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The Dehydration of Alcohols to Ethers or Olefins with Triphenyl[(phenylcarbamoyl)methyl]phosphonium Inner Salt[1]

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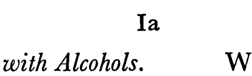
An equilibrium has been set up between benzylidenetriphenylphosphorane with alcohol and the corresponding phosphonium alkoxide, and the equilibrium mixture has been shown to undergo the Wittig reaction successfully.[2,3]

It has been reported, however, by Grayson and Keough[4] that phosphonium salts containing a benzyl group react with ethanolic sodium ethoxide (or butanolic sodium butoxide) to give toluene, ether, and tertiary phosphine oxide, and that the same products are obtained from the corresponding phosphorane and alcohol. In another report, by Speziale and Ratts,[5] dichloromethylenetriphenylphosphorane has been shown to react with *t*-butanol to afford isobutene, along with dichloromethane and phosphine oxide. In these investigations, the reactivities of other types of alcohols have not been studied.

In this paper we wish to describe the reaction of several alcohols, including a diol, and phenol with the title phosphonium inner salt.

Results and Discussion

Triphenyl[(phenylcarbamoyl)methyl]phosphonium Inner Salt (Ia). Ia could be obtained in a 80—90% yield by the treatment of triphenyl[(phenylcarbamoyl)methyl]phosphonium chloride(VIII) with sodium hydride in benzene containing a small amount of dimethyl sulfoxide. Although Trippett and Walker[6] postulated the ylide form of Ia as the intermediate in the reaction of methylenetriphenylphosphorane with two molecules of phenyl isocyanate, the IR and the NMR spectrum of Ia exhibit no N-H peak; therefore, Ia exists in the inner salt form, that is, the betaine form, in which the negative charge can be more delocalized by resonance than in the ylide form:



$$\mathrm{Ph_3\overset{\oplus}{P}\text{-}CH_2\overset{\overset{O^{\ominus}}{|}}{C}\text{-}\ddot{N}\text{-}Ph}$$

Ia

Reaction of Ia with Alcohols. When Ia was allowed to react with alcohol in benzene or excess alcohol under refluxing in a slow stream of nitrogen, an ether and/or an olefin were observed as the volatile products. All the olefins except cyclohexene were allowed to be absorbed in a bromine-dichloromethane solution, and were determined as dibromides. The diethyl ether and cyclohexene were condensed in a cold trap, and the

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[1] Partly presented at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1970.

[2] G. Wittig and W. Haag, *Chem. Ber.*, **88**, 1654 (1955).

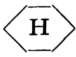
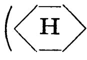
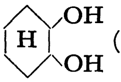
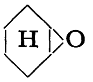
[3] For a review about the Wittig Reaction, see S. Trippett, "Advances in Organic Chemistry, Methods and Results," Vol. 1, ed. by R. A. Raphael, E. C. Taylor, and H. Wynberg, Interscience Publishers, Inc., New York, 1960, pp. 83—102.

[4] M. Grayson and K. W. Keough, *J. Amer. Chem. Soc.*, **82**, 3919 (1960).

[5] A. J. Speziale and K. W. Ratts, *ibid.*, **84**, 854 (1962).

[6] S. Trippett and D. M. Walker, *J. Chem. Soc.*, **1959**, 3874.

Table 1. The ethers and the olefins obtained by the reaction of alcohols with triphenyl[(phenylcarbamoyl)methyl]phosphonium inner salt (Ia)

Alcohol (m*l*)	mmol of Ia	Reflux time (hr)	Ether (Yield, %)	Olefin (Yield, %)
EtOH (50)	20	1	Et_2O (16)	Ethylene (trace)
EtOH (50)	20	3	Et_2O (54)	Ethylene (trace)
n-BuOH (20)	5	1	Bu_2O (60)	1-Butene (trace)
Iso-PrOH (20)	5	3	$(Iso\text{-}Pr)_2O$ (0)	Propene (9)
t-BuOH (20)	5	3	*t*-Bu_2O (0)	Isobutene (0.4)
-OH (20)	5	3	 O (0)	Cyclohexene (13)
-OH (10) + EtOH (10)	5	3	Et_2O (18) + Et-O- (0)	Ethylene (trace) + Cyclohexene (1)
Allyl-OH (20)	5	1	$(Allyl)_2O$ (57)	
n-BuOH (20)	5	a)	Bu_2O (3)	1-Butene (—)
Allyl-OH (20)	5	a)	$(Allyl)_2O$ (11)	
n-BuOHb)	5	3	Bu_2O (2)	1-Butene (0)
$PhCH_2OH$b)	5	3	$(PhCH_2)_2O$ (29)	
 (*trans*)b)	5	3	 (9)	
PhOHb) + MeOH (1)	5	1+1	PhOMe (22)	

a) The temperature of the mixture was maintained at 20°C for 24 hr.
b) A portion of 20 mmol of alcohol in 20 m*l* of benzene was used.

Table 2. The reaction of triphenyl[(phenylcarbamoyl)methyl]phosphonium chloride (VIII) with sodium alkoxide in alcohola)

Alcohol (m*l*)	mmol of VIII	Reflux time (hr)	Ether (Yield, %)	Olefin (Yield, %)
EtOH (50)	20	1	Et_2O (29)	Ethylene (trace)
EtOH (50)	20	3	Et_2O (73)	Ethylene (trace)
Iso-PrOH (20)	5	3	$(Iso\text{-}Pr)_2O$ (0)	Propene (13)
n-BuOH (20)	5	1	Bu_2O (74)	1-Butene (trace)
n-BuOH (20)	5	3	Bu_2O (82)	1-Butene (trace)
t-BuOH (20)	5	3	*t*-Bu_2O (0)	Isobutene (0.4)

a) The amount of sodium alkoxide was 10 percent excess to VIII.

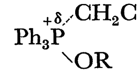
other ethers were detected directly from the reaction mixtures by means of GLC.

Acetanilide (VIa) and triphenylphosphine oxide (VII) were also obtained; for example, the yields of VIa and VII in the reaction of ethanol for 3 hr were 77 and 74% respectively.

The treatment of Ia with phenol in refluxing benzene gave acetanilide; no volatile products were observed in this case. When methanol was added to the above reaction mixture (Ia+phenol), anisole was obtained. The alcohols, the ethers, and the olefins obtained are summarized in Table 1. The reaction of alcohols with Ia can be illustrated as follows:

The final step of this reaction may be analogous to the second step of the Michaelis-Arbusov reaction. On account of the steric hindrance, the secondary and tertiary alcohols are less reactive and gave olefins exclusively in poor yields. The primary alcohols afforded ethers in fairly good yields, and those containing an eliminatable hydrogen atom in the β-position generated olefins as a by-product, whereas no ethylenic product was obtained in the reaction of ethanol or butanol with benzylidenetriphenylphosphorane.4) The high reactivity of allyl and benzyl alcohol is reasonable and parallel with the observation in the reaction of monobromocyanoacetamide and triethyl phosphite with these alcohols.7)

Reaction of Phosphonium Chlorides with Alcoholic Sodium Alkoxides. Table 2 shows the yields of ethers and olefins in the reactions of the corresponding phosphonium chloride (VIII) with sodium alkoxide in alcohol. The yields of ethers are higher in the reactions of VIII than in those of Ia, probably because of the relative stability of Ia in alcohol. Table 3 shows the results of the reactions of the related phosphonium salts with butanolic sodium butoxide. In Scheme 1, the driving force for the collapse of III to IV is attributed to a weakening of the P–C bond, because the negative



$$Ph_3\overset{+\delta}{P}\begin{array}{l}\diagup \overset{-\delta}{C}H_2CONHR'\\ \diagdown OR\end{array}$$

charge of the leaving group can be delocalized. Therefore, if the R′ of the leaving group is electron-attractive, III can probably alter to IV with ease.8) On the other hand, the electron-attractive ability of R′ may facili-

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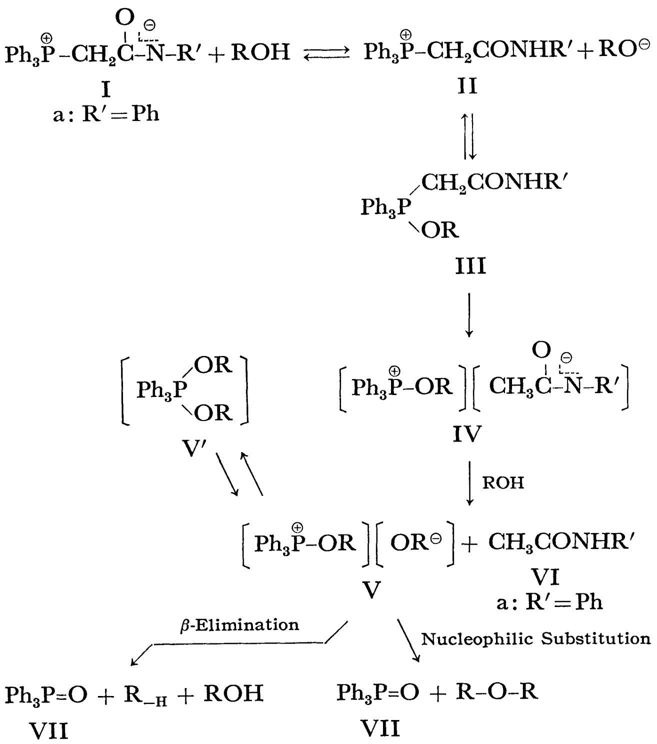
7) T. Mukaiyama, O. Mitsunobu, and T. Obata, *J. Org. Chem.*, **30**, 101 (1965).

8) Grayson and Keough4) observed the decreased reactivity of the unsubstituted benzyltriphenylphosphonium chloride compared to the *p*-nitro homolog and the inertness of the butyltriphenylphosphonium salt in the ether-formation reaction.



Scheme 1

TABLE 3. THE REACTION OF PHOSPHONIUM CHLORIDE, $Ph_3^{\oplus}CH_2CONHR'$ $Cl^{\ominus}$ WITH SODIUM BUTOXIDE IN *n*-BUTANOL[a)]

-R′	Yield of Bu_2O (%)
-Ph	74
$-C_6H_4$-Me(-*p*)	47
$-C_6H_4$-OMe(-*p*)	35
$-C_6H_4$-Cl(-*p*)	62
$-CH_2Ph$	58
-H	46

a) A portion of 5 mmol of the phosphonium chloride was allowed to react with 5.5 mmol of sodium butoxide in 20 m*l* of refluxing butanol for 1 hr.

tate the abstraction of the amido proton by a base and may also cause the stabilization of I. In view of these opposite effects, it may be difficult to obtain an unequivocal relationship between the nature of the *N*-substituents of the phosphonium chlorides and their reactivity in this reaction.

Experimental[9)]

Triphenyl[(phenylcarbamoyl)methyl]phosphonium Inner Salt (Ia). A mixture of 12.9 g (0.03 mol) of triphenyl (phenylcarbamoyl)-methyl phosphonium chloride(VIII) and 80 m*l* of dry benzene was refluxed under a nitrogen atmosphere for 2 hr with 1.1 g (0.033 mol) of dispersed sodium hydride in mineral oil (72%) and 2 g of dimethyl sulfoxide. The reaction mixture was then cooled, and a small amount of precipitates was removed by decantation. Crystallization was then induced by scratching the flask containing the solution. After standing for 2 hr, the resulting crystalline precipitate was filtered, washed with two 10-m*l* portions of benzene, and dried *in vacuo*. The yield of Ia was 10.4 g (87%). The recrystallization of Ia from benzene gave pale yellow needles; mp 122—125°C.

Found: C, 79.11; H, 5.67; N, 3.13%; mol wt (MS), 395 Calcd for $C_{26}H_{22}NOP$: C, 78.97; H, 5.61; N, 3.54%; mol wt 395.5.

The treatment of Ia with gaseous hydrogen chloride in benzene afforded the starting quaternary phosphonium salt quantitatively.

Reaction of Ia with Ethanol.[10)] A mixture of 7.91 g (0.02 mol) of Ia and 50 m*l* of absolute ethanol was refluxed for 3 hr in a slow stream of nitrogen. In a cold trap (−70°C) connected to the reaction flask through a condenser, was condensed diethyl ether (54%), which was determined by means of GLC using a 2.25-meter polyethylene glycol-6000 column at 50°C. The reaction mixture was cooled, concentrated, and then chromatographed on 40 g of 100-mesh silica gel (2.2×30 cm; benzene-ether, and benzene-ethanol) to give 2.08 g (77%) of acetanilide(VIa, mp 114—115°C) 4.11 g (74%) of triphenylphosphine oxide(VII, mp 156—157°C). VIa (82%) could be detected also directly from the reaction mixture by means of GLC using a 2.25-meter silicone grease DC-550 column at 200°C.

Reaction of Triphenyl[(phenylcarbamoyl)methyl]phosphonium Chloride (VIII) and Related Compounds with Alcoholic Sodium Alkoxide. Phosphonium Chlorides. These compounds were prepared from triphenylphosphine (0.2 mol) and the corresponding halides (0.2 mol) by a modification of the procedure of Fuerst and his associates[11)] by treatment in refluxing ethanol (50—70 m*l*) for 3—4 hr. Yields: 80—90% (except one example). Triphenyl[(benzylcarbamoyl)methyl]phosphonium chloride: colorless prisms; mp 230—233°C; yield, 80%.

Found: C, 72.38; H, 5.78; N, 3.08%. Calcd for $C_{27}H_{25}NOP$: C, 72.74; H, 5.65; N, 3.14%. Triphenyl[(*p*-nitrophenylcarbamoyl)methyl]phosphonium chloride: pale yellow prisms; mp 212—213°C;[12)] yield, 24%. (Found: C, 65.38; H, 4.77; N, 5.79%).

Reaction of VIII with Sodium Butoxide in Butanol.[13)] A mixture of 2.16 g (0.005 mol) of VIII and 20 m*l* of *n*-butanol containing 0.0055 mol of sodium butoxide was refluxed for 1 hr in a stream of nitrogen. The 1-butene thus generated was allowed to be absorbed in a bromine—dichloromethane solution in a trap connected to the reaction flask through a condenser. The reaction mixture was cooled, and then dibutyl ether (74%) in butanol was detected by means of GLC using a 2.25-meter silicone grease DC-550 column at 80°C.

[9)] Melting points are uncorrected. The yields of the products are shown in mole percentage. For the micro-analysis, a Perkin-Elmer Elemental Analyzer Model 240, and a Shimadzu Gas Chromatograph Model GC-2C for the GLC determination were employed.

[10)] The reactions of Ia with alcohols were represented by this example.

[11)] H. Fuerst, G. Wetzke, W. Berger, and W. Schubert, *J. Prakt. Chem.*, **17**, 299 (1962).

[12)] Fuerst *et al.*[11)] reported the melting point of this compound to be 79°C.

[13)] The reactions of the phosphonium chlorides with alcoholic sodium alkoxides were represented by this example.