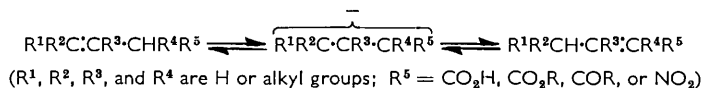


649. *The Prototropic Isomerization of Unsaturated Organophosphorus Compounds.*

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Diallylphenylphosphine oxide, allylphenylphosphinic acid, allylphosphonic acid, and diallylphenylphosphine have been wholly or partly converted into mixtures of the corresponding propenyl isomers by treatment with inorganic base.

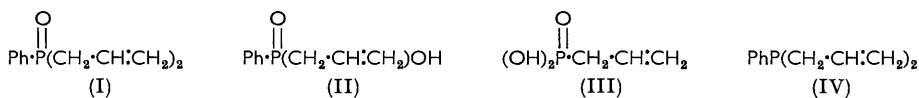
PROTOTROPIC isomerization of three-carbon systems has been much studied,¹ and is known to involve abstraction of a proton from the aliphatic carbon atom of the system to give a carbanion to which a proton may then be added to form either the original olefin or the isomer.¹⁻³



For the system to be mobile, a +*E* substituent must be present to stabilize the intermediate carbanion.

Phosphorus and sulphur may stabilize carbanions by overlap of their *d*-orbitals with the *p*-orbital of the carbon atom containing the unbonded electrons.⁴⁻⁷ For this reason, groups containing phosphorus and sulphur, exhibiting a +*E* effect, confer some degree of mobility on three-carbon systems to which they are attached. For example, diallyl sulphide is converted into the propenyl isomer by treatment with base,⁵ and unsaturated phosphonium salts⁸ and sulphones⁹ also exhibit prototropy.

We report here a number of mobile three-carbon systems in which the activating group contains phosphorus.



¹ Kon, Linstead, and their collaborators, *J.*, 1931, 2496 and preceding Papers; 1934, 1995 and preceding Papers; 1934, 614 and preceding Papers.

² Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 562.

³ Dewar, "Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 104.

⁴ Rothstein, *J.*, 1953, 3991.

⁵ Tarbell and Lovett, *J. Amer. Chem. Soc.*, 1961, **78**, 2259.

⁶ Cram and Partos, *J. Amer. Chem. Soc.*, 1963, **85**, 1093; Cram and Pine, *ibid.*, 1963, **85**, 1096.

⁷ Cram, Scott, and Nielsen, *J. Amer. Chem. Soc.*, 1961, **83**, 3696.

⁸ Rothstein and his co-workers, *J.*, 1963, 1036, and preceding Papers.

⁹ Culvenor, Davies, and Savige, *J.*, 1949, 2198.

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Diallylphenylphosphine oxide (I) was converted into a mixture of isomers when refluxed with 0.01N-methanolic potassium hydroxide. The mixture showed intense infrared absorption at 978 cm^{-1} , characteristic of *trans*-RCH:CHR', and internal comparison of the intensity of the band due to terminal unsaturation (920 cm^{-1}) with that due to aromatic CH out-of-plane vibration (700 cm^{-1}) indicated that the mixture contained 5–10% of the concentration of allyl groups present in the original. Refluxing with aqueous potassium hydroxide or potassium *t*-butoxide in benzene had the same effect. The mixture had melting point ranges of about 20° owing to the presence of combinations of geometric and positional isomers of which six are possible. A phosphine oxide, obtained by reaction of *n*-propenylmagnesium bromide with phenyldichlorophosphine followed by oxidation of the resulting phosphine possessed an infrared spectrum almost identical with that of the isomeric mixtures obtained by treatment of diallylphenylphosphine oxide with base. Rather unexpectedly, the phosphine and phosphine oxide also contained terminal unsaturation, not present in the original propenyl bromide, which must have been due to isomerization of the Grignard reagent. Hydrogenation at 20–25 lb./sq. in. over Adams catalyst of this phosphine oxide and of diallylphenylphosphine oxide and the oxides obtained by treatment of it with base gave high yields of phenyl-di-*n*-propylphosphine oxide. Diallylphenylphosphine oxide itself differed from the base-treated compound and the phosphine oxide obtained from propenylmagnesium bromide in that it could also be hydrogenated at atmospheric pressure.

Allylphenylphosphinic acid (II), obtained as a viscous liquid by acid hydrolysis of allyl allylphenylphosphinate, was converted into a crystalline acid, m. p. 65°, when refluxed with 4N-methanolic potassium hydroxide. The cyclohexylammonium salt of the liquid acid showed infrared bands at 906 and 993 cm^{-1} , characteristic of terminal unsaturation, which were absent from the spectrum of the salt of the crystalline acid, being replaced by a band at 978 cm^{-1} due to *trans*-RCH:CHR'. The proton resonance spectra of the free acids confirmed that the liquid acid was the allyl isomer and the crystalline acid the propenyl isomer.

Allylphosphonic acid (III) was obtained, by acid hydrolysis of diallyl allylphosphonate, as crystals, m. p. 47–50°. Refluxing for prolonged periods with 4N-aqueous potassium hydroxide caused the appearance of a very weak band at 980 cm^{-1} in the spectrum of the cyclohexylammonium salt, characteristic of *trans*-RCH:CHR'.

Diallylphenylphosphine (IV) was unaffected by refluxing 2N-ethanolic potassium hydroxide, but refluxing 2N-ethanolic sodium ethoxide caused conversion into a mixture of isomers containing about 10% of the terminal unsaturation originally present.

It is possible that the mobility conferred upon three-carbon systems by phosphinoxy- (in I), phosphinic (in II), and, to a lesser extent, phosphonic (in III) groups could be due solely to inductive effects. The possibility of stabilization of carbanions by phosphinoxy- and sulphinyl groups by this means has been discussed in a recent publication,⁶ but in the case of the phosphine (IV) no such explanation could apply, and it seems more probable, especially in view of the high mobility of diallylphenylphosphine oxide, that the common anion in these systems is stabilized to some extent by *d-p* overlap between the phosphorus atom and the alkyl anion.

EXPERIMENTAL

Infrared spectra were determined for Nujol mulls unless otherwise stated. Nuclear magnetic resonance spectra were obtained for deuteriochloroform solutions.

Treatment of Diallylphenylphosphine Oxide with Methanolic Potassium Hydroxide.—The phosphine oxide¹⁰ (13 g.; m. p. 52°) was dissolved in 0.01N-methanolic potassium hydroxide (50 ml.) and the solution refluxed for 72 hr. The solution was cooled, and passed down a column of Amberlite IR 120 (H⁺) ion-exchange resin. The eluate and washings were evaporated and

¹⁰ Beynon, *J. Polymer Sci., Part A, General Papers*, 1963, **1**, 3357.

the residue distilled, to give a crystalline material (11.5 g., 90%) b. p. 118—120°/0.1 mm., m. p. 60—75°, ν_{\max} (liquid) 920w ($\text{CH}_2\text{:CHR}$), 978s (*trans*-RCH:CHR'), 995sh ($\text{CH}_2\text{:CHR}$), and 1630 cm^{-1} (C:C). An approximate estimate of the proportion of allyl groups remaining was made by comparing the intensity of the band at 920 with that of the aromatic C:H out-of-plane bending at 700 cm^{-1} . Assuming the ratio for diallylphenylphosphine oxide to represent 100%, this indicated that the base-treated material contained only 5—10% of the allyl groups present in the starting material.

Treatment of the phosphine oxide with aqueous base or with potassium t-butoxide in benzene gave similar results. It was unaffected by aqueous pyridine.

Hydrogenation of Base-treated Diallylphenylphosphine Oxide.—The phosphine oxide which had been refluxed with 0.01N-methanolic potassium hydroxide was hydrogenated at 20—25 lb./in.² over Adams catalyst in industrial methylated spirit at room temperature for 16 hr., to give phenyldi-n-propylphosphine oxide* (85%), b. p. 105°/0.1 mm., m. p. 38—41°; the infrared spectrum was identical with that of an authentic sample and the mixed m. p. with a sample of m. p. 43.5° was 38—43°. The lower melting point was probably due to the presence of a small quantity of the compound produced by addition of methanol across the double bonds. The base-treated phosphine oxide would not absorb hydrogen at atmospheric pressure.

Phenyldi-n-propenylphosphine.—A Grignard reagent was prepared from n-propenyl bromide (7.5 g., 0.0889 mole) and magnesium (21.5 g., 0.985 mole) in dry tetrahydrofuran according to the method of Normant.¹¹ A solution of phenyldichlorophosphine (0.3 mole, 53.7 g., 40.7 ml.) in dry benzene (100 ml.) was added to this, with stirring, at 5—10° (ice-cooling), and the mixture set aside overnight. Pyridine (14.5 g., 1.778 moles) was added, followed by light petroleum (b. p. 30—40°; 200 ml.), and after 1 hr. the mixture was altered. The filtrate was evaporated under reduced pressure almost to dryness, mixed with light petroleum (b. p. 30—40°; 200 ml.), and filtered. This was a lengthy process owing to the colloidal nature of the precipitate. Solvents were removed under reduced pressure and the residue distilled, to give phenyldi-n-propenylphosphine* (30.5 g., 53% on phenyldichlorophosphine), b. p. 92—94°/1.5 mm., n_D^{20} 1.5755 (Found: C, 75.6; H, 7.9; P, 16.5. $\text{C}_{12}\text{H}_{15}\text{P}$ requires C, 75.75; H, 7.95; P, 16.3%), ν_{\max} (liquid) 910w ($\text{CH}_2\text{:CHR}$), 970s (*trans*-RCH:CHR'), and 1620 cm^{-1} (C:C). The presence of terminal unsaturation was most probably due to rearrangement of the Grignard reagent.

Phenyldi-n-propenylphosphine Oxide.—Phenyldipropenylphosphine (27 g.) in light petroleum (b. p. 40—60°; 150 ml.) was added to a vigorously stirred suspension of freshly prepared manganese dioxide¹² (110 g.) in light petroleum. The temperature rose from 15 to 30° during the addition ($\frac{1}{2}$ hr.). The mixture was stirred for 18 hr. at 40° and then filtered through a bed of a filter aid (Clarcel). The filter bed was washed copiously with industrial methylated spirit and the combined filtrate and washings evaporated at room temperature under reduced pressure. The residue (25 g.) was distilled *in vacuo*, to give unsaturated semisolid phosphine oxide (15.7 g., 53%), b. p. 130—140°/0.6 mm. (Found: C, 69.7; H, 7.2; P, 14.8. $\text{C}_{12}\text{H}_{15}\text{PO}$ requires C, 69.88; H, 7.3; P, 15.0%), ν_{\max} (liquid) 920w ($\text{CH}_2\text{:CHR}$), 995w ($\text{CH}_2\text{:CHR}$), 987s (*trans*-RCH:CHR'), and 1630 cm^{-1} (C:C). The spectrum closely resembled that of base-treated diallylphenylphosphine oxide.

Hydrogenation of this material by the method already described gave a quantitative yield of phenyldi-n-propylphosphine oxide, b. p. 106—108°/0.15 mm., m. p. 38—41°. The infrared spectrum was identical with that of an authentic sample, and the mixed m. p. with a sample of m. p. 43—45° was 38—42°.

Phenyldi-n-propylphosphine Oxide.—A Grignard reagent was prepared from n-propyl bromide (0.5 mole) and magnesium turnings (0.55 mole) in dry ether (250 ml.). To this solution a solution of phenylphosphonic dichloride (33.7 g., 28.2 ml., 0.17 mole) in dry ether (70 ml.) was added with stirring at 5—10°. The mixture was set aside overnight and hydrolysed with ammonium chloride solution (17 g. in 100 ml. of water).

Benzene (100 ml.) was added and the organic layer separated. The aqueous layer was extracted with benzene (3 × 10 ml.); the extracts were combined with the organic layer, dried, and solvents removed under reduced pressure. Distillation of the residue (30 g.) gave phenyldi-n-propylphosphine oxide* (25 g., 69% on phenylphosphonic dichloride), b. p. 120°/0.4 mm., m. p. 43.5° (Found: C, 68.7; H, 8.9; P, 14.9. $\text{C}_{12}\text{H}_{19}\text{OP}$ requires C, 68.55; H, 9.1; P, 14.75%).

* Berlin and Butler, *J. Amer. Chem. Soc.*, 1960, **82**, 2712.

¹¹ Normant, *Adv. Org. Chem.*, 1960, **2**, 1.

¹² Attenburrow, Cameron, Chapman, Evans, Hems, Jansen, and Walker, *J.*, 1952, 1094.

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Treatment of Diallylphenylphosphine with Base.—Diallylphenylphosphine¹³ (12.3 g.; b. p. 81°/1.5 mm., n_D^{20} 1.5700) was dissolved in ethanol (50 ml.) containing sodium ethoxide (from 3.5 g. of sodium), and the solution refluxed under nitrogen for 24 hr., cooled, diluted with water (50 ml.), and extracted with ether. The extract was dried and evaporated, and the residue (10 g.) distilled, to give mixed phosphines (8 g.; b. p. 86—88°/1.5 mm., n_D^{20} 1.5723), ν_{\max} . (liquid) 910w ($\text{CH}_2\text{:CHR}$), 970s (*trans*-RCH:CHR'), and 1620 cm^{-1} (C:C). The peak at 995 cm^{-1} ($\text{CH}_2\text{:CHR}$) present for the diallyl compound was absent. Comparison of the intensity of the peak at 910 ($\text{CH}_2\text{:CHR}$) with that at 700 cm^{-1} (aromatic CH out-of-plane bending) showed that 5—10% of the allyl groups present before base-treatment remained.

The mercuric chloride adduct, m. p. 105—130°, was prepared by mixing the phosphine with an equimolar quantity of mercuric chloride in ethanol (Found: C, 31.1; H, 3.4; P, 6.6. $\text{C}_{12}\text{H}_{15}\text{Cl}_2\text{HgP}$ requires C, 31.2; H, 3.3; P, 6.7%). Admixture with the mercuric chloride complex of diallylphenylphosphine (m. p. 127—128°) lowered the melting point to 105—120°.

Allyl Allylphenylphosphinate.—This was prepared by treatment of diallyl phenylphosphinate with allyl bromide under nitrogen at 100°.¹⁴

Allylphenylphosphinic Acid.—Allyl allylphenylphosphinate (25.3 g.) was dissolved in 4N-sulphuric acid made up in equal volumes of glacial acetic acid and water (100 ml.), and the solution refluxed under nitrogen for 16 hr., cooled, diluted with water (50 ml.), and evaporated under reduced pressure to its original volume. This process was repeated until the acetic acid has been completely removed. The residual mixture of oil and water was extracted with ether, the extract dried (MgSO_4), ether removed under reduced pressure, and the residue (18 g.) dissolved in acetone (100 ml.) and mixed with a solution of cyclohexylamine (13 g.) in acetone (100 ml.). The solid which separated was collected and extracted repeatedly with cold ethanol. Evaporation of the ethanolic extracts under reduced pressure gave the cyclohexylammonium salt of *allylphenylphosphinic acid*, needles (21.3 g., 67%) (from methylated spirit-acetone), m. p. 192° (Found: C, 64.1; H, 8.5; N, 4.9. $\text{C}_{15}\text{H}_{24}\text{NO}_2\text{P}$ requires C, 64.05; H, 8.6; N, 5.0%), ν_{\max} . 906, 993 ($\text{CH}_2\text{:CHR}$), and 1625 cm^{-1} (C:C).

The cyclohexylammonium salt (10.6 g.) was dissolved in water (50 ml.) and acidified with sulphuric acid. The mixture of oil and water was extracted with ether, and the extracts dried and evaporated, leaving allylphenylphosphinic acid as a viscous oil (5.6 g., 81%) which could not be caused to crystallize (Found: Acid value, 305 mg. KOH/g. Required, 308). This material was not suitable for infrared spectroscopy as it exhibited very broad peaks, but the proton resonance spectrum confirmed the presence of terminal unsaturation.

Phenyl-n-propenylphosphinic Acid.—Allylphenylphosphinic acid (3 g.) was dissolved in 4N-methanolic potassium hydroxide (20 ml.) and refluxed for 16 hr. The solution was cooled, neutralized with dilute sulphuric acid, and diluted with water (20 ml.). Methanol was removed under reduced pressure, and the aqueous solution acidified with 9N-sulphuric acid (100% excess). The mixture of oil and water was extracted with ether and the ether washed with water (10 ml.) and dried. Evaporation of the ether left *phenyl-n-propenylphosphinic acid* as an oil which crystallized on scratching (2.6 g., 87%), m. p. 65°.

The cyclohexylammonium salt, prepared in acetone-methylated spirit, crystallized from the same mixture as needles (Found: C, 64.2; H, 8.5; N, 5.1. $\text{C}_{15}\text{H}_{24}\text{NO}_2\text{P}$ requires: C, 64.05, H, 8.6; N, 5.0%). The melting point depended upon the rate of heating but was over 200° on rapid heating, ν_{\max} . 978 (*trans*-RCH:CHR') and 1630 cm^{-1} (C:C). The proton resonance spectrum of the free acid was completely different from that of the allyl compound and was consistent with the presence of propenyl groups.

Diallyl Allylphosphonate.—Triallyl phosphite¹⁵ (40 g.) and allyl bromide (1.5 ml.) were kept at 140—150° for 20 hr. under a stream of dry nitrogen. Distillation gave diallyl allylphosphonate (35 g., 88%), b. p. 124°/12 mm., n_D^{20} 1.4620 (lit.,¹⁵ 1.462) (Found: C, 53.2; H, 7.3; P, 15.5. Calc. for $\text{C}_9\text{H}_{15}\text{PO}_3$: C, 53.45; H, 7.5; P, 15.3%).

Allylphosphonic Acid.—Diallyl allylphosphonate (26 g.) was refluxed for 24 hr. with 4N-sulphuric acid made up in equal quantities of glacial acetic acid and water (100 ml.). The mixture was cooled, diluted with water and evaporated to its original volume several times to remove acetic acid, and neutralized (pH 9) with barium hydroxide solution. Barium sulphate was filtered off and washed, and the filtrates evaporated to 50 ml. under reduced pressure and passed

¹³ Jones, Davies, Bowden, Edwards, Davis, and Thomas, *J.*, 1947, 1448.

¹⁴ Kamai and Kukhtin, *J. Gen. Chem. (U.S.S.R.)*, 1955, 1985.

¹⁵ Kennedy, Lane, and Robinson, *J. Appl. Chem.*, 1958, 8, 459.

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down a column of Amberlite IR 120 (H^+) ion-exchange resin. The eluate and washings were evaporated under reduced pressure and the residue (11.6 g.) dissolved in methylated spirit (100 ml.) and mixed with sufficient cyclohexylamine (18.8 g., 23 ml.) to form the dicyclohexylammonium salt. The solution became alkaline when half of the amine had been added. The precipitate was collected and crystallized from aqueous methylated spirit, to give the monocyclohexylammonium salt of *allylphosphonic acid* (12.8 g., 45% on the diallyl ester) as large needles, decomp. 236° (Found: C, 48.6; H, 9.0; N, 6.4. $C_9H_{20}NO_3P$ requires: C, 48.85; H, 9.1; N, 6.35. $C_{15}H_{33}N_2O_3P$ requires C, 56.25; H, 10.4; N, 8.75%), ν_{max} . 905, 1000 ($CH_2:CHR$), and 1630 cm^{-1} (C:C).

The cyclohexylammonium salt (5 g.) was dissolved in water (50 ml.) and passed down a column of Amberlite IR 120 (H^+) ion-exchange resin. The eluate and washings were evaporated and the residue was dried at $60^\circ/0.05\text{ mm.}$, to give allylphosphonic acid as a deliquescent crystalline solid (2.5 g., 90%), m. p. $47-50^\circ$ (Found: Acid value, 1st end-point 467, 2nd end-point 934 mg. KOH/g. Required, 459 and 918).

Treatment of Allylphosphonic Acid with Base.—The cyclohexylammonium salt (2 g.) was refluxed with 4*N*-aqueous potassium hydroxide (20 ml.) for 48 hr. The solution was cooled, extracted with ether, and passed down a column of Amberlite IR 120 (H^+) ion-exchange resin. Evaporation of the eluate and washings gave an oily residue which was dissolved in methylated spirit and mixed with a slight excess of cyclohexylamine. The solid which separated was unchanged starting material (1 g., 50%), decomp. 240° . The mother-liquor was evaporated to 50 ml. and diluted with acetone (50 ml.). The precipitate (0.6 g., 3.5%), decomp. 240° , had an infrared spectrum identical with that of the starting material except for the presence of weak absorption at 980 cm^{-1} (*trans*-RCH:CHR').

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