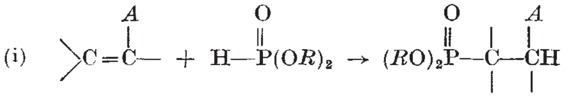
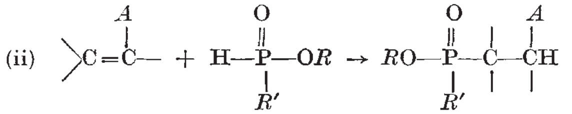
Formation of C—P Bonds by Addition of Di-Alkyl Hydrogen Phosphonates and Alkyl Hydrogen Phosphinates to Activated Ethylenic Derivatives

In the course of a study in these laboratories of new methods for the formation of C—P bonds, the possibility was considered of addition of organic phosphorus compounds of the $>\underset{\underset{\textstyle O}{\|}}{P}—H$ type to activated ethylenic derivatives. This would offer a new approach to a synthesis of various organic oxyacids of phosphorus. Recently, we have been able to show that the reaction is promoted by basic catalysts, sodium derivatives of hydrogen phosphonates and hydrogen phosphinates being the most effective.

Thus, ethylenic derivatives of the α,β double-bond type $>C{=}\overset{|}{C}—A$, in which A is $>CO$, $—COOR$, $—CN$, add dialkyl hydrogen phosphonates (i) and alkyl hydrogen phosphinates (ii) in exothermic reaction :



$$\text{(i)}\quad >C{=}\overset{\textstyle A}{\overset{|}{C}}— \;+\; H—\overset{\textstyle O}{\overset{\|}{P}}(OR)_2 \rightarrow (RO)_2\overset{\textstyle O}{\overset{\|}{P}}—\underset{|}{\overset{|}{C}}—\underset{|}{\overset{\textstyle A}{\overset{|}{C}}}H$$



$$\text{(ii)}\quad >C{=}\overset{\textstyle A}{\overset{|}{C}}— \;+\; H—\underset{\underset{\textstyle R'}{|}}{\overset{\textstyle O}{\overset{\|}{P}}}—OR \rightarrow RO—\underset{\underset{\textstyle R'}{|}}{\overset{\textstyle O}{\overset{\|}{P}}}—\underset{|}{\overset{|}{C}}—\underset{|}{\overset{\textstyle A}{\overset{|}{C}}}H$$

Addition takes place in a sense opposed to Markownikow's rule, resembling the Michael type of reaction. The temperature of the reaction was kept by external cooling below 25° and often as low as 10°.

Addition products forming colourless viscous high-boiling liquids were isolated in good yield and then hydrolysed to give the corresponding crystalline phosphonic and phosphinic acids.

Most of the products obtained have not hitherto been described in the chemical literature and their proposed structures will be further investigated. As an example of the application of this novel method the following reactions can be reported.

Vinyl cyanide (I) adds dibutylhydrogenphosphonate, $(n\text{-}BuO)_2PO.H$ (II), dibutyl-β-cyanoethylphosphonate, $(n\text{-}BuO)_2PO.CH_2CH_2CN$ (III), being formed in 84 per cent yield (b.p. 143–144°/0·8 mm. mercury ; found : C, 53·2 ; H, 9·1 ; N, 5·7 ; P, 12·8 ; $C_{11}H_{22}O_3NP$ requires : C, 53·4 ; H, 9·0 ; N, 5·7 ; P, 12·5 per cent). Hydrolysis of (III) by concentrated hydrochloric acid gave β-phosphonopropionic acid, $(HO)_2PO.CH_2CH_2COOH$ (IV), with 87 per cent yield (colourless plates from water ; m.p. 167–168° ; found : P, 20·1 ; calc. for $C_3H_7O_5P$: P, 20·1 per cent). (IV) was recognized as β-phosphonopropionic acid, described by Arbusov and Dunin (ref. 1).

(I) and diethylhydrogenphosphonate, $(EtO)_2PO.H$, gave diethyl-β-cyanoethylphosphonate $(EtO)_2PO.CH_2CH_2CN$ (V) with 73 per cent yield (b.p. 127–128°/1·5 mm. mercury ; found : P, 16·0 ; $C_7H_{14}O_3NP$ requires : P, 16·2 per cent). Hydrolysis of (V) gave (IV) (identified by mixed melting point with an authentic specimen).

(I) and monobutylphenylhydrogenphosphinate $(n\text{-}BuO)C_6H_5PO.H$ (VI) gave monobutylphenyl-β-cyanoethylphosphinate $(n\text{-}BuO)C_6H_5PO.CH_2CH_2CN$ (VII) in 70 per cent yield (b.p. 110–113°/0·01 mm. mercury ; found : C, 61·8 ; H, 7·4 ; N, 5·6 ; P, 12·3 ; $C_{13}H_{18}O_2NP$ requires : C, 62·1 ; H, 7·2 ; N, 5·6 ; P, 12·3 per cent). Hydrolysis of (VII) gave β-phenylphosphinopropionic acid, $HOC_6H_5PO.CH_2CH_2COOH$ (VIII), in 88 per cent yield (colourless needles from water, m.p. 159–160° ; found : C, 50·5 ; H, 5·4 ; P, 14·6 ; $C_9H_{11}O_4P$ requires : C, 50·5 ; H, 5·2 ; P, 14·5 per cent).

Ethyl crotonate and (II) gave ethyl dibutylphosphono-β-butyrate, $(n\text{-}BuO)_2PO.CHMeCH_2COOEt$ (IX), in 82 per cent yield (b.p., 83–84°/0·02 mm. mercury ; found : C, 54·3 ; H, 9·6 ; P, 10·0 ; $C_{14}H_{29}O_5P$ requires : C, 54·5 ; H, 9·5 ; P, 10·05 per cent). Hydrolysis of (IX) gave β-phosphonobutyric acid, $(HO)_2PO.CHMeCH_2COOH$, with 85 per cent yield (colourless micro-needles from acetic acid ; m.p. 149–150° ; found : C, 28·7 ; H, 5·6 ; P, 18·4 ; $C_4H_9O_5P$ requires : C, 28·6 ; H, 5·4 ; P, 18·4 per cent).

Methyl acrylate (X) adds (II) ; the crude product was hydrolysed as above, yielding (IV), identified by mixed melting point.

(X) and (VI) gave methyl-β-monobutylphenylphosphinopropionate, $n\text{-}BuOC_6H_5PO.CH_2CH_2COOMe$ (XI), with 75 per cent yield (b.p., 108°/0·02 mm. mercury ; found : C, 58·9 ; H, 7·6 ; P, 10·8 ; $C_{14}H_{21}O_4P$ requires : C, 59·1 ; H, 7·45 ; P, 10·9 per cent). Hydrolysis of (XI) gave (VIII), identical with the specimen obtained by hydrolysis of (VII).

Ethyl cinnamate and (II) gave ethyl β-dibutylphosphono-β-phenylpropionate, $(n\text{-}BuO)_2PO.CHPhCH_2COOEt$ (XII), with 40 per cent yield (b.p. 123°/0·02 mm. mercury ; found : C, 61·3 ; H, 8·7 ; P, 8·2 ; $C_{19}H_{31}O_5P$ requires : C, 61·7 ; H, 8·4 ; P, 8·3 per cent). Hydrolysis of (XII) gave β-phosphono-β-phenylpropionic acid, $(HO)_2PO.CHPhCH_2COOH$, in very good yield (colourless needles from acetic acid ; m.p. 200–202° ; found : C, 46·6 ; H, 4·9 ; P, 13·2 ; $C_9H_{11}O_5P$ requires : C, 47·0 ; H, 4·8 ; P, 13·5 per cent).

Benzylidenacetone and (II) gave 1-phenyl-1-dibutylphosphono-butan-3-on, $(n\text{-}BuO)_2PO.CHPhCH_2.CO.CH_3$, with 68 per cent yield (b.p., 117°/0·02 mm. mercury ; found : C, 63·3 ; H, 8·7 ; P, 8·9 ; $C_{18}H_{29}O_4P$ requires : C, 63·5 ; H, 8·6 ; P, 9·1 per cent).

A full account of this investigation will be published elsewhere. We are indebted to Prof. O. Achmatowicz for his interest and for discussions. One of us (J. M.) desires to thank the Science Support Committee of the Ministers' Council of the Polish Government for a fellowship which enabled him to take part in the research.

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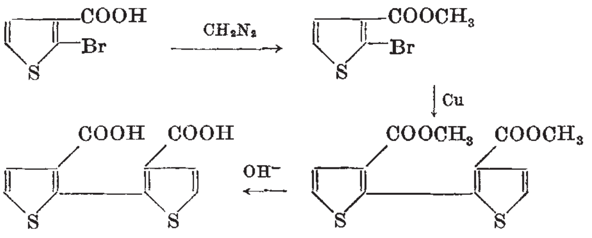
[1] Arbusov, A. E., and Dunin, A. A., *Ber.*, **60**, 291 (1927).

Symmetrical Bi-Aromatics

Recorded instances of the preparation of symmetrically substituted bithienyls appear only scattered in the literature[1]. Furthermore, no work has been published concerning the symmetrically substituted 3,3′-bithienyls.

In the course of studies on the chemistry of heterocyclics[2], initiated in this Department, it became necessary to focus our attention on the preparation of 3,3′-dithenic acid, *via* the readily available 2-halo-3-thenoic acids[3].



2-Bromo-3-thenoic acid was esterified with diazomethane, employing nitrosomethylurea as the source of the diazomethane. Evaporation of the ethereal solution and subsequent fractionation afforded methyl 2-bromo-3-thenoate (b.p. 114–115°/4 mm. ; calc. for $C_6H_5O_2SBr$: C, 32·59 ; H, 2·28 ; found : C, 32·85 ; H, 2·45).

This ester was heated and afterwards treated, *in* the usual manner, with excess Baker's precipitated copper. Upon cooling, the solid mass was extracted with ether and filtered. Evaporation of the ethereal solution left methyl 3,3′-dithenate as a residue, which crystallized from ethyl alcohol in yellow plates (yield, 24 per cent ; m.p. 145–147° (all melting points were obtained with the Fisher–John apparatus) ; calc. for $C_{12}H_{10}O_4S_2$: C, 51·05 ; H, 3·57 ; found : C, 50·72 ; H, 3·49).