

SYNTHESIS AND REACTIVITY OF SOME ALKALINE PHOSPHORANES

I.M. ABDEL-ELLAH, R. S. FARAG AND A. N. EL-KHAZANDAR*

Chemistry Department, Faculty of Science, Al-Azhar University, Nasr City, Cairo, Egypt

(Received August 9, 1992, revised February 1, 1993)

Tris-dimethylamino-methylene-phosphorane (I), has been synthesised and its chemical reactivity towards some aldehydes, ketones, acid chlorides and haloesters was studied. The structure of the isolated products was identified on the basis of micro-analytical data, IR spectra and ¹H n.m.r. spectra.

Key words: Alkylene phosphorane, Phosphorus ylides, Phosphine alkylene.

Introduction

Alkylene phosphoranes are species of the type R₃P=CH₂, which were first considered by Staudinger [1] in the 1920's and later developed by Wittig [2], Issleib [3] and Schmidbaur [4]. The most important representatives of this class are the phosphorus ylides, in which the bonding is depicted as:



These canonical formulas are of principal significance for the description of the structure and bonding of these compounds.

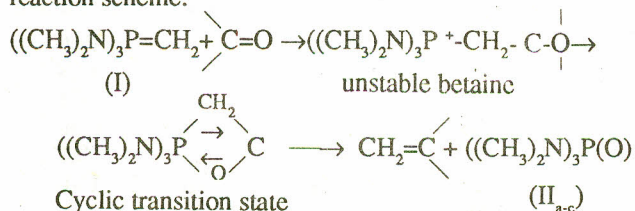
Results and Discussion

In the present work, *tris*-dimethylamino-methylene-phosphorane (I) was prepared essentially by the method of K. Issleib [3], in which *tris*-dimethylamino-phosphine[5], reacted with methyl bromide at -30° to give the corresponding phosphonium salt. The alkylene phosphorane was obtained after treatment of the alkyl phosphonium salt with a suitable base (NaNH₂ in liquid ammonia [6]).

It should be noted that similar alkylene phosphoranes were isolated by S. Trippett [7] and Schmidbaur [4].

The reaction of a carbonyl with phosphorus ylides often referred to under the general heading of carbonyl olefination, has in recent years become one of the most universal methods for the synthesis of unsaturated compounds.

The interaction of *tris*-dimethylamino-methylene-phosphorane (I) with an equimolar ratio of aldehydes or ketones were investigated. The major isolated products from the reaction mixtures were colourless liquids, which gave analytical figures compatible with the empirical formula corresponding to structure (IIa-c), according to the following reaction scheme:



The formation of these compounds in which carbonyl compounds are treated with alkylene phosphorane (I) to give a betaine type intermediate are a typical Wittig reaction. The formed betaine is unstable, which undergoes decomposition through a cyclic transition state into an olefin and a phosphine oxide, (trimethyl methylene phosphorane reacted with benzophenone to give a stable betaine intermediate [8], (CH₃)₃P⁺ - CH₂ - C (C₆H₅)₂).

The ease of isolation of the formed phosphine oxide by distillation make this method more suitable for olefin synthesis.

The isolated olefins (II a-c) were confirmed by their micro-analytical data, infrared spectra and their boiling points, also, by the determination of the m.p. of the prepared derivatives. The obtained data are summarized in Table.1

The structures of the isolated olefins is also supported by the following evidence:

(i) IR spectra showed the characteristic stretching frequencies, (ii) The preparation of derivatives;

Hydrolysis of methylenecyclohexane (II_b) with 3% KMnO₄ gave 1-oxy-methylcyclohexanol as a crystalline substance m. p. 76-78° (Lit. m.p. 75.5-76°).

Also, the bromination of the isolated styrene (II_c) gave the dibromo-derivative which had a m.p. of 73-75° (Lit. m.p. 73-74°).

Attention then turned to the investigation of the reaction of the Wittig reagent (alkylene phosphorane) with functional groups other than carbonyl compounds.

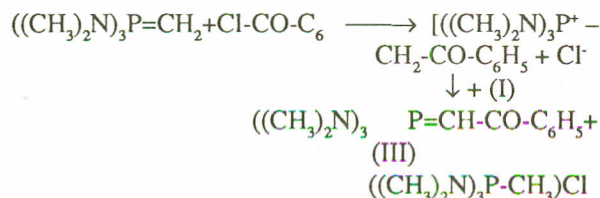
Tris-dimethylamino-methylene-phosphorane (I) reacted

Table 1. DATA OF THE ISOLATED COMPOUNDS (IIa-c).

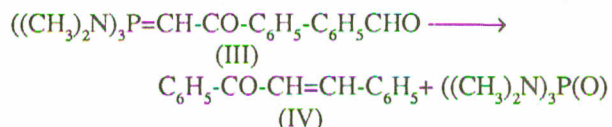
Compd. No.	Reactant	Olefin	Yield %	b.p. °C
II _a	(I)+Benzophenone	1,1-Diphenyl-ethylene	80	11-113/3 mm (Lit.100/1.5 mm)
II _b	(I)+Cyclohexanone	Methylene-cyclohexane	60	104-105/760 mm Lit.103 1760 mm)
II _c	(I)+Benzaldehyde	Styrene	55	53/20 mm (Lit.145/760 mm)

*Chemistry Department, Faculty of Sciences, Islamic University of Gaza, Egypt.

also with acids chlorides to give the corresponding phosphonium salt, which react with another molecule of (I), ((I) acting as a base in this step), to give a new alkylene phosphorane according to the following equations:

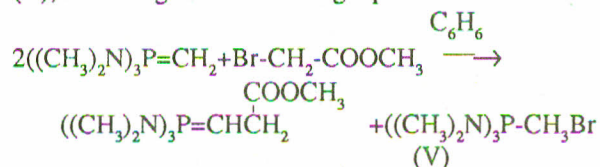


The isolated alkylene phosphorane (III) reacted with benzaldehyde to give *tris*-dimethylamino-phosphine oxide of b.p. 109-115°/16 mm. (Lit. b.p. 115/15 mm.) and benzalacetophenone (IV), having a b.p. of 160-165°/0.7 mm. as a semisolid material, which solidified on standing to give a crystalline substance having a m.p. of 52-54° (Lit. m.p. 56-57°), according to the following scheme:

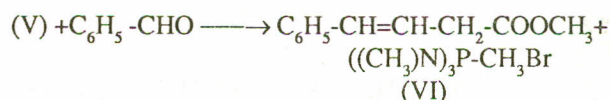
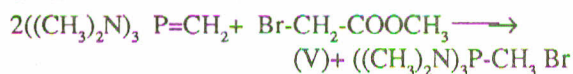


The isolated benzalacetophenone (IV) reacted with bromine to give the dibromo-derivative which had a m. p. of 156-158° (Lit. 156-157°).

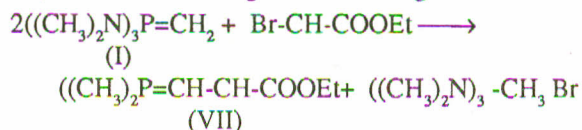
Interaction of *tris*-dimethylamino-methylene-phosphorane (I) with methyl-bromoacetate in molar ratio 2:1 gave after the removal of the formed phosphonium salt (90% yield) and evaporation of the solvent under reduced pressure a new alkylene phosphorane, which corresponds in analysis to structure (V), according to the following equations:



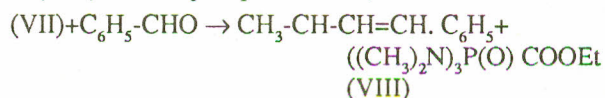
The filtrate from the above experiment, after the removal of the formed phosphonium salt, was left to react with benzaldehyde and then the reaction mixture was distilled under reduced pressure giving (VI), according to the following reaction scheme:



Also, *tris*-dimethylamino-methylene-phosphorane (I) reacts with bromo-methyl-ethylacetate in a molar ratio of 2:1 in benzene to give, after the removal of the formed phosphonium salt (94% yield) and evaporation of the solvent under reduced pressure, the corresponding alkylene phosphorane (VII) as a viscous substance according to the following reaction scheme:



The isolated alkylene phosphorane (VII) reacted with benzaldehyde to give the corresponding unsaturated compound (VIII) and the phosphine oxide, as follows:



¹H n.m.r. spectra of the isolated alkylene phosphorane measured on a 100 MHz NMR spectrometer, showed the following signals:

- I = 1.0 ppm. (2H, d, J_{H-P} = 13 Hz, *p*-CH₂).
- = 2.37 ppm. (18 H, d, J_{H-P} = 9.5 Hz, P-N-CH₃).
- III δ = 1.08 ppm. (1H, d, J_{H-P} = 15 Hz, P-CH).
- δ = 2.78 ppm. (18 H, d, J_{H-P} = 10 Hz, P-N-CH₃).
- δ = 7.32 ppm. (5H, broad signal, ArH).
- V δ = 1.1 ppm. (1H, dd, J_{H-P} = 15 Hz, P-CH).
- δ = 2.79 ppm. (18H, d, J_{H-P} = 10 Hz, P-N-CH₃).
- δ = 4.3 ppm. (2H, t, J_{H-H} = 7.0 Hz, -CH₂).
- δ = 1.3 ppm. (3H, s).
- VII δ = 1.1 ppm. (1H, d, J_{H-P} = 14 Hz P-CH).
- δ = 2.79 ppm. (18 H, d, J_{H-P} = 10 Hz, P-N-CH₃).

The interpretation of the other signals was complicated due to signal overlap (s = singlet; d = doublet; t = triplet).

IR spectra of the isolated compounds showed the characteristic stretching frequencies of the various groups present which are summarized in Table 2.

Experimental

All the experiments were carried out under a nitrogen atmosphere using the "Gunter Thomas" technique [9]. Rou-

TABLE 2. INFRARED ASSIGNMENT OF THE ISOLATED COMPOUNDS.

I	II _a	II _b	II _c	III	IV	V	VI	VII	VIII	Assignment
1010m				1000m		980m		1050m		P=C
1190s				1190s		1190s		1180s		P-N
960m										P-CH ₂
	1640s	1640s	1650s		1600m		1620s		1640s	C=C
				1530vs	1660vs					C=O
2940br	2940m	2940m	2940m	2970m	2970m	2980m	2980m	2970m	2979br	C-H
	750s		750s	750s	750s		750s		740s	Ar

All bands in cm⁻¹ and s, m, vs and br represents; strong, medium, very strong and broad bands respectively.

tine infrared spectra were recorded on a Perkin Elmer Spectrometer 125 (range 400-4000 cm^{-1}). The sample were embedded in KBr pellets which were prepared in a dry disc. ^1H n.m.r. spectra were recorded using a Varian HA-100 Spectrometer.

Tris-dimethylamino-methylene-phosphorane (I). The title compound was prepared essentially by the method described by K. Issleib [3] (I) was obtained as a colourless liquid b.p. 87-88°/14 mm.

Found: N, 23.51; P, 17.37; $\text{C}_7\text{H}_{20}\text{N}_3\text{P}$; Req.: N, 23.71; P, 17.48%.

Reaction of tris-dimethylamino-methylene-phosphorane I with carbonyl compounds.

General Procedure. Tris-dimethylamino-methylene-phosphorane (I) (0.05 mole) in 50 ml. dry benzene was added to a well stirred solution of carbonyl compound (0.05 mole) dropwise at room temperature. After the complete addition of the alkylene phosphorane (I), the reaction mixture was heated under reflux for 1 hr. The solvent was distilled under reduced pressure. Tris-dimethyl-amino-phosphine oxide was distilled at b.p. 113-115°/16 mm. (Lit. b.p. 115°/15 mm.).

1, 1-diphenylethylene (IIa) (7.2 g.; 80% yield) was distilled at b.p. 110-115°/3 mm. (Lit. b.p. 110°/1.5 mm.).

Methylene-cyclohexane (IIb) (3.3 g.; 62% yield) was distilled at b.p. 104-105°/760 mm. (Lit. b.p. 102-103°/760 mm.).

Styrene (IIc) (2.6 g.; 55% was distilled at b.p. 53°/20 mm. (Lit. b.p. 42-45°/18 mm. and b.p. 145°/760 mm.).

Preparation of oxy-methylcyclohexanol. To a solution of methylene cyclohexane (IIb) (1.0 g) in 100 ml. water, 3% KMnO_4 solution was added dropwise during 2 hrs. The reaction mixture was stirred at room temperature for 2 hrs, then, filtered and the organic compound was extracted with diethyl ether, dried over anhydrous Na_2SO_4 and the ether was evaporated.

1-Oxy-methyl cyclohexanol was obtained as a crystalline substance of a m. p. 76-78° (Lit. 75.5-76°).

Bromination of styrene (IIc). 3.20 g. of bromine in 10 ml. CHCl_3 was added to a well stirred cold solution of 2.04 g. of styrene (IIc). The chloroform was evaporated which gave the dibromo-derivatives m.p. 72-75° (Lit. m.p. 73-74°).

Reaction of tris-dimethylene-phosphorane (I) with benzoyl chloride. To a cold solution of 14.1 g. (0.08 mole) (I) in 200 ml., dry benzene, 5.6 g. (0.04 mole) benzoyl chloride was added dropwise during 2 hrs. After the complete addition, the reaction mixture was heated under reflux for 1 hr. The formed phosphonium salt (80% yield) was filtered under nitrogen atmosphere, then, washed several times with dry benzene and the solvent was distilled under reduced pressure.

The residue* (III) (9.0 g.; 80% yield) on analysis gave the following data:

(Found: C, 62, 15; H, 8.64; N, 17.40; P, 10.98; $\text{C}_{14}\text{H}_{24}\text{N}_3\text{PO}$; Req.: C, 59.79; H, 8.54; N, 16.95, P, 11.03%.)

* Because of decomposition all attempts to obtain an analytical sample by distillation under reduced pressure (till 0.2 ml.) failed.

Preparation of benzalacetophenone. To a solution of (III) (8.4 g.; 0.03 mole) in 100 ml. dry benzene benzaldehyde (5.2 g. in excess) was added dropwise. The reaction mixture was heated under reflux for 3 hrs. The solvent was removed under reduced pressure and the residue was distilled yielding tris-dimethylamino-phosphine oxide b. p. 109-115°/16 mm (Lit. b.p. 115°/15 mm.) and benzalacetophenone (IV) (6.0 g; 96.7% yield) at b.p. 160-165°/0.7 mm. as a semisolid substance.

4.0 g of (IV) was added to 100 ml water and then extracted with diethyl ether, dried over anhydrous Na_2SO_4 and left to evaporate. This gave benzalacetophenone as a crystalline solid m.p. 52-54° (Lit. 56-57°).

Preparation of the dibromo-derivative. 1.6 gm bromine in 10 ml CHCl_3 was added dropwise to a well stirred solution of 2.08 g of (IV) in 50 ml CHCl_3 evaporated to give the dibromo-derivative as a yellow crystalline substance m.p. 156-158° (Lit. m.p. 156-157°).

Reaction of tris-dimethyl-amino-methylene-phosphorane (I) with bromomethylacetate. To a cold solution of (I) (10.62 g; 0.06 mole) in 200 ml dry benzene, bromo-methylacetate (4.59 g. 0.03 mole) was added dropwise during 2 hrs. After the complete addition, the reaction mixture was heated under reflux for 1 hr. The formed phosphonium salt (5.8 g.; 90% yield) was filtered under nitrogen atmosphere, washed several times with dry benzene and the solvent was distilled under reduced pressure. The residue* (V) (6.5g; 87% yield) on analysis gave the following data:

(Found: N, 16.00; P, 11.80; $\text{C}_{10}\text{H}_{24}\text{N}_3\text{PO}_2$; Req.: N, 16.86, P, 12.45%.)

Reaction of (V) with benzaldehyde. To a solution of (V) (5.0 g.) in 100 ml dry benzene (or the filtrate from the above experiment), benzaldehyde (5.0 g) was added dropwise. The reaction mixture was heated under reflux for three hrs, solvent was distilled under reduced pressure yielding (VI) (5.8g) of b.p. 55-60°/0.2 mm. and the corresponding phosphine oxide.

Reaction of tris-dimethylamino-methylene-phosphorane (I) with bromo-methyl ethyl ethylacetate. To a cold solution of (I) (10.62 g; 0.06 mole) in 200 ml of dry benzene, bromo-methyl ethylacetate (5.43 g; 0.93 mole) was added dropwise during 2 hrs. The reaction mixture was stirred at room temperature for 1 hr. The phosphonium salt so formed (6.0 g.; 94% yield) was filtered under a nitrogen atmosphere, washed several times with dry benzene and the solvent was evaporated under reduced pressure. The residue was distilled under vacuum which gave (VII) (7.5 g; 90% yield) as a viscous substance of b.p. 120-123°/0.6 mm.

Found: C, 50.14; H, 9.94; N, 15.12; P, 11.53; $\text{C}_{12}\text{H}_{28}\text{N}_3\text{PO}_2$; Req.: C, 51.99; H, 10.11; N, 15.11; P, 11.19%.

Reaction of (VII) benzaldehyde. To a solution of (VII) (1.4 g) in 100 ml dry benzene, benzaldehyde (2.0 ml. in excess) was added dropwise. The reaction mixture was heated under

* Because of decomposition all trials to obtain analytical samples by distillation under reduced pressure (0.2 mm) failed.

reflux for 2 hrs. The solvent was removed under reduced pressure yielding (VIII) (1.1. g; 92% yield) as a semisolid material at b.p. 55-58° /0.5 mm, and the corresponding phosphine oxide.

Bromination of (VIII). To a solution of (VIII) 2.5 g.) in CHCl_3 , bromine (0.6 ml.) in CHCl_3 was added dropwise. Evaporation of the solvent gave yellow crystals of m.p. 120-122°.

References

1. H. Staudinger and J. Meyer, *Helv. Chim. Acta.*, **2**, 608 (1919).
2. G. Wittig *Organo-phosphorus Compound*, International Symposium, Heidelberg (1964), pp. 245.
3. K. Issleib and M. Tischewski, *J. Prak. Chem.*, **312**, 135 (1970).
4. H. Schmidbaur, *Chem. Ber.*, **106**, 1238 (1973).
5. H. Oediger and K. Eiter, *Liebigs. Ann. Chem.*, **682**, 58 (1965), V. Mark; *Tetrahedron Letters*, 3139 (1964).
6. S. J. Bestmann, *Chem. Ber.*, **95**, 58 (1962).
7. S. Tripett, *Organo-phosphorus Compounds*, International Symposium, Heidelberg (1964), pp. 256.
8. G. Wittig and H. Rieber, *Ann.*, **562**, 177 (1949).
9. G. Thomas, *Beitrage zur anaeroben Arbeitstechnik chemiker Ztg. Chem. Apparatur* **85**, Jahrgung/Nr. 16 (1961), S. 567-574.