On Olefin Synthesis with Phosphonate Carbanions

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A number of methods to the synthesis of olefins by using organo-phosphorus compounds have been reported.

Wittig⁽¹⁾ has described the conversion of a carbonyl compound into an olefin in which the oxygen atom of the carbonyl group was replaced with an alkylidene group by the reaction of an alkylidene triphenylphosphorane.

Horner and Hoffmann⁽²⁾ have reported the preparation of olefins from phosphine oxides and aldehydes by refluxing the mixture in toluene for about ten hours in the presence of potassium *tert*-butoxide.

Also, Wadsworth⁽³⁾ has recently reported the preparation of olefins by the reaction of phosphonate carbanions which had been prepared by the addition of the phosphonate to a slurry of sodium hydride in 1,2-dimethoxyethane at room temperature with carbonyl compounds.

In this paper, a method of preparing phosphonate carbanions by the action of sodium amide with phosphonates and the reaction of aldehydes and ketones with the carbanions derived from diethyl carbethoxymethylphosphonate, diethyl cyanomethylphosphonate, diethyl formylmethylphosphonate diethylacetal and diethyl acetonylphosphonate are described.

Diethyl carbethoxymethylphosphonate carbanion was prepared by the reaction of diethyl carbethoxymethylphosphonate with sodium amide as a proton-accepter in tetrahydrofuran or in ether as an aprotic solvent at room temperature; it was treated with such aldehydes as *n*-butylaldehyde, crotonaldehyde, benzaldehyde and cinnamaldehyde, or with such ketones as acetone, acetophenone, benzophenone and cyclohexanone.

The reaction proceeded smoothly under mild conditions with a variety of aldehydes and ketones, resulting in α,β-unsaturated esters in fairly good yields.

The reaction can be formulated by the following scheme; the results are summarized in the Table.

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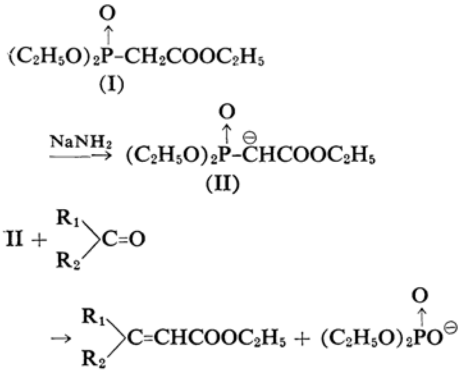
1) U. Schöllkopf, *Angew. Chem.*, **71**, 260 (1959).

2) L. Horner and H. Hoffmann, *Chem. Ber.*, **92**, 2499 (1959).

3) W. S. Wadsworth, *J. Am. Chem. Soc.*, **83**, 1733 (1961).

TABLE

R_1	R_2	Yield %	III Formula	B. p. °C/mmHg
H	$CH_3CH_2CH_2$	67	$C_8H_{14}O_2$	65/12
H	$CH_3CH=CH$	47	$C_8H_{12}O_2$	79∼79.5/13
H	C_6H_5	82	$C_{11}H_{12}O_2$	135∼136/13
H	$C_6H_5CH=CH$	72	$C_{13}H_{14}O_2$	135∼136/3
CH_3	CH_3	61	$C_7H_{12}O_2$	72∼73/49
CH_3	C_6H_5	77	$C_{12}H_{14}O_2$	132∼134/11
C_6H_5	C_6H_5	87	$C_{17}H_{16}O_2$	180∼181/760
$CH_2(CH_2)_4CO$		76	$C_{10}H_{16}O_2$	98∼99/11



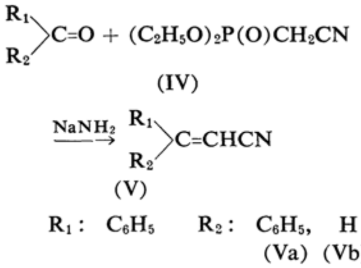
$$(C_2H_5O)_2\overset{\overset{O}{\uparrow}}{P}\text{-}CH_2COOC_2H_5 \quad \text{(I)}$$

$$\xrightarrow{NaNH_2} (C_2H_5O)_2\overset{\overset{O}{\uparrow}}{P}\text{-}\overset{\ominus}{C}HCOOC_2H_5 \quad \text{(II)}$$

$$\text{II} + {}^{R_1}_{R_2}\!\!>\!C=O \rightarrow {}^{R_1}_{R_2}\!\!>\!C=CHCOOC_2H_5 + (C_2H_5O)_2\overset{\overset{O}{\uparrow}}{P}O^{\ominus}$$

(III)

Diethyl cyanomethylphosphonate (IV), prepared from bromoacetonitrile and triethylphosphite, gave an anion when treated with sodium amide at a low temperature; this anion reacted with benzaldehyde and benzophenone to produce cinnamonitrile (Vb) and β-phenylcinnamonitrile (Va).



$${}^{R_1}_{R_2}\!\!>\!C=O + (C_2H_5O)_2P(O)CH_2CN \quad \text{(IV)}$$

$$\xrightarrow{NaNH_2} {}^{R_1}_{R_2}\!\!>\!C=CHCN \quad \text{(V)}$$

R_1: C_6H_5 R_2: C_6H_5, H
(Va) (Vb)

Diethyl formylmethylphosphonate diethylacetal (VI), prepared by the heating of ethyl bromoacetal with triethylphosphite, was added to a suspension of sodium amide in tetrahydrofuran at room temperature, and the resulting diethyl formylmethylphosphonate diethylacetal carbanion was treated with benzaldehyde at about 20°C to give cinnamaldehyde diethylacetal (VII), which was hydrolyzed and identified with 2, 4-dinitrophenylhydrazone.

$$C_6H_5CHO + \underset{\text{(VI)}}{(C_2H_5O)_2P(O)CH_2CH(OC_2H_5)_2}$$

$$\xrightarrow{NaNH_2} \underset{\text{(VII)}}{C_6H_5CH=CHCH(OC_2H_5)_2}$$

In the same way, diethyl acetonylphosphonate carbanion, prepared from diethyl acetonylphosphonate (VIII), was treated with benzaldehyde to give the expected benzalacetone (IX) in a poor yield.

$$C_6H_5CHO + \underset{\text{(VIII)}}{(C_2H_5O)_2P(O)CH_2COCH_3}$$

$$\xrightarrow{NaNH_2} \underset{\text{(IX)}}{C_6H_5CH=CHCOCH_3}$$

Experimental

The phosphonates were prepared by means of the Michaelis-Arbuzov reaction[4]. The sodium amide was a commercial product.

Ethyl Cinnamilideneacetate.—Diethyl carbethoxymethyl phosphonate (11.20 g., 0.05 mol.), prepared from ethyl bromoacetate and triethylphosphite, in dry tetrahydrofuran (20 ml.) was added dropwise with stirring to a suspension of sodium amide (1.95 g., 0.05 mol.) in dry tetrahydrofuran (30 ml.) at about 20°C. The solution was then stirred at room temperature under a slow stream of nitrogen to sweep out the evolved ammonia.

Into the resulting yellow solution, cinnamaldehyde (6.60 g., 0.05 mol.) in the same solvent (20 ml.) was added dropwise over a one-hour period at 20∼25°C. During this addition, a gummy precipitate appeared.

The solvent was removed, and then the residue was taken up in water. The aqueous solution was extracted with ether. The ether extract was dried over sodium sulfate and evaporated, and the residue was distilled under reduced pressure, giving 7.3 g. (72.5%) of liquid; b. p., 135∼136°C/2 mmHg. This product crystallized; m. p., 26∼27°C.

Found: C, 77.10; H, 6.92. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98%.

β-Phenylcinnamonitrile (Va). — Sodium amide (1.95 g., 0.05 ml.) was placed in dry tetrahydrofuran (30 ml.). Diethyl cyanomethylphosphonate (8.86 g., 0.05 mol.), prepared from bromoacetonitrile and triethylphosphite, in dry tetrahydrofuran (20 ml.) was added dropwise with stirring to the suspension at 0∼5°C, and then the resulting red solution was stirred at 15°C for about three hours under a slow stream of nitrogen. After removal of

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[4] G. M. Kosolapoff, "Organophosphorus Compounds", 1st. ed., J. Wiley & Sons, Inc., New York, N. Y. (1950), Chap. 7.

the ammonia, (benzophenone 9.1 g., 0.05 mol.) in the same solvent (20 ml.) was added dropwise with stirring at room temperature, and the solution was allowed to stand overnight. The solvent was removed after cooling, water was added to the residue, and the product was extracted with ether. The ether, after being dried over sodium sulfate, was removed, and the residue was distilled under reduced pressure giving 4.5 g. of liquid (b. p., 170∼171°C/5.5 mmHg), which solidified, giving crystals (m. p. 43∼44°C).

Found: C, 87.50; H, 5.39; N, 6.77. Calcd. for $C_{15}H_{11}N$: C, 87.77; H, 5.40; N, 6.82%.

Cinnamonitrile (Vb). — Diethyl cyanomethylphosphonate carbanion was prepared from diethyl cyanomethylphosphonate (8.86 g., 0.05 mol.) and sodium amide (1.95 g., 0.05 mol.) in the same way. Benzaldehyde (5.3 g., 0.05 mol.) in dry tetrahydrofuran (20 ml.) was added with stirring at −15∼−10°C to the carbanion. After this addition, the solution was stirred for 30 min. at 15°C and allowed to stand overnight. The ether extract was dried over sodium sulfate. After removal of the ether, the residue was distilled, giving 5.5 g. of liquid (b. p., 121∼123°C/9 mmHg). The liquid was hydrolyzed to give crystals of cinnamic acid (m. p., 131∼133°C).

Cinnamaldehyde Diethylacetal (VII). — Diethyl formylmethylphosphonate diethylacetal (12.7 g., 0.05 mol.), prepared from bromoacetoaldehyde diethylacetal and triethylphosphite, in dry tetrahydrofuran (20 ml.) was added dropwise with stirring at 18∼20°C into sodium amide (1.95 g., 0.05 mol.) in dry tetrahydrofran (30 ml.); then nitrogen was passed into the solution for several hours. After removal of the ammonia, benzaldehyde (5.3 g., 0.05 mol.) in the same solvent (20 ml.) was added dropwise with stirring at 17∼18°C. The solution was stirred for an additional three hours and allowed to stand overnight. The solvent was evaporated, and the oily residue was taken up in water. The aqueous solution was extracted with ether, and the ether extract was dried over sodium sulfate and evaporated and the residue was distilled, giving 6.3 g. of liquid (b. p., 126∼127°C/10 mmHg). The product was hydrolyzed and identified with the 2,4-dinitrophenylhydrazone (m. p., 149∼151°C).

Benzalacetone (IX). — Diethyl acetonylphosphonate was prepared from bromoacetone and triethylphosphite. The phosphonate (9.2 g., 0.05 mol.) in dry tetrahydrofuran (20 ml.) was added dropwise with stirring at 3∼5°C into a suspension of sodium amide (1.95 g., 0.05 mol.) in dry tetrahydrofran (30 ml.), and then nitrogen was passed into the solution to sweep out the ammonia. Into the solution, benzaldehyde (5.3 g., 0.05 mol.) in the same solvent was added dropwise with stirring at 5∼8°C. The solution was stirred for an hour and allowed to stand overnight. The solvent was then evaporated. Steam-distillation gave IX; m. p., 39∼40°C.

Found: C, 81.86; H, 7.24. Calcd. for $C_{10}H_{10}O$: C, 82.16; H, 6.90%.

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