781. *The Reaction of Wittig Reagents with Phenyl Isocyanate.*

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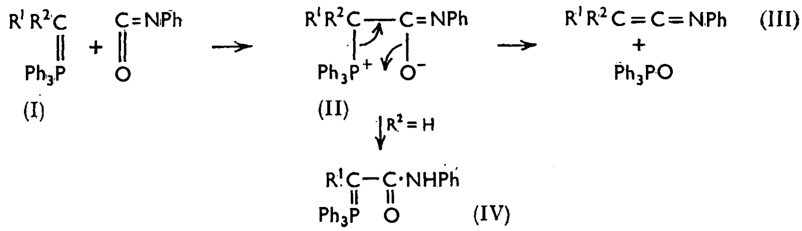
The reaction of a series of Wittig reagents with phenyl isocyanate has been investigated. In general, the intermediate betaines rearranged to more stable Wittig reagents. Nitromethyltriphenylphosphonium bromide with aqueous alkali gave fulminic acid, and pyrolysis of the phosphorane (IX; $R^1 = R^2 =$ Ph) gave diphenylacetylene.

THE only recorded reaction of a Wittig reagent with phenyl isocyanate is that due to Staudinger and Meyer[1] who treated diphenylmethylenetriphenylphosphorane (I; R^1, $R^2 =$ Ph) with phenyl isocyanate in boiling benzene and obtained 1,1-diphenyl-2-phenylimidoethylene (III; $R^1 = R^2 =$ Ph). This may be formulated as a typical Wittig reaction proceeding *via* the betaine (II). It seemed probable that in similar betaines in which R^1 or R^2 was hydrogen, migration of that hydrogen to nitrogen would occur, to give a new Wittig reagent (IV), stabilised by resonance, which might then react with a further molecule of phenyl isocyanate. To investigate this possibility, the reaction of a series of Wittig reagents with phenyl isocyanate has been examined.



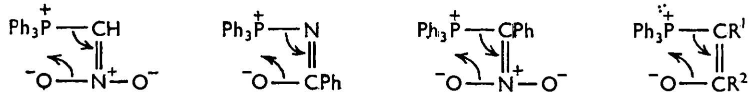
Methylenetriphenylphosphorane (I; $R^1 = R^2 =$ H) with two molecules of phenyl isocyanate gave a betaine, stable to water, and shown to be di(phenylcarbamoyl)methylenetriphenylphosphorane (IV; $R^1 =$ CO·NHPh) by reduction with zinc and acetic acid to malondianilide; in this case, the Wittig reagent (IV; $R^1 =$ H) formed by migration of one hydrogen atom reacted with a second molecule of phenyl isocyanate and gave a stable betaine by means of a second hydrogen transfer. Ethylidenetriphenylphosphorane (I; $R^1 =$ Me, $R^2 =$ H) consumed only one molecule of phenyl isocyanate; the resulting phosphorane (IV; $R^1 =$ Me) decomposed in aqueous solution and was obtained as the corresponding quaternary bromide. Evidently one phenylcarbamoyl group is not sufficient to stabilise a Wittig reagent towards hydroxylic solvents. Isopropylidenetriphenylphosphorane (I; $R^1 = R^2 =$ Me) gave the expected betaine (II; $R^1 = R^2 =$ Me), isolated as the quaternary iodide.

Among the more stable Wittig reagents, ethoxycarbonylmethylenetriphenylphosphorane (I; $R^1 = CO_2Et$, $R^2 =$ H) with one molecule of phenyl isocyanate gave the stable phosphorane (IV; $R^1 = CO_2Et$), whose structure was confirmed by the presence of NH absorption and by the absence of carbonyl absorption below 6 μ in the infrared spectrum. Similar stable phosphoranes were obtained from Wittig reagents in which $R^2 =$ H, and $R^1 =$ CHO, COMe, COPh, or CN. The phosphorane (I; $R^1 = CO{\cdot}NH_2$, $R^2 =$ H) readily decomposed in hydroxylic solvents to triphenylphosphine oxide, and reacted with two molecules of isocyanate; it seems probable that the carbonyl group of the intermediate (IV; $R^1 = CO{\cdot}NH_2$) was sufficiently basic to react with a second molecule of phenyl isocyanate, giving the betaine (IV; $R^1 =$ CO·NH·CO·NHPh).

To complete this series of stable Wittig reagents, an attempt was made to prepare

[1] Staudinger and Meyer, *Ber.*, 1920, **53**, 72.

nitromethylenetriphenylphosphorane. However, an aqueous solution of nitromethyltriphenylphosphonium bromide at 0° with alkali gave an immediate quantitative precipitate of triphenylphosphine oxide. The solution contained fulminate ion, as shown by a positive test with ferrous-ferric ion (fulminate is reduced to cyanide by the ferrous ion [2]), the absence of nitromethane and of hypobromite ion, and the formation, after acidification with nitric acid, of a silver salt partly soluble in aqueous potassium chloride. The initially formed nitromethylenetriphenylphosphorane (VI) may have decomposed *via* a four-



(VI) (VII) (VIII) (IX)

membered state reminiscent of the Wittig reaction and analogous to the decomposition of benzoyliminotriphenylphosphorane (VII) above its melting point to triphenylphosphine oxide and benzonitrile.[3]

Horner *et al.*[4] suggested a similar scheme to account for the probable formation of benzonitrile oxide by the action of dichlorotriphenylphosphorane on phenylnitromethane in the presence of triethylamine, the phosphorane (VIII) being the supposed intermediate. In view of this, the action of heat on the stable phosphoranes (IX; $R^1 = H$, $R^2 = OEt$ or Me) was investigated, but in neither case was the expected acetylene detected. However, when α-benzoylbenzylidenetriphenylphosphorane (IX; $R^1 = R^2 = Ph$), prepared by the action of benzoyl chloride on benzylidenetriphenylphosphorane, was heated above its melting point, it gave triphenylphosphine oxide and diphenylacetylene quantitatively.

Experimental

Di(phenylcarbamoyl)methylenetriphenylphosphorane.—To a stirred suspension of methyltriphenylphosphonium bromide (3·7 g.) in ether (30 ml.) under nitrogen was added ethereal 1·4N-butyl-lithium (8 ml.), followed after 0·5 hr. by phenyl isocyanate (2·58 g.) in ether (10 ml.). After 0·5 hr., the ether was removed under reduced pressure and the residue crystallised from aqueous ethanol. Recrystallisation from butan-1-ol gave the *phosphorane*, m. p. 172—173° (decomp.) (Found: C, 76·8; H, 5·05; N, 5·3. $C_{33}H_{27}O_2N_2P$ requires C, 77·0; H, 5·3; N, 5·45%) Crystallisation from ethanol-dilute hydrochloric acid gave the quaternary *phosphonium chloride*, m. p. 207—209° (Found: C, 71·8; H, 5·0; N, 5·1. $C_{33}H_{28}O_2N_2PCl$ requires C, 71·9; H, 5·1; N, 5·1%).

The above phosphorane (1 g.) in chloroform (30 ml.) and acetic acid (20 ml.) was warmed with zinc dust (10 g.) until this had dissolved. Repeated washing of the resulting solution with water, followed by evaporation to low bulk, gave malondianilide, m. p. and mixed m. p. (from ethanol) 230—231° (Found: C, 70·9; H, 5·5; N, 11·3. Calc. for $C_{15}H_{14}O_2N_2$: C, 70·8; H, 5·5; N, 11·1%).

Triphenyl-α-phenylcarbamoylethylphosphonium Bromide.—To a stirred suspension of ethyltriphenylphosphonium bromide (3·5 g.) in ether (75 ml.) under nitrogen, was added ethereal 1·4N-butyl-lithium (9 ml.), followed after 1 hr. by phenyl isocyanate (1·2 g.) in ether (50 ml.). Evaporation of solvent under reduced pressure, and crystallisation of the residue from ethanol-dilute hydrobromic acid, gave the above quaternary *bromide*, m. p. 276—277° (Found: C, 66·6; H, 5·1; N, 2·95. $C_{27}H_{25}ONBr$ requires C, 66·2; H, 5·1; N, 2·9%).

In a similar way, isopropyltriphenylphosphonium iodide gave (1-*methyl*-1-*phenylcarbamoylethyl*)*triphenylphosphonium iodide*, m. p. (from ethanol) 276—278° (decomp.) (Found: C, 60·8; H, 4·9; N, 2·55. $C_{28}H_{27}ONPI$ requires C, 61·0; H, 4·9; N, 2·5%).

[*α*-*Ethoxycarbonyl*-*α*-(*phenylcarbamoyl*)*methylene*]*triphenylphosphorane.*—Ethoxycarbonylmethylenetriphenylphosphorane (3·5 g.) in chloroform (40 ml.) was treated with phenyl isocyanate (2 g.), and the solution set aside at room temperature for 2 hr. Solvent and excess

[2] Nef, *Annalen*, 1894, **280**, 330.
[3] Staudinger and Hauser, *Helv. Chim. Acta*, 1921, **4**, 861.
[4] Horner and Oediger, *Chem. Ber.*, 1958, **91**, 437.

of isocyanate were then removed at 100°/0·1 mm., and the residue crystallised from butan-1-ol to give the *phosphorane* (90%), m. p. 189—190° (Found: C, 74·35; H, 5·45; N, 2·9. $C_{29}H_{26}O_3NP$ requires C, 74·55; H, 5·5; N, 3·0%).

In a similar way, acetonylidenetriphenylphosphorane gave *α-phenylcarbamoylacetonylidenetriphenylphosphorane*, m. p. (from butan-1-ol) 191—192° (decomp.) (Found: N, 3·1. $C_{28}H_{24}O_2NP$ requires N, 3·2%); benzoylmethylenetriphenylphosphorane gave *[α-benzoyl-α-(phenylcarbamoyl)methylene]triphenylphosphorane*, m. p. (from chloroform–ethanol) 189° (decomp.) (Found: C, 80·05; H, 5·25; N, 3·0. $C_{35}H_{26}O_2NP$ requires C, 80·2; H, 5·0; N, 2·7%); and formylmethylenetriphenylphosphorane [5] gave *[α-formyl-α-(phenylcarbamoyl)methylene]-triphenylphosphorane*, m. p. (from ethanol) 230—231° (decomp.) (Found: N, 3·3. $C_{27}H_{22}O_2NP$ requires N, 3·3%).

α-Cyano-α-(phenylcarbamoyl)methylenetriphenylphosphorane.—Chloroacetonitrile (2 g.) and triphenylphosphine (5·2 g.) were dissolved in nitromethane (30 ml.), and the solution was refluxed for 5 hr. and cooled, to give *(cyanomethyl)triphenylphosphonium chloride*, m. p. 278—279°, $\lambda_{max.}$ 4·42 μ (Found: N, 4·0. $C_{20}H_{17}NPCl$ requires N, 4·15%). The chloride (1 g.) was dissolved in water (20 ml.) and the solution made alkaline with dilute sodium hydroxide solution, giving the *phosphorane*, m. p. (from ethyl acetate) 195—196°, $\lambda_{max.}$ 4·60 μ (Found: C, 79·7; H, 5·3; N, 4·45. $C_{20}H_{16}NP$ requires C, 79·7; H, 5·4; N, 4·65%).

This phosphorane (0·5 g.) in chloroform (10 ml.) was treated with phenyl isocyanate (1 g.) and refluxed for 2 hr. Removal of solvent and repeated crystallisation from butan-1-ol gave *α-cyano-α-(phenylcarbamoyl)methylenetriphenylphosphorane*, m. p. 205—206°, $\lambda_{max.}$ 4·55 μ (Found: N, 7·0. $C_{27}H_{21}ON_2P$ requires N, 6·7%).

Carbamoylmethylenetriphenylphosphorane.—Chloroacetamide (1·9 g.) and triphenylphosphine (5·2 g.) were refluxed in nitromethane (50 ml.) for 30 hr., then cooled, to give *carbamoylmethyltriphenylphosphonium chloride*, m. p. 227—229° (Found: N, 3·9. $C_{20}H_{19}ONPCl$ requires N, 3·94%). The chloride (1 g.) was dissolved in water (20 ml.) at 0° and made alkaline, and the precipitate filtered after not more than 1 min., washed rapidly with water, and dried, to give the *phosphorane*, m. p. 177—178° (Found: N, 4·45. $C_{20}H_{18}ONP$ requires N, 4·4%); this decomposed rapidly in contact with hydroxylic solvents.

The phosphorane (1 g.) was set aside with phenyl isocyanate (1 g.) in chloroform (10 ml.) at room temperature for 1 hr. Removal of solvent and crystallisation of the residue from ethanol gave *[α-phenylcarbamoyl-α-(N′-phenylureidocarbonyl)methylene]triphenylphosphorane* (IV; R^1 = CO·NH·CO·NHPh), m. p. 172—173° (Found: C, 73·0; H, 5·25; N, 7·45. $C_{34}H_{28}O_3N_3P$ requires C, 73·25; H, 5·1; N, 7·5%).

Nitromethyltriphenylphosphonium Bromide.—A solution of bromonitromethane (3·0 g.) in benzene (10 ml.) was slowly added to triphenylphosphine (5·2 g.) in benzene (20 ml.) at 0°, and the resulting solid filtered off and recrystallised from nitromethane, to give *nitromethyltriphenylphosphonium bromide*, m. p. 166° (decomp.) (Found: N, 3·7. $C_{19}H_{17}O_2NPBr$ requires N, 3·5%).

A solution of the bromide (1 g.) in water (20 ml.) at 0° was made alkaline and filtered after less than 1 min., to give triphenylphosphine oxide (0·65 g.), m. p. and mixed m. p. 157–158°.

α-Benzoylbenzylidenetriphenylphosphorane.—To a stirred suspension of benzyltriphenylphosphonium bromide (2·15 g.) in dry ether (100 ml.) under nitrogen was added ethereal 1·12N-butyl-lithium (4·4 ml.), and after 0·5 hr. the resulting solution added slowly to a stirred solution of benzoyl chloride (0·7 g.) in ether (50 ml.) under nitrogen. Evaporation of the ether and crystallisation of the residue from aqueous ethanol gave *α-benzoylbenzylidenetriphenylphosphorane* (0·6 g.), m. p. 191—192° (Found: C, 84·05; H, 5·5. $C_{32}H_{25}OP$ requires C, 84·2; H, 5·5%).

This phosphorane was heated at 300° for 0·5 hr. The distillate (b. p. ~250°) crystallised from aqueous ethanol to give diphenylacetylene, m. p. 58·5—59·5°, having the recorded ultraviolet spectrum.[6] The residue of triphenylphosphine oxide, washed with light petroleum, had m. p. and mixed m. p. 157—158°.

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[5] Unpublished work.
[6] Friedel and Orchin, " Ultraviolet Spectra of Aromatic Compounds," J. Wiley and Sons, New York, 1951.