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STUDY OF THE ALKALINE CLEAVAGE OF THE P-C BOND IN PHOSPHINE OXIDES AND DERIVATIVES OF TRICHLOROMETHANEPHOSPHONATE

Gunnar Aksnes^a; Roald Gierstae^a; Erik A. Wulvik^a

^a Chemical Institute, University of Bergen, Bergen, Norway

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STUDY OF THE ALKALINE CLEAVAGE OF THE P—C BOND IN PHOSPHINE OXIDES AND DERIVATIVES OF TRICHLOROMETHANEPHOSPHONATE

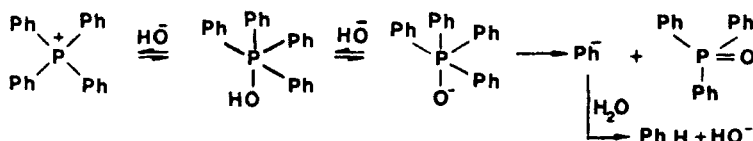
GUNNAR AKSNES, ROALD GIERSTAE and ERIK A. WULVIK

Chemical Institute, University of Bergen, N-5007 Bergen, Norway

(Received March 7, 1988)

A study of alkaline decomposition of several aromatic phosphine oxides containing *p*- and *o*-nitrobenzyl, and trichloromethyl as leaving groups, is reported. The property of the trichloromethyl group as leaving group, and the CCl₃-group's further decomposition in the hydrolysis of diethyl and disodium trichloromethanephosphonates, have also been investigated.

The resistance of alkyl and aryl substituted phosphonium compounds towards cleavage by hydroxyl ions is very dependent on the electronegativity of the substituents, as well as the resonance stabilization of the leaving carbanion. In fact, phosphonium cations containing exclusively alkyl groups require high hydroxyl concentration and high temperature to break the P—C bond.¹ From many rate studies it is well known that the decomposition can be fairly well described by overall third order kinetics, first order in phosphonium ions, and second order in hydroxyl ions. The rate law is in accordance with the following reaction scheme.²⁻⁴



SCHEME 1

Decomposition of the negatively charged pentacovalent intermediate is rate determining, and the transformation of the P—O⁻ bond to the strong P=O bond is supposed to be the driving force during the cleavage of the P—C bond.

Since phosphine oxides already contain the P=O bond it is reasonable that they are more stable than phosphonium compounds towards alkaline cleavage. In fact, it is usually necessary to heat alkyl substituted phosphine oxides with solid sodium or potassium hydroxide in order to break the P—C bond.⁵ However, diphenylbenzyl phosphine oxide has been found to decompose in KOH/DMSO/H₂O solvent mixtures.⁶

With regard to esters of phosphinic and phosphonic acids, it is usually unlikely that they undergo P—C in preference to P—O cleavage during hydrolysis, but an

exception will be reported in the present paper for diethyl trichloromethanephosphonate. However, salts of phosphinic and phosphonic acids undergo P—C cleavage under forced conditions, or when the leaving carbanion is sufficiently resonance stabilized, as f.ex. the *p*-nitrobenzyl group.⁷ The decomposition of disodium trichloromethanephosphonate is reported in this paper.

ALKALINE DECOMPOSITION OF NITROBENZYL SUBSTITUTED PHOSPHINE OXIDES IN METHANOL/WATER SOLVENT MIXTURE

Rate data and activation parameters of the alkaline decomposition of several aromatic phosphine oxides in 90% methanol/water are recorded in Table I. From product analysis it was found that the leaving groups were *p*- or *o*-nitrobenzyl groups in compounds I–IV in Table I. When the rates of III and IV, having the

TABLE I

Rate constants and activation parameters for the alkaline decomposition of aromatic phosphine oxides in 90% methanol/water

		Temp °C	KOH N	Rate const. $l^2 M^{-2} s^{-2}$ $\times 10^5$	Activation energy E kcal/M	Activation entropy, ΔS^\ddagger , E. U.
I		25.00	5.55	1.08	18	-24
		34.15	5.49	2.70		
		42.95	5.57	5.88		
		30.00	—	1.78(calc.)	21	-13
			2.83			
			2.87	0.78		
II		29.50	2.98	2.62	20	-18
		40.15	—	7.21		
		49.70	—	0.81(calc.)		
		30.00	—	0.69	18	-19
		24.90	5.17	1.54		
		34.40	4.78	4.20		
III		44.90	5.44	11.94(calc.)	17	-14
		53.15	5.27	34.6		
		38.40	3.21	62.0		
		44.65	2.39	124	18	+17
		52.70	2.64	15.5(calc.)		
		30.00	—	149		
IV		14.90	2.50	439	25	+4
		25.40	2.36	948		
		33.80	2.36	676(calc.)		
		30.00	—	3.6 × 10 ⁴	18	+5.6
		21.0	1–6 × 10 ⁻⁴	9.6 × 10 ⁴		
		31.0	1–6 × 10 ⁻⁴	9 × 10 ⁴ (calc.)		
V		30.0	—	16.4(2.order)	20	-25
		35.0	0.2476	60.0(2.order)		
		45.0	0.2476	8.1(calc)		
		30.00	—	27.2(2.order)	25	+5.6
		30	At pH = 11			
			in 95%			
VI		40	H ₂ O/EtOH	100	25	+5.6
		80	0.046 M	0.05(1.order)		
			acid in			
		90	0.25 M NaOH	0.11	20	-25
VII						
VIII						

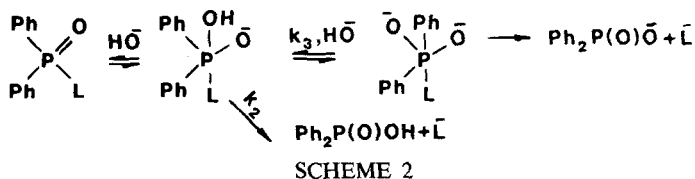
TABLE II

Comparison of second and third order rate constants in the alkaline hydrolysis of $(m\text{-NO}_2\text{Ph})_2\text{P}(\text{O})\text{CH}_2\text{Ph-}p\text{-NO}_2$ at different KOH concentrations. Temp. 25°C

Conc. KOH	Rate constant	
	2. order $1\text{ M}^{-1}\text{ s}^{-1} \times 10^2$	3. order $1^2\text{ M}^{-2}\text{ s}^{-2} \times 10^3$
2.315	0.98	4.24
2.361	1.04	4.39
2.786	1.18	4.23
3.092	1.33	4.29

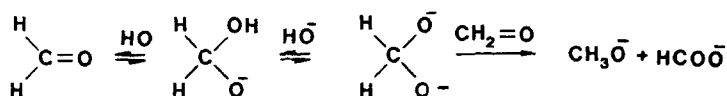
same leaving group (*p*-nitrobenzyl), but where IV has one more *m*-nitrophenyl group than III, the rate of the former is approximately 40 times higher at 30°C. If the statistical factor of two *p*-nitrobenzyl groups in compound III is taken into consideration, the rate accelerating effect is 80 times greater for *m*-nitrophenyl than *p*-nitrobenzyl when present as non-leaving substituent, in accordance with its greater electron attracting power.

The rate constants in Table I are calculated as overall 3. order constants, 1. order in phosphonium ions, and 2. order in hydroxyl ions. Measurements of phosphine oxide III at four concentrations of KOH showed that the rate was better expressed as second than first order in hydroxyl concentration (Table II). Unfortunately, the low reactivity of the *p*- and *o*-nitrobenzyl substituted phosphine oxides prevented studies at low hydroxyl concentrations. But the less stable trichloromethyl substituted phosphine oxide (VI) which could be studied around 0.2 M concentration of hydroxyl ions in 90% methanol/water was found to follow 1. order dependence on hydroxyl ions to at least 70% decomposition. Haake and Allen⁶ have also shown that $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{Ph}$ is decomposed according to 1. order rate dependence on HO^- in the concentration range 0.03–0.1 M KOH in 70.3 mol% DMSO/water where the HO^- ions are extraordinary active. A reaction scheme which may explain the change in reaction order with decreasing hydroxyl concentration is the following:



The kinetic of the reaction route through the double charged pentacovalent anion (Scheme 2) is approx 2. order in hydroxyl when $k_3[\text{HO}^-] > k_2$, but of mixed order when $k_3[\text{HO}^-] \sim k_2$. When $k_2[\text{HO}^-] < k_2$, the kinetic of the overall reaction ought to approach towards 1. order dependence on HO^- -concentration. This means that if the two decomposition routes in Scheme 2 are of comparable magnitude, the route through the dianion will increase more rapidly with increasing hydroxyl concentrations, and the observed change in reaction constants in Table II is accounted for. The suggested reaction scheme has much in common with the Cannizzaro reaction where the hydrid ion is assumed to be displaced

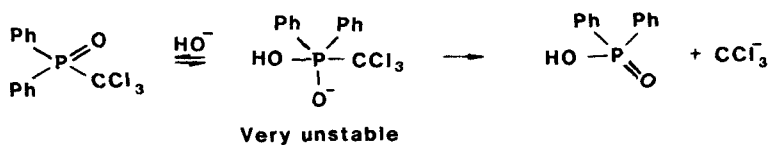
from a double charged anion intermediate:⁸



SCHEME 3

The dependence of the activation parameters on the hydroxyl concentration in the decomposition of phosphine oxides is illustrated by compound I in Table I. The activation energy is approximately 2.5 kcal/M lower in 5.5 M than in 2.8 M KOH solution. This effect is, however, counteracted by a much more unfavourable activation entropy which is 11 E.U. more negative. The change in the activation parameters may reflect mechanistic changes (Scheme 2), but salt effects might also be of considerable importance. It is interesting that the activation energy of displacing the *p*-nitrobenzyl group in the phosphine oxides studied which vary between 17 and 21 kcal/M, is almost equal to the activation energy of displacing the *p*-nitrobenzyl group in *p*-nitrobenzyltriphenylphosphonium bromide (18 kcal/M for V in Table I) in spite of that the rate of the latter is 10^4 – 10^6 times higher than the rate of the phosphine oxides. The rate difference is thus chiefly due to a much more positive activation entropy. The mechanism outlined in Scheme 2 where two negatively charged ions must approach each other in forming the rate determining step, will strongly contribute to such an unfavourable entropy. The opposite effect will dominate in the first step of phosphonium decomposition which represents an encounter of opposite charged ions.

As mentioned previously the trichloromethyl group in diphenyltrichloromethyl phosphine oxide is displaced during alkaline hydrolysis in approximately 0.2 M KOH solution according to 1. order rate dependence on hydroxyl ions (VI in Table I). Although the rate of the decomposition is much faster in comparison with phosphine oxides containing *p*-nitrobenzyl as leaving group (approx. 30 times when the different reaction order is considered), the activation energy is on the average still 6–7 kcal/M higher. But this extra energy is more than compensated for by the activation entropy which is around 20 E.U. more positive. The result is remarkable since entropy values of this magnitude are usually observed only for unimolecular reactions. However, the alkaline hydrolysis of diethyl trichloromethanephosphonate where CCl_3^- is the leaving group (which will be discussed later) has comparable activation parameters, and similar very favourable entropy value (VII in Table I). The effect is therefore most likely connected with the properties of the trichloromethyl group, its high electronegativity, polarisability, and bulky size. When the activation data are viewed in relation to the 1. order rate dependence on HO^- ions, it suggests formation of a very unstable intermediate or transition state:

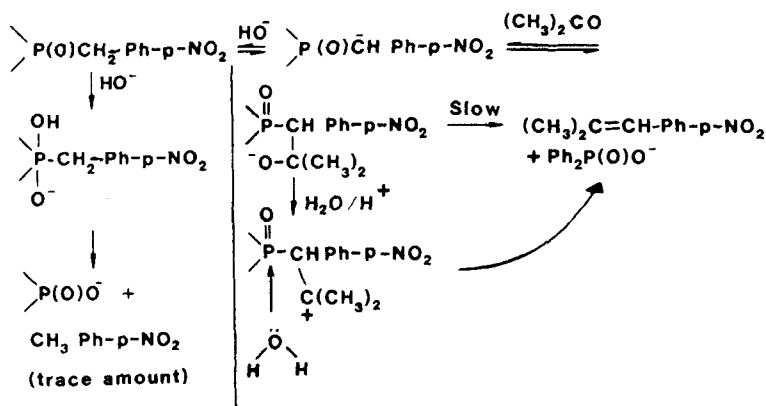


SCHEME 4

ALKALINE DECOMPOSITION OF *p*-NITROBENZYL SUBSTITUTED PHOSPHINE OXIDES IN ACETONE/WATER SOLVENT MIXTURE

$(\text{CH}_3)_2\text{C}=\text{CH}-\text{C}\begin{matrix} \nearrow \text{CH}_3 \\ \searrow \text{O} \end{matrix}$, were detected. The former was identified gaschroma-

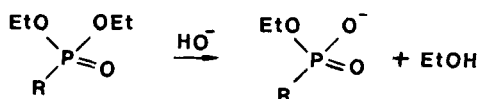
ographically by comparing it with a known specimen. Prolonged reaction time, higher temperature, and greater concentration of KOH resulted in the same olefine together with trace amount of the direct displacement product, *p*-nitrotoluene. The experimental findings are summarized in the reaction Scheme 5, where formation of the tertiary carbonium ion in acid, followed by P—C splitting, is supposed to take place.



SCHEME 5

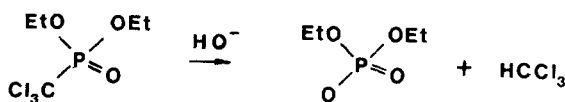
P—C BOND CLEAVAGE IN DERIVATIVES OF TRICHLOROMETHANEPHOSPHINIC ACID

Diethyl methanephosphonate and its mono-, and dichloro-substituted analogs show normal P—O (or C—O) bond cleavage during alkaline hydrolysis ($R = CH_3, CH_2Cl, CHCl_2$):⁹



SCHEME 6

In an unpublished study twenty years ago we observed that the corresponding trichloro-substituted ester reacted differently under the same conditions, giving rise to chloroform:

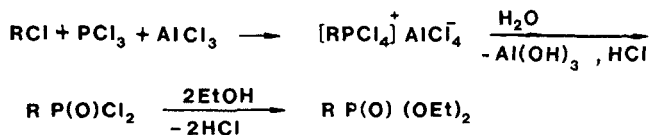


SCHEME 7

The change of mechanism from P—O (or C—O) to P—C bond cleavage seemed so intriguing, especially in relation to similar P—C cleavage in phosphine oxide, and in the dianion of trichloromethanephosphonic acid, that we decided to study the hydrolysis of the diethyl ester in greater details than earlier. Prior to the hydrolytic study we were met with unexpected problems during synthesis of the diester through ethanolysis of trichloromethyl phosphonyldichloride. Since we feel that these findings have relevance to the reactivity properties of phosphonyl compounds containing the CCl_3 -group they are reported here.

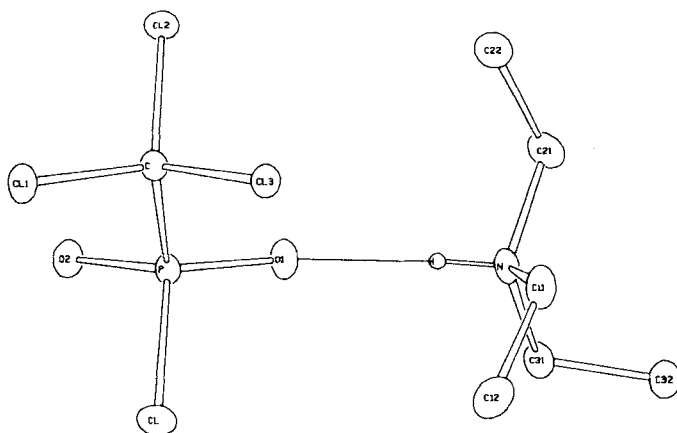
ETHANOLYSIS OF TRICHLOROMETHYL PHOSPHONYL DICHLORIDE

Esters of alkanephosphonic acids are usually synthesised in good yields from the respective phosphonyl dichlorides obtained by the method of Kinnear and Perren:¹⁰



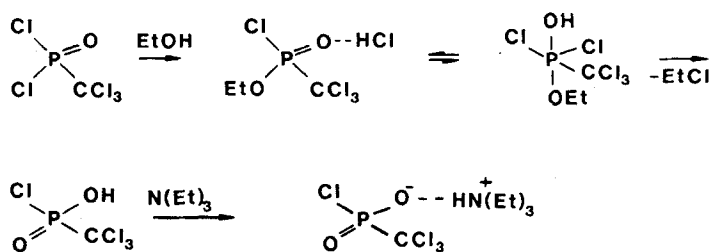
SCHEME 8

Since the ethanolysis in the last step gave unexpected poor yields the CCl_3 group was suspected to interfere in the substitution process. Tertiary base is

FIGURE 1 Structure of $\text{Cl}_3\text{CP}(\text{O})(\text{Cl})\text{O}^- \cdots \text{H}-\text{N}^+(\text{C}_2\text{H}_5)_3$.

usually added in stoichiometric amount in the alcoholysis step to counteract any interference from HCl which is set free in the reaction. But addition of excess alcohol to the phosphonyl dichloride followed by lengthy evacuation at room temperature to get rid of unreacted alcohol and HCl , is also recommended. In our hands, both methods gave very poor yields. Working up of the product from the latter method resulted in a compound where only one of the Cl group had been substituted in the phosphonyl dichloride. When the raw product was treated with triethylamine a crystalline compound was formed. A single crystal of the product was directly subjected to single X-ray diffraction analysis revealing the compound, $\text{Cl}_3\text{CP}(\text{O})(\text{Cl})\text{O}^- \cdots \text{H}-\text{N}^+(\text{Et})_3$, having the structure shown in the computer drawing in Figure 1.¹⁹

The sluggish reaction of the $\text{P}-\text{Cl}$ group in trichloromethyl substituted phosphonyl chlorides has been observed earlier by Kennard and Hamilton¹¹ who report that similar compounds withstand hydrolysis even in basic solution. Since trichloroacetyl chloride is immediately hydrolysed under similar conditions, steric hindrance is hardly the reason for the low reactivity of the trichloromethyl phosphonyl dichloride. But the bulky size and the high electronegativity of the CCl_3 group might stabilize a pentacovalent intermediate formed from the mono-substituted compound and HCl when the CCl_3 group occupies the axial position. When this intermediate undergoes an Arbuzov like $\text{O}-\text{C}$ -splitting the isolated compound (Figure 1) is formed upon adding triethylamine:



SCHEME 9

TABLE III

Complete alkaline decomposition of $\text{CCl}_3\text{P}(\text{O})(\text{OEt})_2$ with different NaOH concentrations in 50% $\text{EtOH}/\text{H}_2\text{O}$ at 100°C

Conc. (M) in reaction solution		Consumption of M NaOH , resp. AgNO_3 during hydrolysis		Ratio of production of total acid, resp. Cl^- , to $\text{CCl}_3\text{P}(\text{O})(\text{OEt})_2$	
$\text{CCl}_3\text{P}(\text{O})(\text{OEt})_2$	NaOH	NaOH	AgNO_3	Acid/ $\text{CCl}_3\text{P}(\text{O})(\text{OEt})_2$	$\text{Cl}^-/\text{CCl}_3\text{P}(\text{O})(\text{OEt})_2$
0.1	0.1	0.1	0.01	1	0.1
0.1	0.25	0.24	0.15	2.4	1.5
0.1	0.50	0.39	0.27	3.9	2.7
0.05	0.50	0.195	0.135	3.9	2.7

decomposition of phosphine oxides progressively changes the order of reaction from 1. to 2. order in OH^- with increasing hydroxyl concentrating (Table II).

When alkaline hydrolysis of diethyl trichloromethanephosphonate studied at low concentrations is compared with the corresponding hydrolysis of unsubstituted, mono-, and dichlorodiethyl methanephosphonates (Table IV), the change of displaced group from EtO^- to CCl_3^- is dramatically illustrated in the corresponding activation parameters. The much higher activation energy, 26 kcal/M in comparison with 12 kcal/M, is expected when $\text{P}-\text{C}$ instead of $\text{P}-\text{O}$ splitting takes place. But the higher energy is more than compensated for by a far more positive activation entropy, +5 E.U. as compared to approx. -30 E.U. The main reason may be the much lower electrostriction of the solvent around the leaving CCl_3^- ion in comparison with the strongly H-bonded EtO^- ion. The similar activation parameters in the alkaline decomposition of trichloromethyl diphenylphosphine oxide (Table I) has already been commented upon.

2. Acid and neutral hydrolysis

When the hydrolysis of $\text{CCl}_3\text{P}(\text{O})(\text{OEt})_2$ is performed in acidic or neutral solution, the ethoxy group is always displaced. Studies of the temperature effects gave the following activation parameters for reaction is 0.05 M HNO_3 in water

TABLE IV
Alkaline hydrolysis of $\text{R P}(\text{O})(\text{OEt})_2$

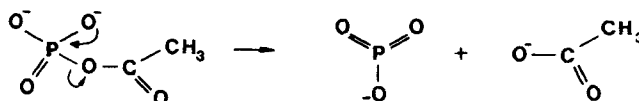
R	Solvent	Rate const. $1 \text{ M}^{-1} \text{ s}^{-1} \times 10^4$			Activation parameters	
		20°	30°	40°C	E kcal/M	ΔS^\ddagger , E.U. 30°C
C_2H_5	H_2O		0.407	0.872	14.0	
	80% H_2O /acetone		0.310	0.642	14.0	-34.8
CH_3	H_2O		3.20	6.57	13.4	
	80% H_2O /acetone		2.40	4.80	13.1	-33.7
CH_2Cl^p	H_2O	25.1	49.8	97.3	12.3	
	80% H_2O /acetone	19.2	37.5	71.5	12.0	-31.9
CHCl_2^p	80% H_2O /acetone	128	258		12.3	-27.0
CCl_3	95% H_2O /alcohol	—	27.2	100	25	+5.6

between 80 and 90°C: $E_A = 19$ kcal/M, $\Delta S^* = -40$ E.U. In neutral solution (pH = 7) in 5–50% EtOH/H₂O between 30 and 50°C: $E_A = 19$ kcal/M, $\Delta S^* = -35$ E.U.

The lower activation energies under acidic and neutral condition in comparison with basic hydrolysis is a consequence of that the ethoxy group instead of the trichloromethyl group has been displaced. From the present data no conclusion concerning P—O and/or C—O bond cleavage under acidic and neutral conditions can be reached. But the small differences in activation parameters at pH 7 and in 0.05 M HNO₃ show that the specific proton catalytic effect is negligible. This is similar to earlier reported findings for hydrolysis of trimethyl phosphate where extensive C—O bond cleavage was observed.¹⁵ Similar C—O bond cleavage seems therefore natural in the present case.

DECOMPOSITION OF DISODIUM TRICHLOROMETHANEPHOSPHONATE

The rate data of the decomposition of the trichloromethane phosphonate anion in water and its activation parameters are recorded in VIII Table I. The activation parameters are compared with the corresponding parameters for the decomposition of the dianion of acetylphosphate Table V.¹⁶ The high value of the entropy of activation, in addition to a negligible volume of activation of the dianion of acetylphosphate was taken as clear evidences for that the compound are decomposed according to a unimolecular mechanism, giving the metaphosphate ion as an unstable intermediate:¹⁶



SCHEME 12

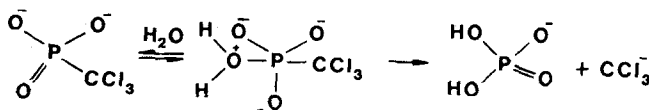
The driving force in the decomposition is the two negatively charged oxygen atoms linked to phosphorus, and the tendency to form a second P=O bond. The resonance stabilized acetate ion is also a good leaving group. The activation entropy of the dianion of trichloromethanephosphonate is, on the other hand,

TABLE V

Comparison of the activation parameters of the decomposition of the dianions of trichloromethanephosphonate and acetylphosphate

Compound	CCl ₃ (P(O)O) ²⁻	CH ₃ C(O)OP(O)O ²⁻
Activation energy, kcal/M	20	26
Activation entropy, E.U.	-25	+3

strongly in disfavour of a unimolecular reaction. The strength of the P—C bond is probably too high for a unimolecular reaction to take place. This may be interpreted that the displacement of CCl_3^- and/or $\text{CCl}_2 + \text{Cl}^-$, needs strong nucleophilic assistance from water in the transition state:



SCHEME 13

EXPERIMENTAL SECTION

1 Syntheses

Diphenyl-p- and o-nitrobenzylphosphine oxides (I and II). Ph_2PCL was made according to Horner *et al.*¹⁷ from PCl_3 , AlCl_3 , and benzene, bp.₁₂ 175°C, lit. 178°C.

Ph_2OMe : 7.6 g (0.24 M) methanol, 24 g (0.33 M) triethylamine dissolved in 250 ml dry ether was cooled. To the mixture was added slowly 52 g (0.24 M) Ph_2PCL . The amine salt was filtered off, and the filtrate distilled giving 41 g (82%) Ph_2OMe , bp.₁₁ 158°C, lit. bp.₁₀ 152°C.

$\text{Ph}_2\text{P(O)CH}_2\text{Ph-p-NO}_2$: 1.4 g (0.0065 M) Ph_2POMe and 1.4 g (0.0065 M) $\text{BrCH}_2\text{Ph-p-NO}_2$ was mixed and carefully heated. The solid product was recrystallized five times from ethanol. Light yellow needles, mp. 223–224°C. $\text{C}_{19}\text{H}_{16}\text{NO}_3\text{P}$: C, 67.70, H, 4.78, requires: C, 68.10, H, 4.70.

$\text{Ph}_2\text{P(O)CH}_2\text{-Ph-o-NO}_2$: 1.4 g (0.0065 M) Ph_2POMe and 1.4 g (0.0061 M) $\text{BrCH}_2\text{-Ph-o-NO}_2$ was mixed and carefully heated. The solid product was recrystallized five times from ethanol. Light needles, mp. 179–180°C.

Di(p-nitrobenzyl)-m-nitrophenylphosphine oxide(III). $\text{PhP(O)(CH}_2\text{Ph)}_2$ was made according to Mann *et al.*,¹⁸ $\text{C}_{19}\text{H}_{17}\text{OP}$: C, 78.41, H, 6.25, requires: C, 78.58, H, 6.00.

$m\text{-NO}_2\text{-PhP(O)(CH}_2\text{-Ph-p-NO}_2)_2$: 20 g $\text{PhP(O)(CH}_2\text{Ph)}_2$ was added in small portions under rapid stirring to a mixture of 20 ml conc. HNO_3 and 20 ml conc. H_2SO_4 . After 30 min. at room temperature the reaction mixture was poured on 300 g ice. The solid product was filtered and recrystallized several times from acetone/benzene, mp. 227–228°C. $\text{C}_{20}\text{H}_{16}\text{N}_3\text{O}_7\text{P}$: C, 54.55, H, 3.66, requires: C, 54.96, H, 3.84.

Di(m-nitrophenyl)-p-nitrobenzylphosphine oxide(IV). $\text{Ph}_2\text{P(O)CH}_2\text{Ph}$: 24 g (1 M) Mg and 150 g (1 M) PhBr in 600 ml dry ether was treated dropwise with 40 g (0.29 M) $\text{Ph}_2\text{P(O)H}$ in 100 ml ether. 49.3 g (0.39 M) PhCH_2Cl was thereafter added under stirring. The Mg-complex was decomposed with 600 ml 1 M HCl . After working up of the product, and several recrystallizations from benzene/petroleum, 60% yield of $\text{Ph}_2\text{P(O)CH}_2\text{Ph}$, was obtained mp. 201–202°C, Lit. 197–198°C. $\text{C}_{19}\text{H}_{17}\text{OP}$: C, 78.10, H, 5.53, requires: C, 78.26, H, 5.63.

$(m\text{-NO}_2\text{Ph)}_2\text{P(O)CH}_2\text{Ph-p-NO}_2$: To a mixture of 40 ml conc. HNO_3 and 40 ml H_2SO_4 was carefully added 40 g (0.14 M) $\text{Ph}_2\text{P(O)CH}_2\text{Ph}$ under rapid stirring. The reaction mixture was poured on 500 g ice and then filtered. After several recrystallizations from $\text{H}_2\text{O/EtOH}$ the product melted at 217–18°C.

$\text{C}_{19}\text{H}_{14}\text{N}_3\text{O}_7\text{P}$ H_2O : C, 51.48, H, 3.18, requires: C, 51.97, H, 3.10.

Diphenyltrichloromethylphosphine oxide (VI). $\text{Ph}_2\text{P(O)CCl}_3$: 5.65 g (0.025 M) Ph_2OMe was added to excess CCl_4 under stirring, keeping the temperature below boiling. The mixture was thereafter boiled for 1/2 h, and the product worked up and recrystallized two times from ethanol, yield 79%, mp. 145–146°C. $\text{C}_{13}\text{Cl}_3\text{H}_{10}\text{OP}$: C, 49.00, H, 3.15, requires: C, 49.86, H, 3.01.

Diethyl trichloromethanephosphonate(VII). The synthesis is described by Kosolapoff.¹³ Yield 95%, bp.₁₅ 137°C, n_D²³: 1.4590, lit. bp.₁₆: 137°C, n_D²⁵: 1.4582.

Disodium trichloromethanephosphonate(VIII). $\text{CCl}_3\text{P}(\text{O})\text{Cl}_2$: The dichloride was made according to Kinnear and Perren,¹⁰ mp 154°C, lit. 155–156°C. The dichloride was then hydrolysed with excess water. After evaporation of H_2O and HCl and prolonged evacuation, the free acid was obtained in crystalline form. Due to its hygroscopic character the disodium salt was made immediately by neutralization with NaOH . The salt solution was used directly without further purification.

Synthesis of $\text{CCl}_3\text{P}(\text{O})(\text{Cl})\text{O}^- - \text{H}-\text{N}^+(\text{Et})_3$. 10 g $\text{CCl}_3\text{P}(\text{O})\text{Cl}_2$ was added dropwise to 10 ml absolute ethanol at room temperature. After prolonged evacuation of the reaction mixture the reaction product was dissolved in methylene chloride and neutralized with triethylamine. The crystalline compound was directly subjected to single X-ray analysis proving the above structure. (See computer drawing Figure 1).

2 Hydrolysis

Alkaline hydrolysis of $m\text{-NO}_2\text{-PhP}(\text{O})(\text{CH}_2\text{Ph-}p\text{-NO}_2)_2$ in acetone/water mixture. To a solution of 10^{-3} M phosphine oxide in 90% acetone/water was added an equivalent amount of 10^{-3} M KOH at room temperature. The reaction mixture obtained immediately a pink colour which after 24 hours standing had changed to light yellow. A toluene extract of the reaction mixture after 24 hours standing showed no presence of β, β , dimethyl- p -nitrostyrene by gaschromatographic analysis. A portion of this reaction mixture (after 24 hours standing) was then made acidic with HCl and again extracted with toluene. The gaschromatogram showed a strong peak, identified as β, β , dimethyl- p -nitrostyrene, and a very small peak, assumed to be $\text{CH}_2=\text{C}(\text{CH}_3)\text{Ph-}p\text{-NO}_2$.

By heating the 10^{-3} M phosphine oxide solution with excess KOH , the β, β -dimethyl- p -nitrostyrene and trace amount of p -nitrotoluene was detected after a short reaction time.

Spectrophotometric measurements of the rate of alkaline hydrolysis of nitrobenzyl substituted phosphine oxides. The phosphine oxides were studied in the concentration interval 10^{-4} – $5 \cdot 10^{-3}$ M in 90% methanol/water. The base concentration varied from 2.2–5.6 M KOH . The effect of temperature was studied in the region 15–55°C. The alkaline solution of p - and o -nitrobenzyl substituted phosphine oxides investigated had characteristic absorption peak in the region 520–530 nm due to ylid formation. When the hydroxyl ion concentration is constant during hydrolysis (great excess of HO^-) the amount of ylid is directly proportional to the amount of phosphine oxide present. Thus, the decrease in ylid absorption as function of time due to the hydrolysis will therefore follow a 1. order rate dependence (pseudo 1. order). The cell of the Beckman photometer was thermostated, and the temperature measured directly in the reaction solution.

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