viscous, a factor which made accurate pipetting of samples more difficult, but this does not explain the deviations between separate runs. It was felt that perhaps the solvent used for each run was not uniform, but redistillation and immediate use of the alcohol in simultaneous runs did not offer a solution and as yet the problem has not been resolved. It is evident however that the data can be used, in a qualitative sense, to indicate the nature and extent of the effect of solvent dielectric and ionizing power upon the reaction. Table II shows the effect of *p*-substituents on the reaction rate.

From the rate data obtained at 40° and 50° in toluene solution, the free energy, enthalpy and entropy of activation were calculated and are listed in Table II.

In addition to the rate data reported, several runs were discarded or not continued, especially in the alcohol and ketone solvents, because it was obvious that a gross discrepancy was present.

[CONTRIBUTION FROM ROHM AND HAAS CO., PHILADELPHIA 37, PENNA.]

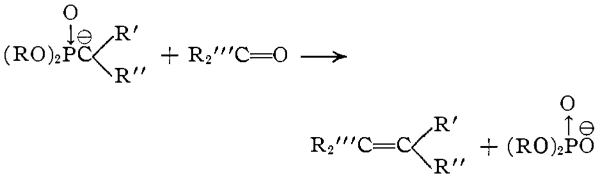
The Utility of Phosphonate Carbanions in Olefin Synthesis

BY WILLIAM S. WADSWORTH, JR., AND WILLIAM D. EMMONS

RECEIVED OCTOBER 28, 1960

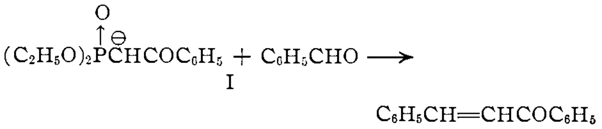
The reaction of phosphonate carbanions containing electron-withdrawing groups with aldehydes or ketones in an aprotic solvent constitutes a useful olefin synthesis. These reagents were, in general, more reactive than the analogous triarylphosphoranes or "Wittig" reagents and have a number of special features which enhance their utility.

In connection with another problem we have studied the reaction of phosphonate carbanions with ketones and aldehydes to produce olefins. The reaction proceeds smoothly under mild conditions to give fair to excellent yields of olefins and, indeed, this synthesis is a very useful supplement to the well known "Wittig" reaction.[1] The structures of the olefins were in every case deduced from their physical properties, infrared spectra and, where appropriate, by analysis.



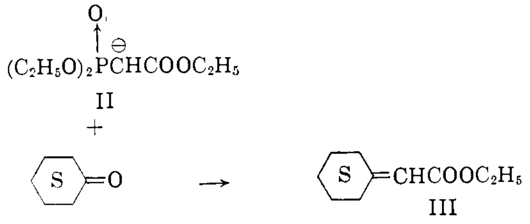
$$(RO)_2\overset{O}{\overset{\downarrow}{P}}\overset{\ominus}{C}\begin{smallmatrix}R'\\R''\end{smallmatrix} + R_2'''C{=}O \longrightarrow R_2'''C{=}C\begin{smallmatrix}R'\\R''\end{smallmatrix} + (RO)_2\overset{O}{\overset{\uparrow}{P}}O^{\ominus}$$

The phosphonate anions have in many instances a number of advantages over the triarylphosphoranes or "Wittig" reagents. They are in most cases much less expensive and they react with a wider variety of ketones and aldehydes, usually under much milder conditions. The reaction, for example, of triphenylphenacylidenephosphorane with benzaldehyde has been carried out by refluxing the reagents in tetrahydrofuran for thirty hours.[2] The analogous reaction using diethyl phenacylphosphonate anion (I) was exothermic at room temperature and gave comparable yields of olefin after immediate workup.



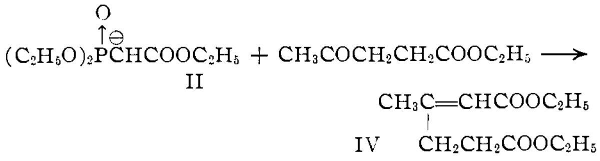
$$\underset{\text{I}}{(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}\overset{\ominus}{C}HCOC_6H_5} + C_6H_5CHO \longrightarrow C_6H_5CH{=}CHCOC_6H_5$$

Also, whereas triphenylcarbethoxymethylidenephosphorane reacts with benzaldehyde it fails to react with cyclohexanone in a normal manner.[3,4] Carbethoxymethylphosphonate anion (II) on the other hand, reacted exothermically with cyclohexanone to give the olefin III in good yield.



$$\underset{\text{II}}{(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}\overset{\ominus}{C}HCOOC_2H_5}$$

Unlike the triarylphosphoranes which give undesirable side products with keto esters,[5] the phosphonate anions react in a normal manner without reverse addition.



$$\underset{\text{II}}{(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}\overset{\ominus}{C}HCOOC_2H_5} + CH_3COCH_2CH_2COOC_2H_5 \longrightarrow \text{IV}\ \ CH_3\underset{CH_2CH_2COOC_2H_5}{\underset{|}{C}}{=}CHCOOC_2H_5$$

Horner and co-workers[6] recently have reported the preparation of olefins from phosphine oxides and aldehydes. The conditions for the reaction were relatively rigorous, requiring the use of refluxing toluene over a period of ten to twelve hours in the presence of potassium *t*-butoxide. These workers also reported that diethyl benzylphosphonate (V) reacted with benzaldehyde under comparable conditions to give stilbene. Obviously, only the most stable ketones or aldehydes could be used under these conditions. The use of a preformed phosphonate anion, on the other hand, allows all but the most hindered ketones to be used with equal ease.

A convenient method for preparing the anion consists of adding the phosphonate at room temperature to a slurry of sodium hydride in 1,2-dimethoxyethane. Elevated temperatures were detrimental, due to the facile self-condensation of the anion. Indeed, simple alkyl phosphate anions which did not contain an activating group could not be prepared, for the anions once formed were unstable at the elevated temperatures needed for

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(1) For an excellent review of the "Wittig" reagent see U. Schöllkopf, *Angew. Chem.*, **71**, 260 (1959).

(2) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

(3) G. Wittig and W. Haag, *Chem. Ber.*, **88**, 1654 (1955).

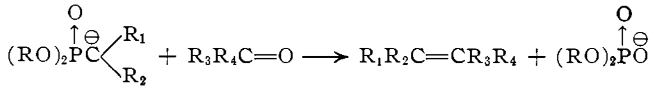
(4) M. Vilkas and N. A. Abraham, *Compt. rend.*, **246**, 1434 (1958).

(5) F. Bohlmann and E. Inhoffen, *Chem. Ber.*, **89**, 1276 (1956).

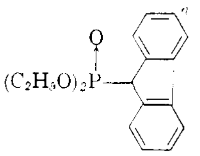
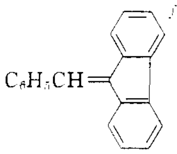
(6) L. Horner, H. Hoffmann, H. G. Wippel and G. Klahre, *ibid.*, **92**, 2499 (1959).

TABLE I

PREPARATION OF OLEFINS



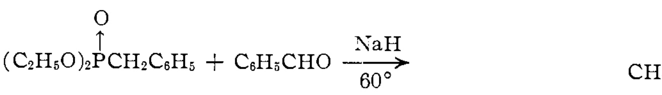
$$(RO)_2\overset{O}{\overset{\uparrow}{P}}\overset{\ominus}{C}\begin{matrix}R_1\\R_2\end{matrix} + R_3R_4C{=}O \longrightarrow R_1R_2C{=}CR_3R_4 + (RO)_2\overset{O}{\overset{\uparrow}{P}}\overset{\ominus}{O}$$

Phosphonate	Aldehyde or ketone	Olefin	B.p. °C.	Mm.	Yield, %	$n^{25}D$	Infrared stretching frequency (C=C), cm.$^{-1}$
$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}CH_2C_6H_5$	$(C_6H_5)_2C{=}O$	$(C_6H_5)_2C{=}CHC_6H_5$[c]	67 (m.p.)		78		1590
	$C_6H_5CH{=}CHCHO$	$C_6H_5CH{=}CHCH{=}CHC_6H_5$[d]	151 (m.p.)		58	....	1592
$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}CH_2COOC_2H_5$	C_6H_5CHO	$C_6H_5CH{=}CHCOOC_2H_5$	70	0.1	84	1.5562	1625
	$(CH_3)_2CHCHO$	$(CH_3)_2CHCH{=}CHCOOC_2H_5$[e]	65	15	74	1.4284	1650
 [a]	C_6H_5CHO	 [f]	74–75 (m.p.)		80	....	1591
$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}CH_2CN$	C_6H_5CHO	$C_6H_5CH{=}CHCN$[g]	130	16	66	1.5828	1605
$(C_2H_5O)\overset{O}{\overset{\uparrow}{P}}CH_2COOC_2H_5$	CCl_3CHO	$CCl_3CH{=}CHCOOC_2H_5$[h]	86	10	50	1.4798	1650
$(CH_3O)_2\overset{O}{\overset{\uparrow}{P}}CH_2COOC_2H_5$	$(CH_3)_2C{=}O$	$(CH_3)_2C{=}CHCOOC_2H_5$[i]	150	760	70	1.4331	1650
$(C_2H_5O)_2P(O)\underset{CH_2COOC_2H_5}{CH}COOC_2H_5$[b]	C_6H_5CHO	$C_6H_5CH{=}\underset{CH_2COOC_2H_5}{C}COOC_2H_5$[j]	119	0.1	61	1.5068	1640

[a] B. E. Smith and A. Burger, *J. Am. Chem. Soc.*, **75**, 5891 (1953). [b] Prepared by treating the half-ethyl ester of maleic acid with triethyl phosphite; F. Johnson, U. S. Patent 2,754,319. [c] H. Adkins and W. Zortman, *Org. Syntheses*, **17**, 89 (1937). [d] B. B. Corson, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 229. [e] Calcd. for $C_8H_{15}O_2$: C, 67.65; H, 9.87. Found: C, 67.66; H, 9.91. [f] J. Thiele and F. Hende, *Ann.*, **347**, 296 (1906). [g] K. V. Auwers and B. Ottens, *Ber.*, **58**, 2071 (1925). [h] K. V. Auwers and M. Schmidt, *ibid.*, **46**, 487 (1913). [i] W. Massot, *ibid.*, **27**, 1226 (1894). [j] H. Stobbe, *J. prakt. Chem.*, **90**, 551 (1914).

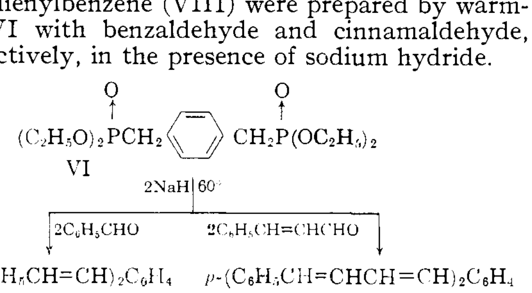
their preparation. As the ketone or aldehyde was added to the anion in solution, a precipitate of sodium diethyl phosphate was formed. The products, Table I, were isolated by dilution with water and extraction with ether.

Diethyl benzylphosphate (V) was intermediate in its ability to form a stable carbanion. A solution of the phosphonate when heated with sodium hydride at 60°, the temperature necessary for hydrogen evolution, gave only an intractable unreactive resinous product. When the anion was prepared in the presence of a ketone or aldehyde, however, good yields of olefin were obtained. Thus, stilbene was prepared in 63% yield.



$$\underset{V}{(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}CH_2C_6H_5} + C_6H_5CHO \xrightarrow[60°]{NaH} C_6H_5CH{=}CHC_6H_5$$

Likewise, distyrylbenzene (VII) and *p*-bis-4-phenylbutadienylbenzene (VIII) were prepared by warming VI with benzaldehyde and cinnamaldehyde, respectively, in the presence of sodium hydride.



VI

2NaH | 60°

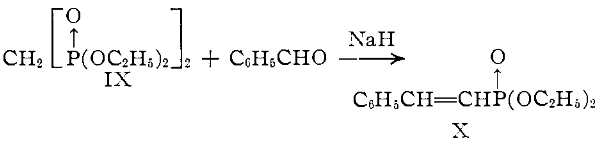
$2C_6H_5CHO$ $2C_6H_5CH{=}CHCHO$

p-$(C_6H_5CH{=}CH)_2C_6H_4$ VII

p-$(C_6H_5CH{=}CHCH{=}CH)_2C_6H_4$ VIII

It is interesting to note that in the case of stilbene only the *trans* isomer was obtained. It is probable that the reaction is not stereospecific and that initially both *cis* and *trans* isomers are formed as in the "Wittig" reaction.[1] In this instance, however, under strongly basic conditions at elevated temperatures the isomerization of any *cis*-stilbene to the stable *trans* isomer would be expected.

Phosphonate anions can be formed easily when the carbon atom attached to phosphorus is negatively substituted. Tetraethylmethylene bisphosphonate (IX), prepared from methylene iodide and triethyl phosphite,[7] gave off hydrogen when added to a slurry of sodium hydride at room temperature. The resulting anion when treated with benzaldehyde gave the vinyl phosphonate X.



$$\underset{IX}{CH_2\left[\overset{O}{\overset{\uparrow}{P}}(OC_2H_5)_2\right]_2} + C_6H_5CHO \xrightarrow{NaH} \underset{X}{C_6H_5CH{=}CH\overset{O}{\overset{\uparrow}{P}}(OC_2H_5)_2}$$

Diethyl fluorenyl phosphonate (XI), prepared from 9-bromofluorene and triethyl phosphite, gave an anion when treated with sodium hydride which reacted exothermically with paraformaldehyde to give 9-methylenefluorene (XII). This product, which absorbed bromine to give the 9,10-dibromo derivative in high yield, quickly polymerized when the solvent was evaporated. The high yield obtained in this reaction makes it the method of choice for the preparation of solutions of 9-methylenefluorene.[8,9]

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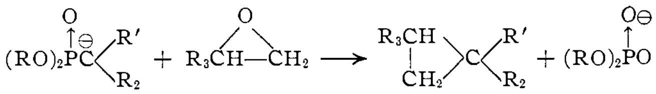
(7) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **75**, 1500 (1953).

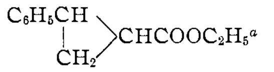
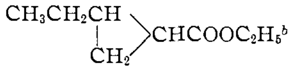
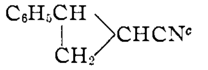
(8) H. Wieland, F. Reindel and J. Femer, *Ber.*, **55B**, 3313 (1922).

(9) H. Wieland and O. Probst, *Ann.*, **530**, 274 (1937).

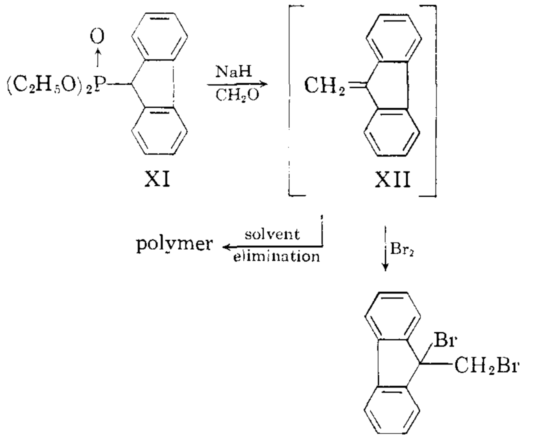
TABLE II

PREPARATION OF CYCLOPROPANES

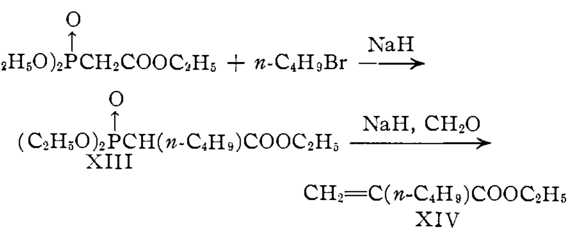


Phosphonate	Oxide, R_3 =	Cyclopropane	B.p. °C.	B.p. Mm.	M.p., °C.	Yield, %	$n^{25}D$
$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}CH_2COOC_2H_5$	C_6H_5		100–102	0.5	37–38	42	1.5121
$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}CH_2COOC_2H_5$	CH_3CH_2		55	15	. . .	21	1.4215
$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}CH_2CN$	C_6H_5		80	0.2	26–27	51	1.5226

[a] A. Burger and W. L. Yost, *J. Am. Chem. Soc.*, **70**, 2198 (1948). [b] Calcd. for $C_8H_{14}O_2$: C, 67.63; H, 9.86. Found: C, 67.33; H, 10.26. [c] R. J. Mohrbacker and N. H. Cromwell, *J. Am. Chem. Soc.*, **79**, 401 (1957).

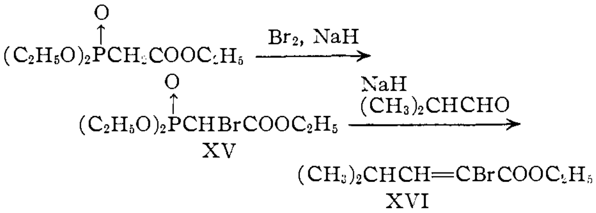


The enhanced reactivity of phosphonate anions over the triaryl phosphoranes may also be utilized to advantage in other ways. Phosphonate anions react with alkyl halides to give α-substituted phosphonates.[10] These in turn will react with excess sodium hydride if present yielding a new anion which can be treated with an aldehyde or ketone to give olefins. Thus, *in situ* alkylations may be carried out and the phosphonate so obtained used without isolation in olefin synthesis. In the example shown below ethyl α-*n*-butylacrylate was obtained in 60% over-all yield.



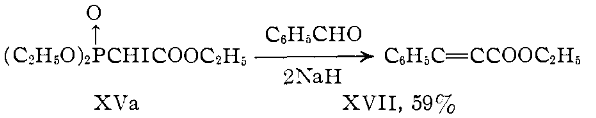
$$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}CH_2COOC_2H_5 + n\text{-}C_4H_9Br \xrightarrow{NaH} \underset{\text{XIII}}{(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}CH(n\text{-}C_4H_9)COOC_2H_5} \xrightarrow{NaH,\ CH_2O} \underset{\text{XIV}}{CH_2{=}C(n\text{-}C_4H_9)COOC_2H_5}$$

Similarly, halogenation of a phosphonate anion *in situ* followed by the addition of an aldehyde or ketone gave vinyl halides. By the use of this technique XVI was obtained in over 60% yield.



$$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}CH_2COOC_2H_5 \xrightarrow{Br_2,\ NaH} \underset{\text{XV}}{(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}CHBrCOOC_2H_5} \xrightarrow[(CH_3)_2CHCHO]{NaH} \underset{\text{XVI}}{(CH_3)_2CHCH{=}CBrCOOC_2H_5}$$

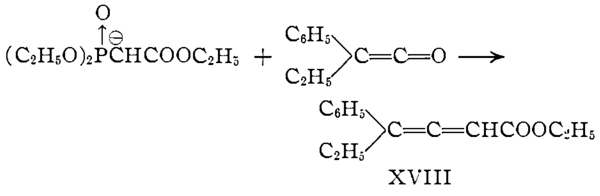
In an additional example the iodophosphonate XVa was treated with benzaldehyde in the presence of two equivalents of sodium hydride and under these conditions a good yield of the propiolate XVII was obtained.



$$\underset{\text{XVa}}{(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}CHICOOC_2H_5} \xrightarrow[2NaH]{C_6H_5CHO} \underset{\text{XVII, 59\%}}{C_6H_5C{\equiv}CCOOC_2H_5}$$

Thus, a one-pot synthesis of substituted acetylenes is possible using halophosphonates directly or halophosphonates prepared *in situ* without the isolation of intermediate vinyl halides.

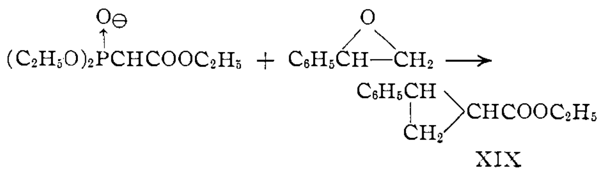
Allenes can be prepared by treating a phosphonate anion with a ketene.



XVIII

In the one instance examined, the reaction proceeded smoothly at room temperature although yields were reduced by resin formation during the distillation of the product.

The reaction of phosphonate anions with epoxides gave cyclopropanes in fair yields; see Table II.



XIX

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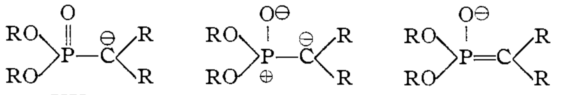
(10) A. E. Arbuzov and A. F. Razumov, *J. Russ. Phys. Chem. Soc.*, **61**, 623 (1929).

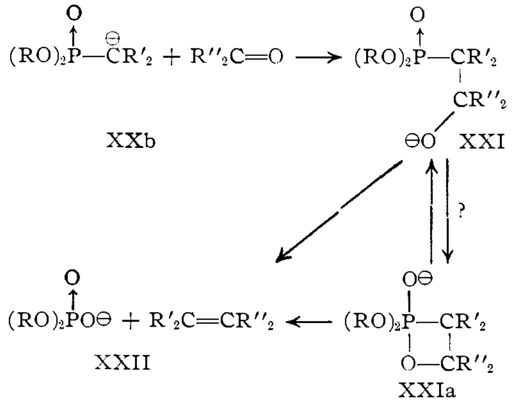
The use of phosphonate anions in cyclopropane synthesis is restricted to those phosphonates which contain an activating group such as the carboethoxy or cyano radical. The diethyl benzylphosphonate anion, for example, did not react with styrene oxide even though the anion was prepared *in situ*. While this work was in progress, Denney and Boskin[11] reported that triarylphosphoranes also react with epoxides to give cyclopropanes. Whereas phosphonate anions gave cyclopropanes under relatively mild conditions, the phosphoranes require rigorous conditions (heating to 200° in a sealed bomb) and give much lower yields.

The phosphonate anion can be looked upon as a resonance hybrid having three contributing structures



XXa XXb XXc

The structures XXa and XXc make use of a phosphorus d-orbital in a manner similar to the phosphoranes. It is well known that the P=O bond in phosphates, phosphonates, etc., has some single bond character which enables structures XXb and XXc to contribute. The first step in the reaction of a phosphonate anion with an aldehyde or ketone is addition of the anion to the carbonyl group forming XXI. The intermediate XXI may or may not be in equilibrium with a four-membered ring, XXIa, but in any event undergoes fragmentation to yield olefin and phosphate anion.

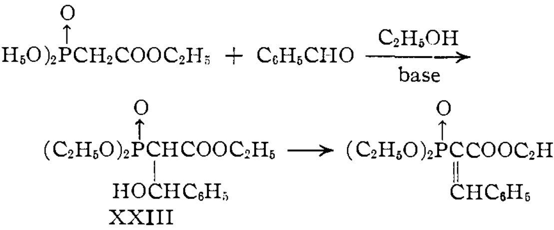


XXb XXI XXII XXIa

$$(RO)_2\overset{O}{\overset{\uparrow}{P}}-\overset{\ominus}{C}R'_2 + R''_2C=O \longrightarrow (RO)_2\overset{O}{\overset{\uparrow}{P}}-CR'_2-CR''_2-O^{\ominus}$$

$$(RO)_2\overset{O}{\overset{\uparrow}{P}}O^{\ominus} + R'_2C=CR''_2$$

It is interesting to note that in the presence of a proton-donating solvent Patai and Schwartz[12] have found that dehydration products of the adduct XXIII are obtained, a result which conforms to our proposed mechanism.



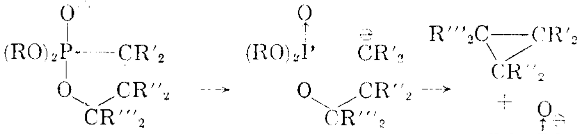
XXIII

$$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}CH_2COOC_2H_5 + C_6H_5CHO \xrightarrow[\text{base}]{C_2H_5OH}$$

$$(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}\underset{HOCHC_6H_5}{\underset{|}{C}}HCOOC_2H_5 \longrightarrow (C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}\underset{CHC_6H_5}{\underset{\|}{C}}COOC_2H_5$$

Under these conditions proton transfer is favored and hence fragmentation of the intermediate to give olefin and phosphate is not observed.

The reaction of phosphonate anions with epoxides to give cyclopropanes may involve a five-membered ring.



XXIV XXV

It is probable that the P–C bond in XXIV breaks first in the collapse of the intermediate to give products. The stability of the resulting carbanion XXV, which is enhanced by having R′ an electron-withdrawing group, may be a deciding factor in this reaction. Although the formation of cyclopropanes is undoubtedly not stereospecific, only *trans*-1-carbethoxy-2-phenylcyclopropane[11] was obtained from the reaction of styrene oxide and triethyl phosphonoacetate anion. The *cis* isomer formed initially undoubtedly was converted under the reaction conditions to the thermodynamically more stable product.

The mechanism of olefin formation is similar to that proposed by Wittig[3] for the reaction of triarylphosphoranes with aldehydes and ketones. The driving force for the reaction is provided undoubtedly by the formation of the stable phosphate anion XXII, which is certainly a more thermodynamically stable species than the phosphonate anion XXI. The enhanced reactivity of a phosphonate anion over a comparable phosphorous ylid may simply reflect the fact that the former species is a saturated carbanion having a high degree of charge separation while the triarylphosphoranes have relatively little charge separation and are accordingly less reactive.

Acknowledgment.—Analyses were carried out under the supervision of Mr. Clyde Nash.

Experimental

The phosphonates were prepared by means of the Michaelis–Arbuzov reaction.[13] Either triethyl or trimethyl phosphite, supplied by the Eastman Kodak Co., was used. The alkyl halides were common reagents supplied from commercial sources and in some cases purified before use. The phosphonates were purified by distillation or crystallization and their physical properties compared with published data.

Sodium hydride, 50% in mineral oil, was supplied by Metal Hydrides Inc. The solvent 1,2-dimethoxyethane was obtained from the Ansul Chemical Co. and dried over calcium hydride just before use.

Benzalacetophenone.—Sodium hydride (50%, 2.4 g., 0.05 mole) was placed in 100 cc. of dry 1,2-dimethoxyethane. The slurry was cooled to 20° and diethyl phenacylphosphonate (11.4 g., 0.05 mole) was added dropwise with stirring. After the addition, the solution was stirred at room temperature for 1 hour until gas evolution had ceased. To the yellow solution, maintained below 25°, was added dropwise benzaldehyde (5.3 g., 0.05 mole). During the addition, a gummy precipitate appeared. The solution was stirred at room temperature for 1 hour and refluxed for 0.5 hour. After cooling, a large excess of water was added and the product extracted with ether. The ether, after being dried over magnesium sulfate, was removed and the crystalline residue recrystallized twice from isooctane. A yield of 6.3 g. (61%), m.p. 52–53°, was obtained.

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[11] D. B. Denney and M. J. Boskin, *J. Am. Chem. Soc.*, **81**, 6330 (1959).

[12] S. Patai and A. Schwartz, *J. Org. Chem.*, **25**, 1232 (1960).

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

The infrared spectrum of the product was identical with that of an authentic sample.

Ethyl Cyclohexylideneacetate (III)[14]—Triethyl phosphonoacetate (11.2 g., 0.05 mole) was added dropwise at 20° to a slurry of 50% sodium hydride (2.4 g., 0.05 mole) in 100 cc. of dry 1,2-dimethoxyethane. After the addition, the reaction mixture was stirred for 1 hour at room temperature until gas evolution had ceased. Cyclohexanone (4.9 g., 0.05 mole) was added dropwise at such a rate that the temperature was maintained below 30°. After the addition, the solution was stirred for 15 minutes at room temperature during which time a viscous semi-solid appeared. The mixture was taken up in a large excess of water, and the aqueous solution extracted with ether. The ether layer after being dried over magnesium sulfate and evaporated gave a liquid residue, b.p. 88–90° (10 mm.), 5.8 g. (70% yield), $n^{25}\text{D}$ 1.4704. The infrared spectrum of the product contained a strong band at 1660 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.42; H, 9.53. Found: C, 71.48; H, 9.57.

1,2-Dicarbethoxy-2-methylbutene-1 (IV).—Triethyl phosphonoacetate (11.2 g., 0.05 mole) was added dropwise at 20° to a slurry of 50% sodium hydride (2.4 g., 0.05 mole) in 100 cc. of dry 1,2-dimethoxyethane. After the addition, the solution was stirred for 1 hour at room temperature. Ethyl levulinate (7.2 g., 0.05 mole) was added dropwise to the solution and some heat evolution was observed. The solution was heated with stirring at 50–60° for 1 hour during which time a gummy precipitate was produced. The solution was cooled and taken up in a large excess of water. The aqueous solution was extracted with two 100-ml. portions of ether and the ether extract dried over magnesium sulfate and evaporated. The residue was distilled giving 7.1 g. of clear liquid, 78–80° (0.25 mm.), 67% yield, $n^{25}\text{D}$ 1.4506. The infrared spectrum of the product contained a strong band at 1650 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{18}O_4$: C, 61.68; H, 8.14. Found: C, 61.57; H, 8.42.

***trans*-Stilbene.**[15]—Diethyl benzylphosphonate (11.4 g., 0.05 mole), 50% sodium hydride (2.4 g., 0.05 mole) and benzaldehyde (5.3 g., 0.05 mole) were added to 100 cc. of dry 1,2-dimethoxyethane. The mixture was heated slowly to 85° with stirring. At 70° there was a large evolution of gas and the appearance of a semi-solid precipitate. The solution was refluxed for 0.5 hour, cooled and then taken up in a large excess of water. The aqueous solution was filtered and the precipitate recrystallized twice from alcohol giving 5.6 g. (62.6%), of white crystals, m.p. 124.5°. The infrared spectrum of the product was identical with that of an authentic sample of *trans*-stilbene.

Di-styrylbenzene (VII).[16]—Tetraethyl xylylenebisphosphonate (9.45 g., 0.025 mole), 50% sodium hydride (1.2 g., 0.025 mole) and benzaldehyde (2.65 g., 0.025 mole) were added to 100 cc. of dry 1,2-dimethoxyethane. The solution was warmed gradually to 85° with stirring. At approximately 70°, hydrogen evolution became rapid and was controlled by means of an ice-bath. After the gas evolution had ceased the solution was refluxed for 0.5 hour. After being cooled and diluted with a large excess of water, the mixture was filtered giving a pale yellow precipitate. The precipitate was recrystallized twice from 1,2-dimethoxyethane giving 4.5 g. (63% yield) of product, m.p. 259–260°. The product absorbed strongly at 1360 and at 965 cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{18}$: C, 93.61; H, 6.38. Found: C, 93.39; H, 6.41.

***p*-Bis-4-phenylbutadienylbenzene (VIII).**[17]—Tetraethyl xylylenebisphosphonate (9.45 g., 0.025 mole), 50% sodium hydride (2.4 g., 0.05 mole) and cinnamaldehyde (7.6 g., 0.05 mole) were added to 100 cc. of dry 1,2-dimethoxyethane. The solution was heated at 85° for 0.5 hour during which time gas evolution took place. After being cooled and diluted with a large excess of water the solution was filtered. Bright yellow leaflets were obtained which when recrystallized from dimethylformamide gave 3.0 g. (37%) of product, m.p. 290–291° (reported m.p. 288°).

Anal. Calcd. for $C_{26}H_{22}$: C, 93.41; H, 6.58. Found: C, 93.15; H, 6.53.

Diethyl β-Phenylvinylphosphonate (X).[18]—Tetraethylmethylenediphosphonate (5.3 g., 0.018 mole) was added dropwise at room temperature to a slurry of 50% sodium hydride (0.971 g., 0.02 mole) and 100 cc. of dry 1,2-dimethoxyethane. After the addition, the solution was stirred at room temperature for 1 hour. To the solution was added benzaldehyde (2.14 g., 0.02 mole) dropwise with stirring. The addition was exothermic and was carried out at 25°. During the course of the addition, a gummy precipitate appeared. A large excess of water was added, and the aqueous solution extracted with two 100-ml. portions of ether. The residue, obtained after drying the ether over magnesium sulfate and evaporating, was distilled giving 2.4 g. (67%) of colorless liquid, b.p. 116–118° (0.35 mm.), $n^{25}\text{D}$ 1.5208. The product showed the expected infrared spectrum with strong bands at 1610 and 1250 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{17}O_3P$: C, 60.0; H, 7.08; P, 12.91. Found: C, 60.37; H, 7.17; P, 12.19.

9-Methylenefluorene (XII).—Diethyl fluorenylphosphonate (7.55 g., 0.025 mole) was added dropwise to a slurry consisting of 50% sodium hydride, (1.3 g., 0.025 mole) in 100 ml. of dry 1,2-dimethoxyethane keeping the temperature below 25°. After the addition, the solution was stirred for 1 hour until gas evolution ceased. Dry paraformaldehyde (0.8., 0.025 mole) suspended in 1,2-dimethoxyethane was added slowly to the solution at 30°. During the addition a semi-solid precipitate appeared. A large volume of water was added, and the solution extracted with two 100-ml. portions of ether. The ether extract was dried over magnesium sulfate and evaporated. A yellow solid resulted which was insoluble in all common solvents; 30.5 g. (77%).

Anal. Calcd. for $C_{14}H_{10}$: C, 94.38; H, 5.62. Found: C, 94.61; H, 5.67.

A sample of the ether solution absorbed bromine from a bromine–carbon tetrachloride solution. On removal of solvent a crystalline precipitate was obtained, m.p. 144°.[8]

Ethyl α-*n*-Butylacrylate (XIV).—To a slurry of 50% sodium hydride (18.4 g., 0.384 mole) in 100 ml. of dry 1,2-dimethoxyethane was added dropwise at room temperature with stirring, triethyl phosphonoacetate (86 g., 0.384 mole). After the addition the solution was stirred for 1 hour or until gas evolution ceased. N-Butyl bromide (52.6 g., 0.38 mole) was added at room temperature and the solution heated at 50° for 1 hour. The resulting slurry was cooled to 10° and 50% sodium hydride (18.4 g., 0.38 mole) was added all at once. The solution was allowed to come slowly to room temperature during which time rapid evolution of gas took place. After stirring the solution for 1 hour, a slurry of dry paraformaldehyde (12.1 g., 0.38 mole) in 50 cc. of dry 1,2-dimethoxyethane was added at 20° over a period of 1 hour during which time a gummy precipitate appeared. The solution was stirred for 1 hour and then taken up cautiously in a large excess of water. The aqueous layer was extracted with two 100-ml. portions of ether and the ether solution dried over magnesium sulfate and the ether boiled off. The residue was distilled giving 38.4 g. (60%) of product, b.p. 68–69° (100 mm.), $n^{25}\text{D}$ 1.4254. The product absorbed strongly at 1640 cm.$^{-1}$.

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.27; H, 10.25. Found: C, 69.09; H, 10.19.

Ethyl α-Bromo-β-isopropylacrylate (XVI).—Triethyl phosphonoacetate (22.4 g., 0.1 mole) was added dropwise at 20° to a slurry of 50% sodium hydride (4.8 g., 0.1 mole) in 100 cc. of dry 1,2-dimethoxyethane. The solution was stirred for 1 hour or until gas evolution had ceased. Bromine (16.0 g., 0.1 mole) was added dropwise to the solution maintaining the temperature below 25°. The addition of bromine was exothermic and the color was immediately discharged. After the addition, the solution was warmed briefly at 40°, then cooled to 10° and 50% sodium hydride (4.5 g., 0.1 mole) added all at once. The solution was warmed gradually to room temperature during which time rapid gas evolution took place. Isobutyraldehyde (7.3 g., 0.1 mole) was added dropwise at such a rate as to maintain the temperature below 30°. Near the end of the addition the slurry contained a gummy mass. It was taken up in a large excess of water and the aqueous solution extracted

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[14] K. V. Auwers and P. Ellinger, *Ann.*, **387**, 235 (1912).

[15] R. L. Shriner and A. Berger, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 786.

[16] T. W. Campbell and R. N. McDonald, *J. Org. Chem.*, **24**, 1246 (1959).

[17] G. Drefahl and G. Plotner, *Chem. Ber.*, **91**, 1285 (1958).

[18] K. N. Anisimov and A. N. Nesmeyanov, *Isvest. Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk*, 1003 (1955).

with ether. The ether was taken off and the residue distilled giving 14.5 g. (65.6%) of distillate, b.p. 76–78° (10 mm.), n^{25}_D 1.4649. The infrared spectrum of the product showed strong absorption at 1625 cm.$^{-1}$.

Anal. Calcd. for $C_8H_{13}O_2Br$: C, 43.5; H, 5.88; Br, 36.2. Found: C, 43.81; H, 6.04; Br, 36.58.

Ethyl β-Phenylpropiolate (XVII).—Triethyl phosphonoacetate (11.2 g., 0.05 mole) was added at 25° dropwise to a slurry of 50% sodium hydride (2.4 g., 0.05 mole) in 100 cc. of dry 1,2-dimethoxyethane. The solution was stirred for 1 hour until hydrogen gas evolution ceased. To the homogeneous solution was added dropwise iodine (12.7 g., 0.05 mole) dissolved in a minimum of solvent. After the addition, the solution was stirred at room temperature for 1 hour and cooled to 10°; 50% sodium hydride (4.8 g. 0.10 mole) was added to the chilled solution all at once. The mixture was allowed to come to room temperature gradually during which time rapid gas evolution took place. Benzaldehyde (5.3 g., 0.05 mole) was added dropwise keeping the temperature at 25°. After the addition the solution was heated slowly to 40° at which temperature rapid gas evolution took place. After gas evolution had ceased, the solution was cooled and a large excess of water added. The aqueous solution was extracted with two 100-ml. portions of ether, and the ether extract dried over magnesium sulfate and evaporated. The residue now was distilled giving 5.1 g. (59% yield) of distillate, b.p. 78–80° (0.1 mm.), n^{25}_D 1.5800. The product absorbed at 2220 cm.$^{-1}$ and its infrared spectrum was identical with that of an authentic sample.

1-Carbethoxy-3-ethyl-3-phenylallene (XVIII).—Triethyl phosphonoacetate (11.2 g., 0.05 mole) was added dropwise at 25° to a slurry of 50% sodium hydride (2.5 g., 0.05 mole) in 100 cc. of dry 1,2-dimethoxyethane. The solution was stirred for 1 hour until gas evolution had ceased. Phenyl ethyl ketene (7.3 g., 0.05 mole) was added dropwise keeping the temperature below 30°. After the addition, which was exothermic, the solution was heated briefly to 50°, cooled to room temperature and taken up in a large excess of water. The aqueous solution was extracted with two 100-ml. portions of ether, the ether extract dried over magnesium sulfate and evaporated. The residue was distilled giving 3.5 g. (32% yield) of liquid, b.p. 89–90° (0.1 mm.), n^{25}_D 1.5490. The product was unstable, becoming viscous on standing. The infrared spectrum of the product showed strong absorption at 1940 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.82; H, 7.46. Found: C, 77.62; H, 7.74.

1-Carbethoxy-2-phenylcyclopropane (XIX).—Triethyl phosphonoacetate (22.4 g., 0.1 mole) was added dropwise with stirring to a slurry of 50% sodium hydride (5.0 g., 0.014 mole) in 100 cc. of dry 1,2-dimethoxyethane at 25°. After the addition the solution was stirred for 1 hour until gas evolution had ceased. Styrene oxide (12.0 g., 0.1 mole) was added. The solution was refluxed for 4 hours at 85°, cooled to room temperature and taken up in a large excess of water. The aqueous solution was extracted with two 100-ml. portions of ether. The ether extract was dried over magnesium sulfate, evaporated and the residue distilled giving 8.0 g. (42% yield) of distillate, b.p. 100° (0.5 mm.). The distillate crystallized on standing, m.p. 37–38°. The product showed the expected infrared spectrum with the characteristic cyclopropane band at about 1020 cm.$^{-1}$.[19]

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.51; H, 7.36. Found: C, 75.38; H, 7.39.

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[19] V. A. Slabey, *J. Am. Chem. Soc.*, **76**, 3604 (1954).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN 1, N. Y.]

Intramolecular Carboxylate Attack on Ester Groups. II. The Effect of Diastereoisomerism in Polymers and their Low Molecular Weight Models[1]

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The hydrolysis catalyzed by neighboring carboxylate attack on ester groups in copolymers of acrylic acid with small proportions of acrylic or methacrylic esters follows first-order kinetics, but the corresponding reactions of copolymers of methacrylic acid give strongly curved first-order plots and behave as if the copolymers contained two kinds of ester groups with reactivities differing by a factor of about 10. The effect is interpreted as due to steric isomerism of polymer chain sections in the neighborhood of the ester functions and is discussed in terms of present knowledge of conformations of vinyl polymers. To clarify the phenomenon, the hydrolysis rates of monoesters of *meso*- and *rac*-α,β-dialkylsuccinic acids were compared in the *p*H range where the rate is controlled by neighboring carboxylate attack. The difference in the reactivities of the isomers was very slight with methyl substituents; with isopropyl substituents the derivative of the racemic acid was about twice more reactive. The monoesters of the α,β-dialkylsuccinic acids are much more reactive than monoesters of succinic acid and their hydrolyses have lower activation energies. The data imply that the transition state is closer to a *skew* than to an eclipsed conformation and that the increased reactivity of succinic monoesters on α,β-disubstitution reflects the fact that the energy difference of *trans* and *skew* conformations is less in 1,1′,2,2′-tetrasubstituted than in 1,2-disubstituted ethanes.

Introduction

Previous investigations have demonstrated that the hydrolytic rate of carboxylic esters with a free carboxyl attached to the β- or γ-carbon is proportional in the *p*H range 3–7 to the degree of ionization of the carboxyl group.[3-9] The mechanism of the reaction was clarified by Bender and Neveu[8] and by Bruice and Pandit[10] who showed that the attack of the carboxylic acid anion on the ester group results in formation of an acid anhydride.

Experiments with copolymers of acrylic or methacrylic acid with 1–2 mole % of an acrylic or methacrylic *p*-nitrophenyl ester have revealed an unexpected phenomenon: Whereas ester groups in copolymers of methacrylic esters with acrylic acid hydrolyzed by first-order kinetics, copolymers containing methacrylic esters in a methacrylic acid chain gave first-order plots with a pronounced downward curvature.[11,12] The polymer behaved as

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[3] H. Morawetz and P. E. Zimmering, *J. Phys. Chem.*, **58**, 753 (1954).

[4] P. E. Zimmering, E. W. Westhead, Jr., and H. Morawetz, *Biochem. Biophys. Acta*, **25**, 376 (1957).

[5] E. R. Garrett, *J. Am. Chem. Soc.*, **79**, 3401 (1957).

[6] H. Morawetz and I. Oreskes, *ibid.*, **80**, 2591 (1958).

[7] M. L. Bender, F. Chloupek and M. C. Neveu, *ibid.*, **80**, 5384 (1958).

[8] M. L. Bender and M. C. Neveu, *ibid.*, **80**, 5388 (1958).

[9] E. Gaetjens and H. Morawetz, *ibid.*, **82**, 5328 (1960).

[10] T. C. Bruice and U. K. Pandit, *ibid.*, **82**, 5858 (1900).