

Water as an Effective Precursor of Electrogenerated Base. Facile Alkylation of Dialkyl Phosphonates

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A small amount of water has been shown to be a precursor of an effective electrogenerated base *via* the formation of hydroxide ion, as revealed in the electroreductive alkylation of dialkyl phosphonates with alkyl halides.

Electrogenerated bases (EGBs) are of current interest in electro-organic synthesis.¹ A number of base-induced reactions have been accomplished by the electroreduction of azobenzenes,² alkenes,³ pyrrolidin-2-one,⁴ and a hindered phenol.⁵

Our attempts to alkylate dialkyl phosphonates (**1**) electrochemically led us to find the unprecedented effect of water as a new source of EGB. The alkylation of (**1**) with alkyl halides is usually carried out using sodium alkoxide or sodium (the Michaelis–Becker reaction).⁶ Here, we report that the simple, *i.e.*, without addition of any strong base, electroreduction of a wet solution of (**1**) and primary alkyl halides (**2**) results in an

efficient alkylation to give alkane phosphonic esters (**3**) (equation 1).

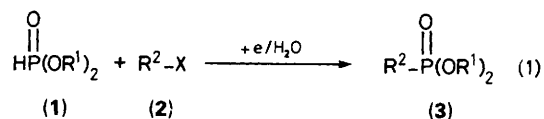
The electroreductive alkylation of (**1**) shows an exclusive *P*-alkylation as in the Michaelis–Becker reaction. Although (**1**) yields an ambidentate anion,[†] no trialkyl phosphate as the *O*-alkylation product was detected. The electrolytic procedure was as follows. An equimolar solution of (**1**) and alkyl halide (**2**) (2 mmol) in dimethylformamide (DMF, 25 ml) containing tetrabutylammonium bromide (4 mmol), as an electrolyte, and water (4 mmol) was electrolysed cathodically with 0.1 A of constant current in a divided cell equipped with platinum sheet electrodes (1 × 3 dm²). After usual work-up and purification, alkane phosphonic ester (**3**) was obtained as a colourless liquid (Table 1). The reaction was completed by passing 1.0–1.2 F mol⁻¹ (*ca.* 0.6 h) in polar aprotic solvents and the yields of (**3**) were good with alkyl iodides and benzyl halides.

The electroreductive alkylation of (**1**) also took place in dry DMF, but two equivalents of alkyl iodides and *ca.* 2 F mol⁻¹ of electricity were required. The most appropriate amount of water was 0.1–0.5 M in DMF. The reported p*K*_a value of H₂O

Table 1. Electroreductive alkylation of (**1**) in the presence of water.^a

R ¹ in (1)	(2)	Yield of (3) ^b /%
Me	Bu-I	53
	C ₈ H ₁₇ -I	62
Et	Bu-I	74
	Bu-Br	49
	PhCH ₂ -Br	60
Pri	PhCH ₂ -Cl	55
	Bu-I	75
Bu	Bu-I	76
	C ₈ H ₁₇ -I	66

^a Two equiv. of water was added to an equimolar solution of (**1**) and (**2**) in DMF. See text for conditions. ^b Yields were determined by GLC and based on (**1**).



[†] Since (**1**) can undergo the tautomerism $\text{HP}(\text{O})(\text{OR})_2 \rightleftharpoons \text{HOP}(\text{OR})_2$, the resulting anion of (**1**) is ambidentate.

is 35 in DMF and 31 in dimethyl sulphoxide (DMSO),⁸ whereas that of (1) with R' = Et is 21 in DMSO.⁹ Thus, OH⁻ ion, once formed, is basic enough to deprotonate (1). The use of a small amount of water under electroreductive conditions will provide a practically useful EGB.

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