Reaction of Phosphorus Compounds. V. Resonance-stabilized α-Halomethylenephosphoranes

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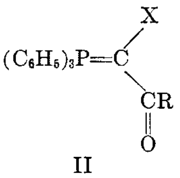
The synthesis of α-halo ylids stabilized by carbethoxy, benzoyl, and carbamyl groups has been demonstrated by two independent general methods. Dehalogenation of the phosphonium salts derived from the reaction of dichloromethylenetriphenylphosphorane and acyl halides constitutes the first method. The second involves dehydrohalogenation of phosphonium salts obtained by halogenation of ylids. These halo ylids undergo the Wittig reaction. A halogen atom attached alpha to a phosphonium group has been shown to be positive in character.

Dihalomethylenephosphoranes (I) react with aldehydes and ketones to give good yields of dihaloölefins.[1] Monochloromethylenephosphoranes have similarly proved useful in the preparation of monochloroölefins.[2] These ylids belong to the nonresonance-stabilized class of phosphinemethylenes and their preparation and use must be accomplished *in situ* because they are unstable under atmospheric conditions. The corresponding compounds (II. X = H)[4] containing an anion stabilizing group are isolable.[3-7] We now wish to report the preparation and Wittig reactions of resonance-stabilized halo ylids (II. X = halogen).

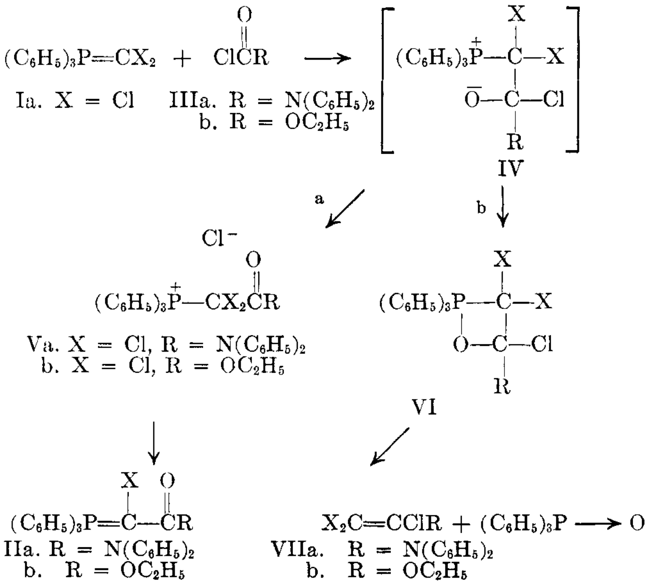
$(C_6H_5)_3P{=}CX_2$

I


$(C_6H_5)_3P{=}C(X)C(=O)R$

II

After our initial study[1] of phosphinedihalomethylenes (I), we turned to an investigation of additional reactions of this class of compounds. The reaction of these reagents with carbamyl chlorides and chloroformates was of special interest because of two possible reaction paths which could be envisioned. These are summarized as follows.



$(C_6H_5)_3P{=}CX_2 + ClC(=O)R \longrightarrow [(C_6H_5)_3\overset{+}{P}{-}CX_2{-}C(\overset{-}{O})(Cl)R]$ IV

Ia. X = Cl IIIa. R = $N(C_6H_5)_2$; b. R = OC_2H_5

$Cl^- \; (C_6H_5)_3\overset{+}{P}{-}CX_2C(=O)R$

Va. X = Cl, R = $N(C_6H_5)_2$
b. X = Cl, R = OC_2H_5

$(C_6H_5)_3P{=}C(X){-}C(=O)R$

IIa. R = $N(C_6H_5)_2$
b. R = OC_2H_5

$X_2C{=}CClR + (C_6H_5)_3P \longrightarrow O$

VIIa. R = $N(C_6H_5)_2$
b. R = OC_2H_5

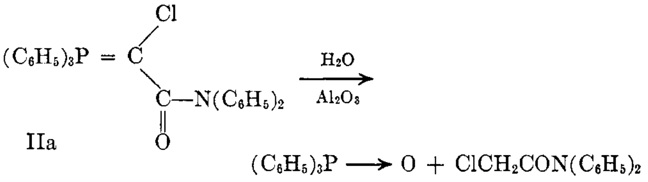
The initial stage of the reaction would undoubtedly proceed *via* the intermediate IV. The subsequent loss of chloride from IV leads to V *via* path a. An alternate possibility, however, involves attack of the oxyanion upon phosphorus to form a four-membered ring Wittig intermediate VI which could cleave to triphenylphosphine oxide and enamine VIIa or vinyl ether VIIb.

The reaction of phosphinemethylenes with acid halides has been reported by Bestmann[8] where R and X are alkyl or aryl groups. The initial product was the phosphonium chloride V rather than a vinyl chloride VII. This leads to the expectation that our reaction would proceed by path a above.

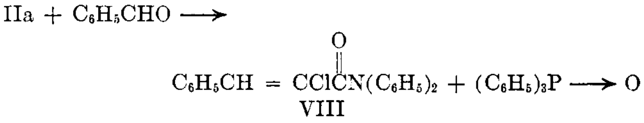
Addition of N,N-diphenylcarbamyl chloride IIIa to a suspension of dichloromethylenetriphenylphosphorane Ia in heptane at 0–5° produced a solid which, based on infrared analysis, contained triphenylphosphine oxide and a phosphonium chloride Va. Treatment of this crude solid with water and methanol produced chloro-N,N-diphenylcarbamylmethylenetriphenylphosphorane (IIa) in 17–24% yield.

The reaction of ethyl chloroformate IIIb with dichloromethylenetriphenylphosphorane, run under essentially similar conditions, gave a brown residue which upon extraction with water and addition of sodium hydroxide to this aqueous extract gave a 14% yield of carbethoxychloromethylenetriphenylphosphorane IIb.

The structure of the ylids (IIa,b) has been proven by hydrolytic cleavage on alumina and by Wittig reaction with aldehydes. The passage of IIa in chloroform over a column of alumina gave triphenylphosphine oxide and N,N-diphenyl-α-chloroacetamide. A Wittig reaction of the ylid IIa with benzaldehyde gave N,N-diphenyl-α-chlorocinnamamide (VIII). Carbethoxychlorometh-


IIa

$(C_6H_5)_3P{=}C(Cl){-}C(=O){-}N(C_6H_5)_2 \xrightarrow[Al_2O_3]{H_2O} (C_6H_5)_3P \longrightarrow O + ClCH_2CON(C_6H_5)_2$


$\text{IIa} + C_6H_5CHO \longrightarrow C_6H_5CH{=}CClC(=O)N(C_6H_5)_2 + (C_6H_5)_3P \longrightarrow O$

VIII

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[1] A. J. Speziale and K. W. Ratts, *J. Am. Chem. Soc.*, **84**, 854 (1962).

[2] (a) D. Seyferth, S. Grim, and T. O. Read, *ibid.*, **82**, 1510 (1960); (b) G. Wittig and M. Schlosser, *Angew. Chem.*, **72**, 324 (1960).

[3] S. Horner and H. Oediger, *Chem. Ber.*, **91**, 437 (1958).

[4] S. Trippett and D. M. Walker, *J. Chem. Soc.*, 3874 (1959).

[5] S. Trippett and D. M. Walker, *ibid.*, 1266 (1961).

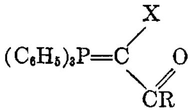
[6] F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

[7] O. Isler, H. Gutmann, M. Montavan R. Ruegg, G. Ryser, and P. Zeller, *Helv. Chim. Acta*, **50**, 1242 (1957).

[8] (a) H. J. Bestmann, *Tetrahedron Letters*, No. **4**, 7 (1960); (b) H. J. Bestmann and H. Schulz, *Angew. Chem.*, **72**, 572 (1960).

TABLE I

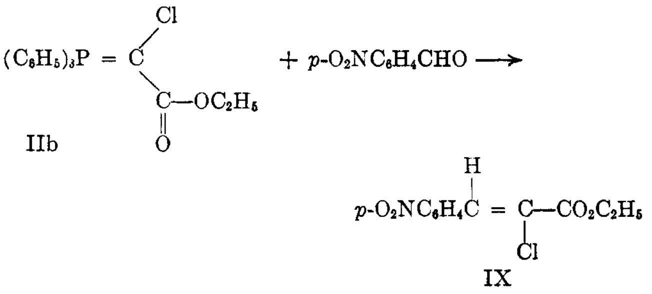
HALO YLIDS



X	R	M.p., °C.	Yield, %	Calcd. C	Calcd. H	Calcd. N	Calcd. P	Calcd. X	Found C	Found H	Found N	Found P	Found X
H	$N(C_6H_5)_2$	dec. ~180	85	81.51	5.56	2.97	6.57	...	81.78	5.46	2.87	6.62	
Cl	$N(C_6H_5)_2$	dec. ~170	67	75.96	4.98	2.77	6.12	7.01	76.35	5.14	2.91	6.15	7.11
Cl	OC_2H_5	147.5–148.5	50	69.01	5.27		8.09	9.26	69.77	5.36		7.90	9.15
Br	OC_2H_5[a]	155–156	91	61.80	4.68		7.27	18.75	61.98	4.65		7.41	19.02
Cl	C_6H_5	156–158	93	75.27	4.86		7.47	8.55	74.80	4.94		7.63	8.52
Br	C_6H_5	dec. prior to 151–152	91	67.98	4.39		6.74	17.40	68.46	4.32		6.89	17.23
I	C_6H_5	dec. prior to 186–187	44	61.67	3.98		6.12	25.06	61.68	3.63		6.23	24.83

[a] Originally prepared by Dr. C. C. Tung who obtained analytical values given.

ylenetriphenylphosphorane (IIb) when allowed to react with *p*-nitrobenzaldehyde gave a 73% yield of *trans*-ethyl-α-chloro-*p*-nitrocinnamate (IX).



IIb

IX

The low yields obtained in the aforementioned sequences led to a consideration of alternate methods for the preparation of resonance-stabilized halo ylids. There were, however, no reported instances of the preparation and use of resonance-stabilized halomethylenephosphoranes at the inception of this work.[9]

Treatment of the corresponding α-halomethylphosphonium salt X with sodium hydroxide or sodium carbonate in aqueous or alcoholic media gave the halo ylids II.

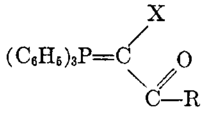
The prepared halogenated ylids, given in Table I, include chlorine, bromine, and iodine as the halogen substituents and carbamoyl, carbethoxy, and benzoyl as the R group.

The spectral properties of the ylids are given in Table II. A band associated with tetravalent phosphorus was found in all the ylids near 1105 cm.$^{-1}$. A strong unassigned band was also found between 1290–1390 cm.$^{-1}$. The carbonyl band was strongly shifted to a lower frequency than ordinarily found for C=O groups. The ultraviolet spectra of most of the ylids in absolute ethanol exhibited a longer wave length band (285–316 mμ). Bands due to the phenyl rings were found in all the ylids (260, 266, and 272 mμ) and are not listed.

The phosphonium salts X were easily prepared in high yields by the addition of halogen to the ylid in chloroform at 0–5°.[10]

TABLE II

Halo Ylids



Infrared spectra[a]

X	R	$\nu_{=C-H}$ cm.$^{-1}$	$\nu_{C=O}$ cm.$^{-1}$	$\nu_{(C_6H_5)_3\overset{+}{P}-}$ cm.$^{-1}$	$\nu_{unassigned}$ cm.$^{-1}$
H	$N(C_6H_5)_2$	888	1570	1105, 1137	1368
Cl	$N(C_6H_5)_2$		1545	1105	1333
H	OC_2H_5	892	1620	1108, 1125	1336, 1380
Cl	OC_2H_5		1665	1105	1260
Br	OC_2H_5		1656	1107, 1101	1310
H	C_6H_5	875, 891	1530	1106	1390
Cl	C_6H_5		1476	1103	1390
Br	C_6H_5		1475	1105	1383
I	C_6H_5		1470	1108	1365

Ultraviolet spectra[b] (absolute ethanol)

X	R	λ_{max} mμ	$\log_{10} \epsilon$
H	$N(C_6H_5)_2$	None	...
Cl	$N(C_6H_5)_2$	None	...
H	OC_2H_5	288 (shoulder)	3.53
Cl	OC_2H_5	288 (shoulder)	3.93
Br	OC_2H_5	299	3.93
H	C_6H_5	321	4.05
Cl	C_6H_5	327	3.72
Br	C_6H_5	318	3.64
I	C_6H_5	291 (shoulder)	3.70

[a] All infrared spectra were obtained as mulls with Nujol on a Beckman IR-5A infrared spectrophotometer. [b] The ultraviolet spectra were obtained using a Beckman DK-2A ratio recording spectrophotometer.

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(9) Subsequently the synthesis and Wittig reactions of II (X = Cl, Br, I; and R = OCH_3) has been reported by G. Markl, *Chem. Ber.*, **94**, 2996 (1961). D. B. Denney and S. T. Ross, *J. Org. Chem.*, **27**, 998 (1962), have also investigated the synthesis of II (X = Cl, Br; R = OC_2H_5 and C_6H_5). In both instances the preparation involved dehydrohalogenation of an α-halomethylphosphonium salt.

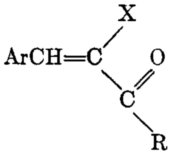
(10) The phenacylidenetriphenylphosphorane was not completely consumed upon treatment with two moles of iodine as it was with one mole of chlorine. The decreased basicity of the ylid due to the benzoyl group and the steric inhibition to addition of the large iodine molecule shifts the following equilibrium to the left.

$$(C_6H_5)_3P{=}CHCOC_6H_5 + I_2 \rightleftharpoons [(C_6H_5)_3\overset{+}{P}CHICOC_6H_5]I^-$$

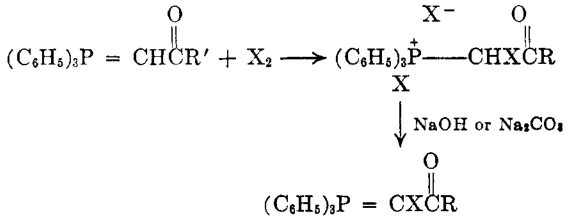
The desired α-halophosphonium salts (X) could not be prepared by nucleophilic displacement of an α-halogen atom by triphenylphosphine from a dichloroamide or ester. In the case of amides this reaction has been shown to lead to appreciable amounts of enamine whereas the reaction of dihalo esters, to our knowledge, has not been reported. For example, an 84% yield of N,N-diphenyl-1,2-dichlorovinylamine is obtained upon reaction of triphenylphosphine with N,N-diphenyl-α,α-dichloroacetamide, see A. J. Speziale and L. R. Smith, *J. Am. Chem. Soc.*, **84**, 1868 (1962). An attempt to prepare the desired phosphonium salt from triphenyl- or tributylphosphine and ethyl chlorofluoroacetate was unsuccessful. Expectedly the attached fluorine atom would decrease the ease of displacement of chloride.

TABLE III

α-HALO-α,β-UNSATURATED COMPOUNDS



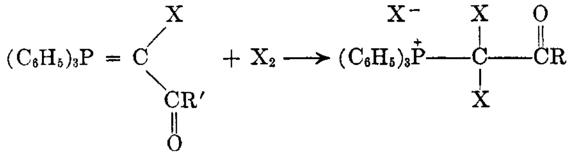
Ar	X	R	M.p., °C.	Yield, %	Calcd.				Found			
					C	H	Cl	N	C	H	Cl	N
C_6H_5	Cl	$N(C_6H_5)_2$	113–114	52	75.55	4.83	10.62	4.20	76.17	4.69	10.28	4.25
4-$O_2NC_6H_4$—	Cl	OC_2H_5	111	73	51.67	3.94	13.87	5.48	52.12	3.95	13.79	5.30
4-$O_2NC_6H_4$—	Cl	C_6H_5	68–69	57	62.62	3.50	12.33	4.87	63.17	3.56	11.94	4.82



$$(C_6H_5)_3P=CH\overset{O}{\overset{\|}{C}}R' + X_2 \longrightarrow (C_6H_5)_3\overset{+}{P}\text{—}CHX\overset{O}{\overset{\|}{C}}R\ \ X^- \xrightarrow{NaOH\ or\ Na_2CO_3} (C_6H_5)_3P=CX\overset{O}{\overset{\|}{C}}R$$

IIa. R = $N(C_6H_5)_2$
b. R = OC_2H_5
c. R = C_6H_5

The halo ylids were also halogenated to give α,α-dihalosubstituted phosphonium halides V as indicated.



$$(C_6H_5)_3P=C\begin{matrix}X\\ \overset{\|}{\underset{O}{C}}R'\end{matrix} + X_2 \longrightarrow (C_6H_5)_3\overset{+}{P}\text{—}\underset{X}{\overset{X}{C}}\text{—}\overset{O}{\overset{\|}{C}}R\ \ X^-$$

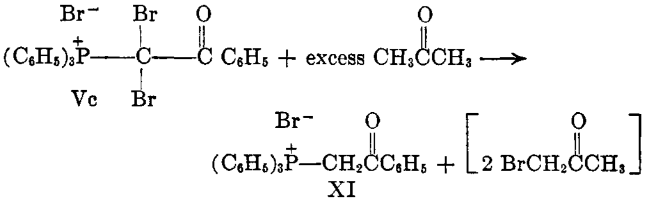
Va. X = Cl, R = $N(C_6H_5)_2$
b. X = Cl, R = OC_2H_5
c. X = Br, R = C_6H_5

This reaction has allowed the preparation of Va and Vb. Although Va was obtained as an oil, its infrared spectrum was almost identical with those of the corresponding salts where one or both α-hydrogen atoms are replaced by halogen. Hydrolytic cleavage of Va on alumina gave triphenylphosphine oxide and N,N-diphenyl-α,α-dichloroacetamide further confirming the proposed structure. Vc was a crystalline compound.

The halo ylids produced by the reaction of N,N-diphenylcarbamyl chloride and ethyl chloroformate with dichloromethylenetriphenylphosphorane must arise from dechlorination of intermediate α,α-dihalosubstituted phosphonium halides (V). The formation of these salts in the initial stage of the reaction, and the fact that no enamine[11] VIIa or vinyl ether VIIb was formed, indicate that the reactions do not proceed *via* a four-membered ring (type VI); but rather that chloride is lost from intermediate IV.

The independent preparation of the proposed intermediates V allowed a more direct study of the dehalogenation step which led to IIa and b in the reaction of dichloromethylenetriphenylphosphorane with N,N-diphenylcarbamyl chloride and ethyl chloroformate. In the original reaction (I→V→II) the ylid II was not produced until water or methanol was added. However, treatment of Va and b with water or methanol alone did not produce any halo ylids in times comparable with the original work-up procedure. Apparently some combination of water or methanol with triphenylphosphine, dichloromethylenetriphenylphosphorane, or potassium *t*-butoxide was the effective dehalogenating agent for Va and b. Treatment of the salt Va with triphenylphosphine in methanol did not cause dehalogenation since no halo ylid was formed. Possibly hydroxides formed by the reaction of dichloromethylenetriphenylphosphorane and potassium *t*-butoxide, under work-up conditions, would effect such a reaction. Indeed, treatment of the phosphonium salts (Va and b) with aqueous sodium hydroxide produced the halo ylids IIa and b in 34 and 30% yield, respectively. Two conceivable points of attack of hydroxide on such phosphonium salts would be at the phosphorus atom, leading to triphenylphosphine oxide and dichloroamide, and at the carbonyl carbon which would lead to hydrolysis of the amide or ester grouping. The formation of the chloro ylids means that attack on halogen is competing effectively with the other possibilities.[12]

The positive nature of halogen atoms attached to an alpha carbon atom of a phosphonium salt must be related to the large resonance stabilization of the derived ylid. The use of these phosphonium salts as halogenating agents has been demonstrated by the bromination of acetone with α,α-dibromophenacyltriphenylphosphonium bromide (Vc). Phenacyltriphenylphosphonium bromide (XI) was obtained in 89% yield indicating that the intermediate α-bromophenacyltriphenylphosphonium bromide (X. X = Br, R = C_6H_5) is also capable of brominating acetone. Bromoacetone was isolated as the acetonyltriphenylphosphonium bromide derivative in 44% yield (assuming two equivalents should be formed).



$$(C_6H_5)_3\overset{+}{P}\text{—}\underset{Br}{\overset{Br}{C}}\text{—}\overset{O}{\overset{\|}{C}}C_6H_5\ Br^- + \text{excess } CH_3\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow (C_6H_5)_3\overset{+}{P}\text{—}CH_2\overset{O}{\overset{\|}{C}}C_6H_5\ Br^- + \left[2\ BrCH_2\overset{O}{\overset{\|}{C}}CH_3\right]$$

Vc

XI

Table III gives the α-halo-α,β-unsaturated carbonyl compounds prepared by the reaction of halo ylids with aldehydes. The reactions were carried out by refluxing the reactants in chloroform solution for varying periods of time. The *cis–trans* geometry of only one of the products (IX) is known. The fact that IX is *trans* suggests that the other products (VIII; IX. OEt = C_6H_5) probably have the same geometry. We have

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[11] N,N-Diphenyl-1,2,2-trichlorovinylamine has been shown to be isolable. [A. J. Speziale and R. C. Freeman, *J. Am. Chem. Soc.*, **82**, 903 (1960)].

[12] Seyferth has shown that the action of strong bases such as alkyllithium compounds will remove halogen from halomethylphosphonium halides competitively with removal of hydrogen halides, see D. Seyferth, J. Heeren, and S. Grim, *J. Org. Chem.*, **26**, 4784 (1961). This dehalogenation is similar to our reaction in that it may be initiated by a nucleophilic attack of the carbanion of the organometallic compound upon halogen.

observed no evidence for the formation of any other isomers. Although more work on this point is forthcoming, the reactions appear to a large extent to be stereospecific.[13]

Halo ylids are hereby made available by two synthetic procedures. This new class of phosphinemethylenes was prepared by dehydrohalogenation of α-halophosphonium salts obtained by halogenation of known ylids. An interesting preparation of the same halo ylids involving dehalogenation of α,α-dihalophosphonium salts by base provides an alternate synthesis. The reaction of the newly prepared halo ylids with aldehydes provides a useful synthesis of α-halo-α,β-unsaturated compounds.

Experimental[14]

Chloro-N,N-diphenylcarbamylmethylenetriphenylphosphorane (IIa). A. From Dichloromethylenetriphenylphosphorane.—N,N-Diphenylcarbamyl chloride (23.2 g., 0.1 mole) in benzene (60 ml.) was added to a suspension of dichloromethylenetriphenylphosphorane[1] (0.1 mole) in *n*-heptane (100 ml.). The mixture was stirred at 45° for 3 hr. and filtered. The residue was washed with *n*-heptane (2 × 250 ml.) and the washings combined with the filtrate. The filtrate and washings were concentrated to an oil which was crystallized from methanol to give 10.8 g. (47%) of N,N-diphenylcarbamyl chloride. Concentration of the mother liquor gave a gummy solid, 11.6 g., which was shown by infrared analysis to be a mixture of N,N-diphenylcarbamyl chloride and triphenylphosphine oxide. The residue (38.4 g.) was digested with methanol (100 ml.) and the mixture filtered to give an amorphous solid and a dark brown filtrate. Concentration of the filtrate gave 21.5 g. (77%) of triphenylphosphine oxide. The solid was washed with water (200 ml.) to leave 8.5 g. (17%) of chloro-N,N-diphenylcarbamylmethylenetriphenylphosphorane, decomposition at 170°, which was unchanged upon two recrystallizations from chloroform–hexane. Potentiometric analysis of the water extract indicated 0.093 mole of chloride ion.

The experiment was repeated using a slight excess of potassium *t*-butoxide (0.13 mole) to give 12.0 g. (24%) of the product.

B. From Chloro-N,N-diphenylcarbamylmethyltriphenylphosphonium Chloride.—Chloro-N,N-diphenylcarbamylmethyltriphenylphosphonium chloride (5.4 g., 0.01 mole) was dissolved in water (1 l.) and 40 ml. of 0.5 *N* sodium hydroxide was added with stirring at room temperature. The mixture was filtered and the filter cake air dried to give 5.2 g. of solid. The infrared spectrum of the crude material was identical to the once-recrystallized (chloroform–hexane) chloro-N,N-diphenylcarbamylmethylenetriphenylphosphorane, 3.6 g. (67%), m.p. decomposition at about 170°. The above procedure is representative of that used in the preparation of other halo ylids.

Chloro-N,N-diphenylcarbamylmethyltriphenylphosphonium Chloride [X. X = Cl, R = $N(C_6H_5)_2$].—Triphenylphosphine (26.2 g., 0.1 mole) and N,N-diphenyl-α-chloroacetamide (25.5 g., 0.1 mole) were refluxed for 27 hr. in benzene (100 ml.). The mixture was filtered to yield 39.5 g. (83%) of N,N-diphenylcarbamylmethyltriphenylphosphonium chloride, decomposition at about 200°.

Anal. Calcd. for $C_{32}H_{27}ClNOP$: C, 75.66; H, 5.36; total and ionic Cl, 6.98; N, 2.76; P, 6.10. Found: C, 75.29; H, 5.05; total Cl, 6.99; ionic Cl, 6.88; N, 2.90; P, 6.12.

The infrared spectrum (Mull) exhibits the following bands: $_{C=O}$ 1675 cm.$^{-1}$; $\nu_{(C_5H_5)_3P^{\pm}}$ 1111 cm.$^{-1}$; $\nu^{+}{-}\overset{|}{\underset{|}{C}}{-H}$ 2725 cm.$^{-1}$.

Repetition of this preparation on a 0.3-mole scale using a 2-day reflux period gave an 89% yield.

To a solution of 15.6 g. (0.033 mole) of the above phosphonium salt in water (300 ml.) at 0° was added 140 ml. (0.07 mole) of 0.5 *N* sodium hydroxide. The mixture was stirred 10–15 min. and filtered. Upon drying the solid and recrystallizing it from chloroform–hexane there was obtained 11.9 g. (85%) of N,N-diphenylcarbamylmethylenetriphenylphosphorane, decomposition about 180°.

Repetition of the above experiment on a 0.275-mole scale in 6 l. of water gave an 86% yield.

The above ylid (4.7 g., 0.01 mole) was dissolved in chloroform (20 ml.) and chlorine (4.0 g., 0.011 mole) was added at 0°. The solution was allowed to warm to room temperature and then concentrated to an oil. Benzene (50 ml.) was added and the mixture evaporated until a solid formed. The hygroscopic solid was removed by filtration to give 5.0 g. (93%) of chloro-N,N-diphenylcarbamylmethyltriphenylphosphonium chloride, decomposition about 185–190°.

Anal. Calcd. for $C_{32}H_{26}ClNOP$: total Cl, 13.07; ionic Cl, 6.54. Found: total Cl, 12.77; ionic Cl, 6.32.

The infrared spectrum (Mull) exhibited characteristic bands: $\nu_{C=O}$ 1660 cm.$^{-1}$; $\nu_{(C_6H_5)_3\overset{+}{P}-}$ 1116 cm.$^{-1}$, and $\nu_{\overset{+}{P}}\ \overset{|}{\underset{|}{C}}{-H}$ 2720 cm.$^{-1}$.

Repetition of the above experiment, but saturating the ylid solution with chlorine, at 0° gave a 73% yield.

Carbethoxychloromethylenetriphenylphosphorane (IIb). A. From Dichloromethylenetriphenyl Phosphorane.—Ethyl chloroformate (10.8 g., 0.1 mole) was added to a suspension of dichloromethylenetriphenylphosphorane (0.1 mole) in *n*-heptane (100 ml.) at 0–10°. The mixture was stirred at room temperature for 7 hr. and let stand 9 hr. The brown residue was removed by filtration and added to 2 l. of ice–water. After thorough stirring the solid was removed by filtration and sodium hydroxide (0.5 *N*) was added to neutralize the aqueous phosphonium salt (to phenolphthalein). The supernatant liquid was decanted and the residual gum dissolved in methylene chloride. The aqueous supernatant liquid was extracted with 200 ml. of methylene chloride three times, and the washings combined with the methylene chloride solution. The organic layer was dried over magnesium sulfate and concentrated to an oil. Crystallization of this oil from chloroform–pentane gave 5.2 g. (14%) of carbethoxychloromethylenetriphenylphosphorane. Triphenylphosphine oxide in 56% yield and 0.09 mole of chloride was isolated from the residues, mother liquors, and aqueous portions which remained. The mother liquors from the chloro ylid also yielded 0.7 g. (2%) of carbethoxymethylenetriphenylphosphorane.

B. From Carbethoxychloromethyltriphenylphosphonium Chloride.—Chlorine (21.3 g., 0.3 mole) was dissolved in chloroform (400 ml.) at 0° and carbethoxychloromethylenetriphenylphosphorane[7] (104.5 g., 0.3 mole) in chloroform was added whereupon immediate decoloration occurred. After allowing it to warm to room temperature, the solution was concentrated.

The oil was dissolved in methylene chloride (500 ml.), and the solution extracted three times with an equivalent of sodium carbonate in 200 ml. of water. The organic layer was dried over magnesium sulfate and concentrated. Addition of pentane gave 79.5 g. (69%) of carbethoxychloromethylenetriphenylphosphorane, m.p. 146–148°. The above procedure is representative of an alternate procedure used in the preparation of other haloylids.

Cleavage of Chloro-N,N-diphenylcarbamylmethylenetriphenylphosphorane on Alumina.—The above ylid (2.0 g.) was dissolved in chloroform (25 ml.) and chromatographed on a 3 × 10 cm. column of Fischer A540 alumina with chloroform. The eluant (250 ml.) was collected and concentrated to 2.0 g. of a yellow oil. Crystallization of the oil from benzene–hexane gave 0.8 g. yellow solid which by infrared analysis was a mixture of starting material and triphenylphosphine oxide. Concentration of the mother liquor gave an additional 0.8 g. which possessed infrared bands characteristic of triphenylphosphine oxide and C=O, 1670 cm.$^{-1}$. The latter 0.8 g. was chromatographed in benzene to give a colorless solid which upon three recrystallizations from benzene–hexane gave N,N-diphenyl-α-chloroacetamide, m.p. 117.5–118.5. A chromatography in chloroform on a column of Fischer A540 alumina yielded a product which upon two recrystallizations from ethanol gave N,N-diphenyl-α-chloroacetamide, m.p. 118–119°, directly.

N,N-Diphenyl-α-chlorocinnamamide (VIII).—Chloro-N,N-diphenylcarbamylmethylenetriphenylphosphorane (7.7 g., 0.015 mole) and benzaldehyde (1.1 g., 0.010 mole) were dissolved in 100 ml. chloroform and refluxed 26 hr., then let stand at room temperature 2 days. No infrared bands near 1342 cm.$^{-1}$ and 1550 cm.$^{-1}$ remained at this point. The solution was concentrated and the resulting oil was extracted with hexane to leave 2.2 g. The hexane extract was evaporated to a small volume and 1.8 g. (70%) crude triphenylphosphine oxide was removed by filtration. The hexane filtrate was concentrated and the residue twice re-

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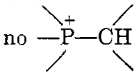
[13] H. O. House and G. H. Rasmusson, *J. Org. Chem.*, **26**, 4278 (1961); reaction of α-carbomethoxyethylidenetriphenylphosphorane with acetaldehyde has been observed to be stereospecific in that the majority (96.5%) of the product obtained was *trans*.

[14] All melting points are uncorrected. Microanalyses were performed by Clark Microanalytical Laboratory, Urbana, Ill.

crystallized from ethanol to give 1.7 g. (52%), m.p. 113–114°, of N,N-diphenyl-α-chlorocinnamamide.

Ethyl *trans*-α-Chloro-*p*-nitrocinnamate (IX).—Carbethoxychloromethylenetriphenylphosphorane (12.8 g., 0.033 mole) and *p*-nitrobenzaldehyde (4.5 g., 0.030 mole) were dissolved in chloroform and refluxed 64 hr. The solvent was removed *in vacuo*, benzene (100 ml.) added, and followed by addition of hexane. Eight and seven-tenths grams of solid (by infrared analysis mostly triphenylphosphine oxide) was removed by filtration of the above mixture. The filtrate was concentrated to 8.0 g. of solid which was recrystallized from ethanol to give 2.7 g., m.p. 103.5–104.0°; 0.5 g., m.p. 93–98°. The above 8.7 g. of crude triphenylphosphine oxide was chromatographed in benzene on alumina to give an eluent containing a carbonyl compound which was combined with the above 2.7 g. and 0.5 g. and recrystallized to give 5.6 g. (73%) of ethyl *trans*-α-chloro-*p*-nitrocinnamate,[15] m.p. 111–121°.

Dichloro-N,N-diphenylcarbamylmethyltriphenylphosphonium Chloride (Va).—Chloro-N,N-diphenylcarbamylmethylenetriphenylphosphorane (10.1 g., 0.02 mole) was dissolved in chloroform, cooled and chlorine added for ~10 min. The solution was concentrated to an oil which could not be crystallized by azeotropic removal of water with benzene. The infrared spectrum indicates the following: no  $>\overset{+}{P}-CH<$ near 2720 cm.$^{-1}$; C=O, 1650 cm.$^{-1}$; unassigned band, 1100 cm.$^{-1}$, no ylid bands near 1350 cm.$^{-1}$ or 1560 cm.$^{-1}$. There were no bands present due to the starting ylid.

Dechlorination of Va with Sodium Hydroxide.—The phosphonium salt (0.004 mole) in 50 ml. of water was treated with 20 ml. of 1 *M* sodium hydroxide. A yellow solid formed immediately. It was removed by filtration from the mixture and dissolved in chloroform. The solution was dried over magnesium sulfate and upon addition of excess hexane gave 0.70 g. (35%) of chloro-N,N-diphenylcarbamylmethylenetriphenylphosphorane.

Repetition of the experiment on a 0.01-mole scale gave a 24% yield of ylid.

Dechlorination of Carbethoxydichloromethyltriphenylphosphonium Chloride (Vb) with Sodium Hydroxide.—Carbethoxychloromethylenetriphenylphosphorane (7.7 g., 0.02 mole) was dissolved in chloroform, cooled to 0°, then saturated with chlorine for 15 min. The solution was concentrated to an oil (infrared analysis indicated no starting ylid remained in this oil) and 0.5 *N* sodium hydroxide (50 ml.) added to the oil dissolved in ice–water (100 ml.). After thorough stirring the mixture was separated, the aqueous layer extracted with benzene (100 ml.), and the organic extract combined with the original organic layer. The benzene solution was dried over magnesium sulfate and concentrated to 7.3 g. of a light yellow oil. Crystallization of this oil from chloroform–pentane gave 2.3 g. (30%) of carbethoxychloromethylenetriphenylphosphorane and 2.3 g. (41%) of triphenylphosphine oxide.

Cleavage of Dichloro-N,N-diphenylcarbamylmethyltriphenylphosphonium Chloride on Alumina.—Chloro-N,N-diphenylcarbamylmethylenetriphenylphosphorane (10.1 g., 0.02 mole) was dissolved in chloroform (150 ml.) and saturated with chlorine for 5–10 min. The solution was concentrated to an oil and benzene (100 ml.) added. Removal of the benzene *in vacuo* gave no solid. The oil was dissolved in chloroform and eluted through a 2.5 × 17.0 cm. Fisher A540 alumina column. Concentration of all the eluents gave an oil which crystallized on standing. Filtration of the mixture and recrystallization of the solid gave 3.0 g. of triphenylphosphine oxide. Addition of hexane to the filtrate gave 1.0 g. additional triphenylphosphine oxide; total yield 4.0 g., 72%.

Concentration of the mother liquor from the original filtration gave 4.0 g. oil which exhibited a strong C=O band (1680 cm.$^{-1}$). Two recrystallizations of the oil from ethanol–water gave 1.0 g., m.p. 62–63°. The solid was chromatographed on a 2.5 × 25 cm. Fisher A540 alumina column in benzene to give 0.6 g. (11%) of N,N-diphenyl-α,α-dichloroacetamide, m.p. 79–81°.

α-Chloro-*p*-nitrochalcone.—α-Chlorophenacylidenetriphenylphosphorane (1.0 g., 0.0024 mole) and *p*-nitrobenzaldehyde (0.36 g., 0.0024 mole) were dissolved in chloroform (50 ml.), and refluxed 18 hr. The solvent was removed *in vacuo*, benzene added, and precipitation induced by addition of pentane to give 0.35 g. (52%) of triphenylphosphine oxide. Concentration of the filtrate and addition of a few drops of methanol followed by filtration, gave 0.28 g. (41%) m.p. 67–68°. Concentration of the filtrate gave an additional 0.11 g. (16%) m.p. 64–66°. Recrystallization of the above 0.39 g. gave α-chloro-*p*-nitrochalcone, m.p. 68–69°.

α,α-Dibromophenacyltriphenylphosphonium Bromide. (Vc).—Bromine (3.2 g., 0.02 mole) in chloroform (50 ml.) was added to α-bromophenacylidenetriphenylphosphorane in chloroform (100 ml.) at room temperature. The mixture was concentrated to an oil, benzene (100 ml.) added and then removed *in vacuo* to give an orange solid. After washing this solid with ether, benzene, and chloroform, drying gave m.p. 206.5–207.5° with decomposition.

Anal. Calcd. for $C_{26}H_{20}Br_3OP$: C, 50.43; H, 3.26; Br, 38.72; P, 5.00. Found: C, 47.89; H, 3.02; Br, 40.96; P, 4.84.

This material consistently gave erratic analytical results in spite of repeated recrystallizations. Infrared analysis, however, showed a strong similarity to α-bromophenacyltriphenylphosphonium bromide indicating the compound has a β-ketophosphonium structure.

Bromination of Acetone with α,α-Dibromophenacyltriphenylphosphonium Bromide.—Acetone (200 ml.) was added to α,α-dibromophenacyltriphenylphosphonium bromide (6.2 g., 0.01 mole) and the solution refluxed 24 hr. The mixture was filtered to give 3.5 g. (76%) phenacyltriphenylphosphonium bromide, m.p. 274.5–275.5°. This material was identical with an authentic sample prepared by treatment of the known chloride[16] with concentrated aqueous potassium bromide. Concentration of the remaining acetone solution and addition of benzene gave an additional 0.6 g. (13%) of this product.

Triphenylphosphine (14.0 g.) was added to the benzene solution and the mixture refluxed 2 hr., then filtered to give, upon recrystallization, 3.55 g. (44%) of acetonyltriphenylphosphonium bromide, m.p. 227–229°.

Anal. Calcd. for $C_{21}H_{20}BrOP$: C, 63.17; H, 5.05; Br, 20.02; P, 7.76. Found: C, 63.87; H, 4.95; Br, 20.1; P, 7.62.

An authentic sample, identical in all respects, was prepared in 83% yield by treatment of acetonyltriphenylphosphonium chloride[16] with concentrated aqueous potassium bromide.

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(15) P. Pfeiffer, *Chem. Ber.*, **47**, 1766 (1914).

(16) Prepared by the procedure of Ramirez, ref. 6. *Anal.* Calcd. for $C_{21}H_{20}ClOP$: C, 71.08; H, 5.68; Cl, 9.99. Found: C, 69.96; H, 5.62; Cl, 10.14.