Stokes[6] has suggested that we can use a radiotracer 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's[7] conductiometric 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.

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[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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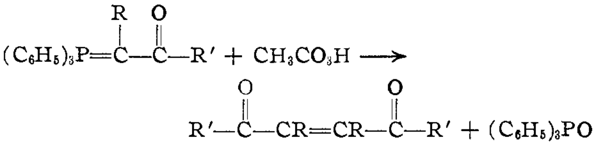
RECEIVED JANUARY 15, 1960

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.



$$(C_6H_5)_3P{=}\overset{R}{\overset{|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}R' + CH_3CO_3H \longrightarrow R'{-}\overset{O}{\overset{\|}{C}}{-}CR{=}CR{-}\overset{O}{\overset{\|}{C}}{-}R' + (C_6H_5)_3PO$$

$R = H, CH_3$; $R' = CH_3, C_6H_5\ OC_2H_5$

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, $(C_6H_5)_3P{=}CHCOC_6H_5$ gave triphenylphosphine oxide (I) in 86% yield and *trans*-dibenzoylethylene (73%), m.p. 110–112° (lit.[2] 111°). The *trans*-dibenzoylethylene was converted to 3,6-diphenylpyridazine, m.p. 220–222° (lit.[2] 221–222°). Similarly, $(C_6H_5)_3P{=}CH{-}COCH_3$ gave I and *trans*-diacetylethylene (52%), m.p. 78–79.5° (lit.[3] 78°), di-2,4-dinitrophenylhydrazone, m.p. 290–292° (lit.[3] 291–292°). Reaction of $(C_6H_5)_3P{=}CHCO_2C_2H_5$ afforded I (96%) and diethyl fumarate (41%), b.p. 100° (block) at 10 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, $(C_6H_5)_3P{=}C(CH_3){-}CO_2C_2H_5$, 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, $(C_6H_5)_3P{=}CH{-}C_6H_5$, 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 Bestmann[7] 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.

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[8] National Science Foundation Coöperative 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), $[\alpha]^{25}{}_D$ $-22.8 \pm 1.0°$ (c, 2.168 in water). In like manner, levorotatory I formed optically pure dextrorotatory II, $[\alpha]^{25}{}_D$ $22.4 \pm 1.0°$.[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

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