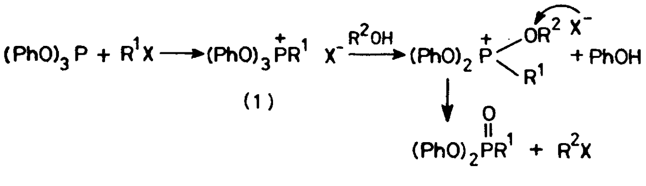
Methyltriphenoxyphosphonium Trifluoromethanesulphonate: A New, Versatile Synthetic Reagent

By EDWARD S. LEWIS,* BRIAN J. WALKER,*† and LUCY M. ZIURYS
(*Department of Chemistry, Rice University, Houston, Texas* 77001)

Summary Methyltriphenoxyphosphonium trifluoromethanesulphonate is used to synthesise a variety of compound types including ethers, esters, nitriles, and diols and in a novel reduction of alkenes to alkanes.

THE generation of Arbusov-type intermediates and their use in synthesis has been the subject of intense recent interest.[1,2] Although these reagents have been used to carry out a wide range of interconversions, the reactions are often very complex and side reactions can reduce yields.[1] Here we report preliminary results with a reagent which is easily prepared, relatively stable, and convenient to handle and undergoes Arbusov-type reactions rapidly, cleanly, and in high yield at room temperature.



SCHEME 1

Rydon reagents (**1**; Scheme 1)[3] have potential as general synthetic reagents, but apart from a single publication[4] their use has been restricted to alkyl halide synthesis owing to the presence of a nucleophilic counter-ion.

Attempts to synthesise the tosylate [**1**; R^1 = Me, X = Ts (Ts = MeC$_6$H$_4$SO$_3$-*p*)], where the counter-ion is of low nucleophilicity, from triphenyl phosphite and methyl tosylate, gave only diphenyl methylphosphonate and phenyl tosylate, presumably *via* the Arbusov-type intermediate (**2**). However the corresponding triflate (trifluoromethanesulphonate) (**1**; R^1 = Me, X = CF$_3$SO$_3$), where the counter-ion nucleophilicity is further reduced, was synthesised in excellent yield from the phosphite and methyl triflate.[5]

The reagent (**1**; R^1 = Me, X = CF$_3$SO$_3$) reacted with methanol, ethanol, and isopropyl alcohol at room temperature to give a high (>90%) yield (g.l.c. on Carbowax 400 at 40 °C) of the corresponding ether, presumably *via* (**3**) (Scheme 2). ^{31}P N.m.r. spectroscopy provided a convenient method of following the course of this reaction; the addition of ethanol (20% v/v) to a solution of (**1**; R^1 = Me, X = CF$_3$SO$_3$) in CDCl$_3$ caused the original proton-decoupled phosphonium resonance at 43·0 p.p.m. to diminish rapidly over 6—8 min, while new resonances appeared at

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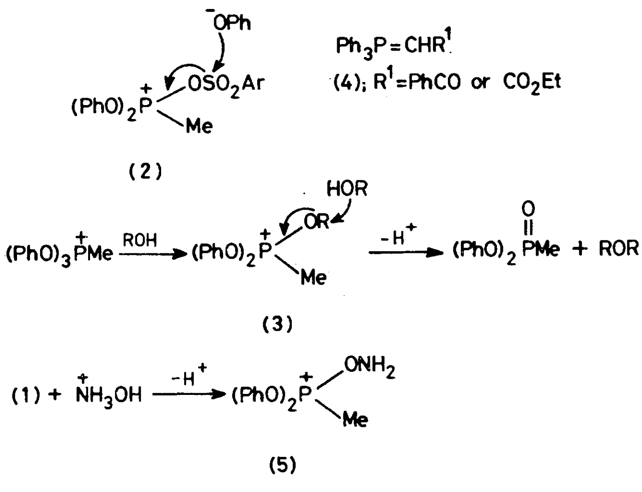
† Present address: Department of Chemistry, David Keir Building, Queen's University of Belfast, Belfast BT9 5AG, N. Ireland.



Scheme 2

40·8 p.p.m. [EtOP$^+$Me(OPh)$_2$] and, more slowly, at 24·5 p.p.m. [(PhO)$_2$P(O)Me].[6] Only trace amounts of the alternative phenyl alkyl ether were observed in these reactions. However, when the salt (**1**; R^1 = Me, X = CF$_3$SO$_3$) was treated with sodium ethoxide in ethanol at room temperature, phenetole (58%) was the major product; phenoxide competes effectively with ethanol as a nucleophile whereas phenol does not. Tertiary alcohols gave high yields (>80%; g.l.c. on Carbowax 400 at 35 °C) of alkene. The rate of the ether-forming reaction is such that other nucleophiles can successfully compete, *e.g.* CN$^-$, NCS$^-$, and I$^-$ give good yields (50—80%)‡ of nitriles, isothiocyanates, and iodides even in alcoholic solution[7] and an alcoholic suspension of sodium acetate gave the corresponding ester in high yield together with some ether.

The results from reactions with carbon nucleophiles were generally disappointing; stabilised phosphorus ylides (**4**) did not react under a variety of conditions and only moderate yields (50%)‡ of alkylation products were obtained from ethyl sodioacetoacetate.[8] However, the ratio of *O*- to *C*-alkylation (4 : 1) in the latter reaction is amongst the highest reported.[9]

Alkylamines and alkoxyamines were not detected (g.l.c. on Carbowax 400 at 20 °C) in reactions of the salt (**1**; R^1 = Me, X = CF$_3$SO$_3$) with alcoholic solutions of ammonia and hydroxylamine, respectively, and since the yields of ether in these reactions were low (< 5%), initial attack at phosphorus by nitrogen, rather than by oxygen, seems likely. However, stirring a suspension of hydroxylamine hydrochloride with the salt (**1**; R^1 = Me, X = CF$_3$SO$_3$) in acetonitrile overnight, followed by the addition of cyclohexene and sodium hydroxide gave cyclohexane (20%; g.l.c. on Carbowax 400 at 40 °C). A di-imide intermediate[10] seems likely, presumably formed by the reaction of hydroxylamine (now protonated at nitrogen) through oxygen to give (**5**), which in the presence of base undergoes substitution and elimination. A similar reaction with hydrazine hydrate also gave cyclohexane, albeit in lower yield (6%), and this is remarkable in that Arbusov-type reactions to give imino-phosphoranes are rare.

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‡ None of the yields quoted have been optimised.

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[6] M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, '^{31}P Nuclear Magnetic Resonance,' Interscience, New York, 1967, p. 294, give for diphenyl methylphosphonate δ = (—) 22·0 and 23·5 p.p.m. in an unspecified solvent.

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