure dextrorotatory I with sodium hydroxide gave optically pure levorotatory methylethylphenylphosphine oxide (II), $[\alpha]^{25}_D -22.8 \pm 1.0^\circ$ (*c*, 2.168 in water). In like manner, levorotatory I formed optically pure dextrorotatory II, $[\alpha]^{25}_D 22.4 \pm 1.0^\circ$.² A kinetic study revealed that the reaction is third order, showing a first-order dependence on the concentration of I and a second-order dependence on the concentration of sodium hydroxide.³

It now has been determined that the Wittig reaction as applied to I is both product specific and stereospecific. Treatment of 0.02 mole of dextrorotatory I with 0.025 mole of phenyllithium in ether solution, and addition of 0.024 mole of

(1) K. F. Kumli, W. E. McEwen and C. A. VanderWerf, *THIS JOURNAL*, **81**, 248 (1959).

(2) K. F. Kumli, W. E. McEwen and C. A. VanderWerf, *ibid.*, **81**, 3805 (1959).

(3) M. Zanger, C. A. VanderWerf and W. E. McEwen, *ibid.*, **81**, 3806 (1959).

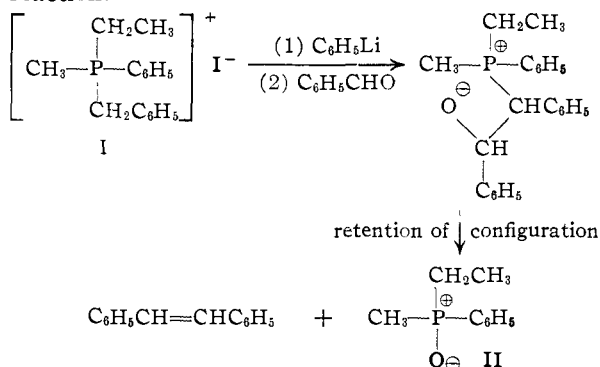
benzaldehyde to the resulting orange mixture, gave a white precipitate of an adduct of II and lithium iodide. Decomposition of the adduct by the action of sodium hydroxide solution, extraction of the phosphine oxide into benzene, and distillation of the extracted material *in vacuo*, gave a 70% yield of II, m.p. 46–50°, $[\alpha]_D^{25}$ 21.5 ± 1.0° (*c*, 2.128 in water).

Anal. Calcd. for C₉H₁₃PO: C, 64.30; H, 7.73; P, 18.46. Found: C, 64.54; H, 7.91; P, 18.22.

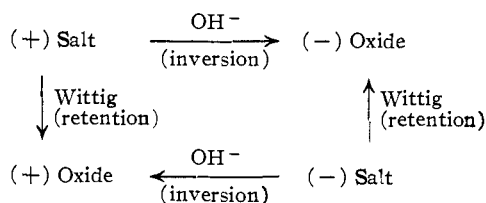
From the ether filtrate there was isolated *trans*-stilbene in 84% yield and *cis*-stilbene in 5% yield.

When levorotatory I was subjected to the Wittig reaction, there was obtained a 68% yield of II, m.p. 47–51°, $[\alpha]_D^{25}$ -21.0 ± 1.0°, an 82% yield of *trans*-stilbene and a 6% yield of *cis*-stilbene.

Since the available evidence indicates that the Wittig reaction takes place by way of a *quasi*-four-membered ring transition intermediate,⁴ it may be assumed that (+)-I and (+)-II belong to the same configurational family. This leads to the conclusion that the decomposition of the phosphonium hydroxides takes place with inversion of configuration since (+)-I gives (-)-II in this reaction.



Consistent with the stereochemical and kinetic data, it may be reasoned that a hydroxide ion can add in a reversible manner to any one of the four faces of the tetrahedral phosphonium cation. Also, the conjugate bases of any of the four trigonal bipyramidal intermediates may be formed by a reversible reaction with a second hydroxide ion. However, owing to the relatively greater stability of the benzyl anion over phenyl, methyl or ethyl anions, only the conjugate base of the pentacovalent phosphorus intermediate in which the negatively charged oxygen atom is colinear with the benzyl group and the phosphorus atom is capable of further reaction to produce II and the benzyl anion. Thus, the stereo-electronic requirements of the decomposition of methylethylphenylbenzylphosphonium hydroxide lead to inversion of configuration of the phosphorus atom.



(4) U. Schollkopf, *Angew. Chem.*, **71**, 260 (1959).

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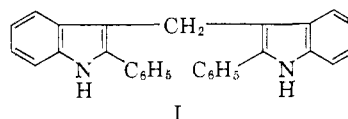
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RECEIVED MARCH 21, 1960

ON THE SYNTHESIS OF 2,2'-DIPHENYL-3,3'-DIINDOLYLMETHANE

Sir:

In a recent paper Leete¹ suggested without evidence that 2,2'-diphenyl-3,3'-diindolymethane (I), m.p. 184–185°, which was synthesized in these



laboratories² from 2-phenylindole (II) and formaldehyde, was identical with the starting material II (m.p. 187–188°). No definite conclusions about the structure can be drawn from the analytical data as the difference in the percentage composition between I and II is very small. However, these other facts will make the case clear.

(a) The melting point of an admixture of I and II is depressed considerably (150–160°).

(b) The infrared and ultraviolet spectra of I and II show beyond a doubt that the two compounds are not identical.

(c) Treatment of an indole unsubstituted in the 3-position with a 3-dialkylaminomethylindole in glacial acetic acid was found to yield 3,3'-diindolymethanes.² 2,2'-Diphenyl-3,3'-diindolymethane (I) also can be obtained in this way from 2-phenylindole and the Mannich base 3-(dimethylamino-methyl)-2-phenylindole. The product formed in this reaction is identical with I prepared from II and formaldehyde and different from II (m.p., mixed m.p. and infrared spectra).

It can be concluded, therefore, that the product with m.p. 184–185° from 2-phenylindole and formaldehyde is a new compound and not the starting material.

(1) E. Leete, *THIS JOURNAL*, **81**, 6023 (1959).

(2) R. Dahlbom and A. Misiorny, *Acta Chem. Scand.*, **9**, 1074 (1955).

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RECEIVED MARCH 8, 1960

THE SOLVOLYSIS OF *EXO* AND *ENDO*-7-ISOPROPYLIDENEDEHYDRONORBORNYL TOSYLATES

Sir:

Although the stability of homoallylic cations has been well established, the structure and bonding in these intermediates is still a matter of much