method of McGrew and Adams,[4] was added dropwise with stirring. The ammonia was driven off by heat, and 1.3 l. of anhydrous ether was added. A solution of 191.5 g. (1.145 moles) of ethyl bromoacetate in an equal volume of dry ether was added dropwise with stirring which was continued for 16 hr. Water was then added dropwise until all salts had dissolved. The ether layer was separated, and the water layer was extracted with ether. The combined ether portions were dried and evaporated. The residue was distilled to give 3-carbethoxymethoxy-1-pentyne.

Preparation[5] of 3-Carbethoxymethoxy-2-pentanone (V, R = H, R' = C_2H_5).—In a 300-ml. flask 0.5 g. of red mercuric oxide and 2 ml. of 50% sulfuric acid were stirred and heated until some white mercuric sulfate was formed. A solution of 7 g. of water in 32 g. of ethanol was added and heated to reflux. Then 47.9 g. (0.282 mole) of 3-carbethoxymethoxy-1-pentyne was added dropwise during 1 hr. Stirring and refluxing were continued for 3 hr. The ethanol was distilled off, and the residue was saturated with sodium chloride. The organic layer was separated, and the water layer was extracted with ether. The combined ether and organic layers were washed with saturated sodium chloride solution, with sodium carbonate solution and again with saturated sodium chloride solution. After drying, the ether was evaporated and the residue was distilled to give 3-carbethoxymethoxy-2-pentanone.

In the preparation of 3-carbethoxymethoxy-3-methyl-2-butanone, the product isolated could not be purified by distillation and was known to contain some starting material. This was shown by the positive test for a terminal acetylene group obtained by adding alcoholic mercuric chloride to an ethanolic sodium ethoxide solution of the compound to give a white precipitate.

In the preparation of 3-carbethoxymethoxy-2-hexanone, an acidic methanol solution was used instead of an ethanol solution. This evidently resulted in some transesterification so that, as indicated by the analysis, the product was a mixture of the methyl and ethyl esters. Purification could not be achieved by distillation. In the hope that the esters could be separated as their 2,4-dinitrophenylhydrazones, this derivative was made of a sample of the mixture.[6] Recrystallization of the derivative gave material with a fairly sharp melting point not improved by repeated recrystallization from ethanol, m.p. 62–63.5°, but the analysis indicated it was still a mixture of the esters. Attempts at purification were abandoned and the mixture was used for the cyclization.

Preparation[7] of 2-Ethyl-2*H*-pyran-3,5(4*H*,6*H*)-dione (VI, R = H, R' = C_2H_5).—In a 1-l. flask 4.8 g. (0.208 atom) of sodium was dispersed in hot toluene which was cooled and replaced by 400 ml. of dry ether. Then 10.0 g. (0.217 mole) of anhydrous ethanol was added, and the solution was stirred until the sodium ethoxide had formed. A solution of 37.0 g. (0.197 mole) of 3-carbethoxymethoxy-2-pentanone in an equal volume of ether was added dropwise. Stirring was continued for 1 hr. The sodium salt was collected, washed with dry ether and added to 70 ml. of 3 *N* sulfuric acid. The aqueous solution was extracted with ether, and the ether was dried and evaporated. The residue was distilled, giving a thick yellow oil, b.p. 108–110° (2 mm.), which crystallized on standing. The product was recrystallized from benzene–petroleum ether (60–62°) to give 2-ethyl-2*H*-pyran-3,5(4*H*,6*H*)-dione.

In the preparation of the 2-isobutyl and 2-*n*-hexyl derivatives the oily products partially decomposed on distillation so they could not be purified in this manner. They were identified through their bis-semicarbazone derivatives which were prepared by the method of Shriner and Fuson[8] and purified by trituration with boiling ethanol.

To characterize further the 2-isobutyl and 2-*n*-hexyl compounds several physical measurements were made on them and these properties compared with those of a pure sample of the 2,2-dimethylpyrandione. The absorption maxima in the infrared for the dicarbonyl system of all three of these compounds appeared at the same wave lengths, 5.82 and 5.74 μ, the latter slightly more intense than the former, and a broad band at 6.25 μ. The last is assigned to the enol form. In the ultraviolet spectra taken in methanol, again the maxima were at the same wave lengths, 251 mμ (ε 14500) and at 278 mμ (ε 26000), *p*H 10.5, which are assigned to the enol and enolate ion, respectively. The titrations in 66% dimethylformamide gave the following results: dimethyl, pK'_a 5.8, apparent molecular weight 145 (theory 142); isobutyl, pK'_a 5.8, A.M.W. 186 (theory 170 or 90% pure); *n*-hexyl, pK'_a 5.9, A.M.W. 237 (theory 198 or 84% pure).

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[4] F. C. McGrew and R. Adams, THIS JOURNAL, **59**, 1497 (1937).

[5] G. F. Hennion and B. R. Fleck, *ibid.*, **77**, 3253 (1955).

[6] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 143.

[7] R. Robinson and R. C. Shah, *J. Chem. Soc.*, 1491 (1934).

[8] R. L. Shriner and R. C. Fuson, ref. 6, p. 142.

INDIANAPOLIS, INDIANA

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT, TEMPLE UNIVERSITY AND SOCONY MOBIL OIL CO., RESEARCH AND DEVELOPMENT LABORATORY]

Disubstituted Phosphine Oxides. IV. Addition Reactions with Aldehydes and Ketones[1]

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Two disubstituted phosphine oxides have been added to a series of aldehydes and ketones in the presence of traces of sodium ethoxide to yield disubstituted phosphinyl alcohols (III). Reduction of α-(dibenzylphosphinyl)-benzyl alcohol (IIIa) with red phosphorus and hydriodic acid gave the known tribenzylphosphine oxide. Heating III with aqueous alcoholic sodium hydroxide resulted in cleavage of the adduct to form the sodium salt of dibenzylphosphinic acid.

Disubstituted phosphine oxides (I) recently have been shown to add in the presence of traces of base to α,β-unsaturated nitriles and carbonyl compounds[1] to form unsymmetrical phosphine oxides. Similar reactions involving dialkyl phosphonates (II) are well known.[4] This paper reports the base-catalyzed addition of I to aldehydes and ketones to form disubstituted phosphinyl alcohols[5] (III). Abramov and co-workers[6] have carried out the

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[1] For the third paper in this series, see R. C. Miller, J. S. Bradley and L. A. Hamilton, THIS JOURNAL, **78**, 5299 (1956).

[2] Abstracted in part from dissertations submitted (R.C.M.) and to be submitted (C.D.M.) to the Temple University Graduate Council in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Experimental Station, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

[4] A. N. Pudovik and B. A. Arbuzov, *Doklady Akad. Nauk S.S.S.R.*, **73**, 327 (1950); *C. A.*, **45**, 2853 (1951).

[5] These compounds were arbitrarily named as substituted alcohols rather than α-hydroxy tertiary phosphine oxides, since no precedence list exists for naming phosphine oxides bearing a hydroxyl substituted side chain.

[6] A few of the series of papers on this subject by Abramov and co-workers are: (a) V. S. Abramov, *Doklady Akad. Nauk S.S.S.R.*, **73**, 487 (1950); *C. A.*, **45**, 2855 (1951); (b) V. S. Abramov, L. P.

analogous base-catalyzed addition of II to aldehydes and ketones to yield dialkyl α-hydroxyalkylphosphonates (IV).

$$\underset{\text{I}}{R_2P(O)H} + R'R''CO \xrightarrow[\text{base}]{\text{trace}} \underset{\text{III}}{R_2P(O)(OH)R'R''}$$

$$\underset{\text{II}}{(RO)_2P(O)H} + R'R''CO \xrightarrow[\text{base}]{\text{trace}} \underset{\text{IV}}{(RO)_2P(O)C(OH)R'R''}$$

The additions of I to aldehydes and ketones involved, for the most part, dibenzylphosphine oxide (Ia). A few additions of di-*n*-octylphosphine oxide (Ib) were also carried out. As in the case of additions to α,β-unsaturated nitriles, ketones and esters,[1] the adducts of Ia with aldehydes and ketones were higher melting compounds than those of Ib. The exothermic additions of I to carbonyl compounds were carried out by adding catalytic amounts of ethanolic sodium ethoxide to an ethanol solution of the reactants.

These addition compounds have also been prepared in another manner. The addition of benzaldehyde (V) to the chloromagnesium salt of Ia followed by hydrolysis gave IIIa ($R = C_6H_5CH_2$, $R' = C_6H_5$, $R'' = H$), identical to that obtained from the base-catalyzed addition of Ia to V.

$$(C_6H_5CH_2)_2P(O)MgCl + C_6H_5CHO \longrightarrow (C_6H_5CH_2)_2P(O)CH(OMgCl)C_6H_5$$

$$(C_6H_5CH_2)_2P(O)CH(OMgCl)C_6H_5 \xrightarrow[H^+]{H_2O} \underset{\text{IIIa}}{(C_6H_5CH_2)_2P(O)CH(OH)C_6H_5}$$

The addition of the halomagnesium salt of II to aldehydes and ketones to form IV was reported recently.[7]

The halomagnesium salt method is useful for making diphenylphosphine oxide (Ic) adducts. Williams and Hamilton[8] were unable to isolate pure Ic after hydrolysis of the bromomagnesium salt (VI) formed by adding three moles of phenylmagnesium bromide to di-*n*-butyl phosphonate. This was attributed to the probable instability of Ic.

$$3C_6H_5MgBr + (n\text{-}C_4H_9O)_2P(O)H \longrightarrow \underset{\text{VI}}{(C_6H_5)_2P(O)MgBr} + C_6H_6 + Mg(OC_4H_9)Br$$

$$\text{VI} \xrightarrow{H_2O,\ H^+} \underset{\text{Ic}}{[(C_6H_5)_2P(O)H]}$$

Upon addition of V to VI followed by hydrolysis, a moderate yield of a 1:1 adduct IIIc, melting at 178.0–179.5°, was obtained. Conant and co-workers[9] reported the preparation of an unspecified amount of a compound, melting at 230°, which was considered to be IIIc. This reaction, the addition of diphenylchlorophosphine to V in glacial acetic acid, was repeated. The only pure compound that could be isolated was identical to the product obtained from the reaction of VI and V.

$$\text{VI} + \text{V} \longrightarrow \xrightarrow{H_2O,\ H^+} \underset{\text{IIIc}}{(C_6H_5)_2P(O)CH(OH)C_6H_5}$$

The adducts III were white solids (except for faintly yellow colored compounds containing nitro groups) whose analyses and infrared spectra[10] agreed with the proposed structure. Furthermore, a chemical proof of structure of IIIa was made by reduction with concentrated hydriodic acid and red phosphorus. The reduction product, tribenzylphosphine oxide, was formed in only 35% yield, as a simultaneous cleavage of IIIa occurred to yield dibenzylphosphinic acid. A stepwise chlorination with phosphorus pentachloride and a similar reduction using hydriodic acid and red phosphorus resulted in a somewhat higher yield of tribenzylphosphine oxide.

The adducts of I with both aldehydes and ketones are thermally unstable. Several of the high-melting adducts of Ia decomposed markedly on melting. For example, a 34% yield of acetone (isolated as the 2,4-dinitrophenylhydrazone) was obtained by heating 2-dibenzylphosphinyl-2-propanol to its melting point. All of the higher-melting III compounds suffered a depression of melting point, if dried in a vacuum pistol at 100°. Heating with aqueous alcoholic hydrochloric acid appeared to cleave IIIa slowly into Ia and V. After refluxing IIIa with hydrochloric acid for 9 hr., 76% was recovered unchanged. A yield of 70% of benzaldehyde as the 2,4-dinitrophenylhydrazone was obtained (yield based upon unrecovered IIIa).

The adducts are much more susceptible to the action of hot caustic solution. After IIIa had stood for 12 hr. at room temperature with aqueous alcoholic sodium hydroxide, 85% of the starting adduct was recovered. However, after refluxing the same mixture for 12 hr. under nitrogen followed by acidification, no unreacted IIIa could be found, and a 66% yield of dibenzylphosphinic acid was obtained. A similar treatment of 2-dibenzylphosphinyl-2-butanol gave a 59% yield of dibenzylphosphinic acid, while the treatment of IIIc with hot alkali gave the corresponding diphenylphosphinic acid as a product.

The initial step in the basic hydrolysis of III is believed to be a cleavage of the adduct to form I and the carbonyl compound. This type of splitting has been observed with IV by Mosher[11] and by Abramov.[6b] Mosher reported the recovery of 90–100% of the theoretical amount of aldehyde upon heating IV in a 5% sodium hydroxide solution. The second step is believed to be a disproportionation reaction of I to form the dibenzylphosphinic acid. The other product of this reaction has not as yet been isolated. To test this hypothesis, Ia was refluxed with aqueous alcoholic sodium hydroxide in the presence or absence of V under a nitrogen atmosphere. After acidification, dibenzylphosphinic acid was obtained in 60–65% yields.

Semenova and L. G. Semenova, *Doklady Akad. Nauk S.S.S.R.*, **84**, 281 (1952); *C. A.*, **47**, 3227 (1953); (c) V. S. Abramov and A. S. Nazmutdinova, *J. Gen. Chem. U.S.S.R.*, **25**, 1095 (1955).

(7) O. Gawron, C. Grelecki, W. Reilly and J. Sands, THIS JOURNAL, **75**, 3591 (1953).

(8) R. H. Williams and L. A. Hamilton, *ibid.*, **74**, 5418 (1952).

(9) J. B. Conant, J. B. S. Braverman and R. E. Hussey, *ibid.*, **45**, 165 (1923).

(10) Further consideration of the infrared spectra of these compounds will be published later.

(11) R. A. Mosher, Dissertation, Univ. of Chicago, Dec., 1950.

TABLE I

DISUBSTITUTED PHOSPHINYL ALCOHOLS FROM THE BASE-CATALYZED ADDITION OF DISUBSTITUTED PHOSPHINE OXIDES TO ALDEHYDES AND KETONES, $R_2P(O)C(OH)R'R''$

R	Substituent R'	R''	Yield,[a] %	M.p., °C.	Phosphorus, % Calcd.	Phosphorus, % Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
$C_6H_5CH_2$	CH_3	H	64	153.7–154.0	11.3	11.4	...	...	..	..
$C_6H_5CH_2$	CH_3CH_2	H	77	165.8–166.4	10.7	10.5	70.81	70.53	7.34	7.35
$C_6H_5CH_2$	$CH_3CH_2CH_2$	H	92	169.1–169.8	10.2	10.2	71.50	71.49	7.67	7.72
$C_6H_5CH_2$	$(CH_3)_2CH$	H	81	175.0–175.6[b]	10.2	10.2	...	...	..	..
$C_6H_5CH_2$	C_6H_5	H	85	163.2–164.0	9.2	9.3	74.98	74.91	6.29	6.30
$C_6H_5CH_2$	$2\text{-}O_2NC_6H_4$	H	65	187.1–187.5	8.1	8.2	3.7[d]	3.6[d]	..	..
$C_6H_5CH_2$	$3\text{-}O_2NC_6H_4$	H	90	176.7–177.0	8.1	7.9	3.7[d]	3.6[d]	..	..
$C_6H_5CH_2$	$4\text{-}O_2NC_6H_4$	H	87	186.5–187.0	8.1	8.1	3.7[d]	3.6[d]	..	..
$C_6H_5CH_2$	$2\text{-}ClC_6H_4$	H	82	173.8–174.5	8.4	8.4	...	...	..	..
$C_6H_5CH_2$	$4\text{-}(CH_3)_2NC_6H_4$	H	73	153.6–154.2	8.2	8.2	3.7[d]	3.6[d]	..	..
$C_6H_5CH_2$	$2\text{-}HOC_6H_4$	H	74	133.7–134.2	8.8	8.8	...	...	..	..
$C_6H_5CH_2$	$2\text{-}\underbrace{C{:}CHCH{:}CHO}$	H	92	170.8–171.7	9.5	9.5	69.93	70.12	5.87	6.10
$C_6H_5CH_2$	$3,4\text{-}CH_2O_2C_6H_3$	H	46	195.5–196.3	8.1	8.0	...	...	..	..
$C_6H_5CH_2$	CH_3	CH_3	59	144.5–145.5[b]	10.8	10.7	70.81	70.83	7.34	7.37
$C_6H_5CH_2$	CH_3CH_2	CH_3	70	153.5–154.0[b]	10.2	10.2	71.50	72.03	7.67	7.83
$C_6H_5CH_2$	Tetramethylene		70	184.3–185.0[b]	9.9	9.8	72.59	72.51	7.38	7.44
$C_6H_5CH_2$	Pentamethylene		89	170.0–170.6[b]	9.4	9.3	...	...	..	..
C_6H_5	C_6H_5	H	46[c]	178.0–179.5	10.0	10.0	74.01	74.42	5.56	5.69
$n\text{-}C_8H_{17}$	C_6H_5	H	38	62.5–64.0	8.1	8.0	...	...	..	..
$n\text{-}C_8H_{17}$	$2\text{-}O_2NC_6H_4$	H	87	122.2–122.6	7.3	7.2	3.3[d]	3.1[d]	..	..
$n\text{-}C_8H_{17}$	$2\text{-}ClC_6H_4$	H	84	97.5–98.1	7.5	7.4	...	...	..	..
$n\text{-}C_8H_{17}$	CH_3	CH_3	28	54.5–56.0	9.3	9.5	...	...	..	..
$n\text{-}C_8H_{17}$	Pentamethylene		63	67.5–68.1	8.3	8.3	...	...	..	..

[a] Yields after recrystallization to constant melting point. [b] Melts with evolution of gas. [c] Prepn. by addition of Grignard complex to benzaldehyde. [d] Nitrogen, %.

Experimental

Reagents.—The di-*n*-octyl- and dibenzylphosphine oxides were prepared by the action of the appropriate Grignard reagent upon di-*n*-butyl phosphonate as previously described.[1,8] The carbonyl compounds were Eastman Organic Chemicals and used as received except for the acetaldehyde. The latter was obtained by heating Eastman paraldehyde with a trace of sulfuric acid.

Base-catalyzed Addition of Disubstituted Phosphine Oxides to Aldehydes and Ketones.—An equimolar mixture of 0.03–0.05 mole of I and the aldehyde or ketone in 15–25 ml. of absolute ethanol was treated with a few drops of a solution of sodium ethoxide in ethanol. After the evolution of some heat, the white crystalline products from Ia precipitated from solution. The more soluble products of Ib were obtained after evaporation of the alcohol and addition of a small amount of *n*-hexane. The products were recrystallized to a constant melting point[12]—adducts of Ia from aqueous alcohol and adducts of Ib from *n*-hexane. The compounds were dried overnight at room temperature in an evacuated drying pistol containing phosphorus pentoxide. Table I lists the melting points and analytical data of the addition products.

Addition of the Grignard Complex of Disubstituted Phosphine Oxides to Benzaldehyde. α-(Dibenzylphosphinyl)-benzyl Alcohol (IIIa).—A solution of 27.2 g. (0.140 mole) of di-*n*-butyl phosphonate in 100 ml. of benzene was added with stirring under an atmosphere of nitrogen over a 45-minute period to a Grignard solution (from 52.0 g. (0.413 mole) of benzyl chloride and 10.0 g. (0.412 g. atom) of magnesium in 150 ml. of diethyl ether). An additional 200 ml. of benzene was added, and the gelatinous gray mass was refluxed for 30 minutes. Finally, 15.0 g. (0.141 mole) of benzaldehyde in 100 ml. of benzene was added over a 0.5-hr. period, during which a faintly exothermic reaction occurred, and the gelatinous mass went into solution. The mixture was refluxed for 90 minutes and allowed to stand overnight. After hydrolysis with 250 ml. of 3:1 aqueous sulfuric acid, the organic layer was washed with 25% aqueous potassium carbonate solution and with water. The solution was evaporated under nitrogen to a 150-ml. volume, and 350 ml. of *n*-heptane was added. Upon cooling, 31.0 g. of a white solid, melting at 161–163°, was obtained. After two recrystallizations from aqueous alcohol, 23.9 g. of product, melting at 162.5–163.0°, was obtained whose melting point was not depressed when mixed with IIIa from the base-catalyzed addition of Ia to V.

Anal. Calcd. for $(C_6H_5CH_2)_2P(O)CH(OH)C_6H_5$: C, 74.98; H, 6.29; P, 9.2; neut. no., nil. Found: C, 74.98; H, 6.51; P, 9.2; neut. no., 0.4.

α-(Diphenylphosphinyl)-benzyl Alcohol (IIIc).—In a reaction similar to the preparation of IIIa, 35.0 g. (0.180 mole) of di-*n*-butyl phosphonate was added to an ethereal solution of phenylmagnesium bromide (from 82.0 g. (0.52 mole) of bromobenzene, 13.0 g. (0.535 g. atom) of magnesium and 300 ml. of ether). No gelatinous material was noted in this case. After the addition of 19.0 g. (0.179 mole) of benzaldehyde in 300 ml. of benzene and a brief reflux, the dark green solution was hydrolyzed with 250 ml. of 3:1 aqueous sulfuric acid. Upon cooling, 34.0 g. of a white solid was obtained, melting at 176.0–178.5°. When this product was recrystallized three times from aqueous alcohol, 21.5 g. (45.5% yield) of white needles, melting at 178.0–179.5°, was obtained.

Anal. Calcd. for $(C_6H_5)_2P(O)CH(OH)C_6H_5$: C, 74.01; H, 5.56; P, 10.0; neut. no., nil. Found: C, 74.42; H, 5.69; P, 10.0; neut. no., 0.2.

Reaction of Diphenylchlorophosphine with Benzaldehyde.—Following the method of Conant,[9] 8.30 g. (0.0376 mole) of freshly distilled diphenylchlorophosphine (as prepared by Gilman[13]) was added to a mixture of 4.00 g. (0.0377 mole) of benzaldehyde and 2.40 g. of glacial acetic acid. After the exothermic reaction was complete, the viscous clear liquid was poured into 200 ml. of water and the gummy mass eventually solidified. The solid mass was dissolved in 600 ml. of benzene and extracted twice with 10% aqueous potassium hydroxide and once with water. After the benzene solution was evaporated to a volume of 300 ml., 4.50 g. of a white powder was obtained, melting at 169–174°. Three recrystallizations from 1:1 aqueous alcohol gave 3.20 g. (27.6% yield) of white needles, melting at 177.2–179.0°, which failed to depress the melting point of IIIc from VI and V.

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[12] All melting points uncorrected.

[13] H. Gilman and G. E. Brown, THIS JOURNAL, **67**, 824 (1945).

Anal. Calcd. for $(C_6H_5)_2P(O)CH(OH)C_6H_5$: P, 10.0. Found: P, 9.9.

Further evaporation of the benzene filtrate gave 3.20 g. of an impure white solid, melting at 125–151°. No higher melting solid such as described by Conant was found.

Reduction of α-(Dibenzylphosphinyl)-benzyl Alcohol (IIIa) to Tribenzylphosphine Oxide. (1) Direct Reaction with Red Phosphorus and Hydriodic Acid.—A mixture of 4.60 g. (0.0137 mole) of IIIa, 100 ml. of glacial acetic acid, 60 ml. of 48.3% hydriodic acid and 0.60 g. of red phosphorus was refluxed for 41 hr. On cooling, the colorless solution was filtered and poured into 1800 ml. of water. Filtration yielded 3.65 g. of a yellowish solid melting at 181–185°. Recrystallization from 100 ml. of 2:1 aqueous alcohol containing 0.5 g. of potassium hydroxide gave 1.10 g. (35.0% yield) of white needles melting at 210–212°. One recrystallization from 1:1 aqueous alcohol yielded 0.95 g. of tribenzylphosphine oxide melting at 211.5–212.1°.

Anal. Calcd. for $(C_6H_5CH_2)_3PO$: P, 9.7. Found: P, 9.5.

This product failed to depress the melting point of an authentic sample as prepared by the addition of $POCl_3$ to benzylmagnesium chloride.[14]

Acidification of the alkaline filtrate gave 1.35 g. (40.1% yield) of dibenzylphosphinic acid as shiny white plates, melting at 188.5–189.5°.

Anal. Calcd. for $(C_6H_5CH_2)_2P(O)OH$: P, 12.6; neut. equiv., 246. Found: P, 12.5; neut. equiv., 246.

A sample of the acid did not depress the melting point of an authentic sample of dibenzylphosphinic acid prepared by the oxidation of Ia.[1]

(2) Stepwise Reaction. Chlorination and Reduction.—A mixture of 5.00 g. (0.0149 mole) of IIIa, 3.10 g. (0.0149 mole) of phosphorus pentachloride and 50 ml. of benzene was refluxed under nitrogen for 1 hr. The benzene was stripped off by heating at reduced pressure to 40°, leaving a crude yellowish solid which was used without purification. The solid was dissolved in 100 ml. of glacial acetic acid and refluxed for 8 hr. with 60 ml. of concentrated hydriodic acid and 0.60 g. of red phosphorus. The mixture was treated as before to yield 2.20 g. (46.0% yield) of tribenzylphosphine oxide and 1.25 g. (34.1% yield) of dibenzylphosphinic acid.

Cleavage Reactions of α-(Dibenzylphosphinyl)-benzyl Alcohol (IIIa). (1) Acid Cleavage.—A mixture of 2.05 g. (0.0061 mole) of IIIa, 10 ml. of concentrated hydrochloric acid, 10 ml. of water and 35 ml. of alcohol was refluxed under nitrogen for 9 hr. After cooling, the clear solution was poured into 150 ml. of water, and 1.65 g. of a white solid, melting at 157–159°, was obtained. Recrystallization from 1:1 aqueous alcohol gave 1.55 g., melting at 161.4–162.5°, which did not depress the melting point of IIIa. The acidic filtrate was treated with an aqueous solution of 2,4-dinitrophenylhydrazine hydrochloride to yield 0.30 g. of a yellow product, melting at 231–233°. This substance did not depress the melting point of an authentic sample of the 2,4-dinitrophenylhydrazone of benzaldehyde.

(2) Basic Cleavage. (a) Room Temperature.—A mixture of 2.00 g. of IIIa, 3.5 g. of sodium hydroxide, 8 ml. of water and 35 ml. of alcohol was allowed to stand at room temperature for 12 hr. The mixture was poured into 100 ml. of water to give, after recrystallization, 1.70 g. of IIIa (85% recovery).

(b) Reflux Temperature.—A similar mixture was refluxed under nitrogen for 12 hr. and poured into 150 ml. of water. Filtration of the cloudy solution yielded only 0.01 g. of an impure white solid. The filtrate was acidified with 15 ml. of concentrated hydrochloric acid to give 1.40 g. of white product melting at 178–185°. Two recrystallizations from 1:1 aqueous alcohol gave 0.98 g. (66% yield) of dibenzylphosphinic acid melting at 189.4–189.9°. Treatment of the acidic filtrate with aqueous 2,4-dinitrophenylhydrazine hydrochloride gave less than 0.01 g. of a yellow-brown solid melting at 201–223°.

Basic Cleavage of Other Adducts of Disubstituted Phosphine Oxides. α-(Diphenylphosphinyl)-benzyl Alcohol (IIIc).—A mixture of 5.15 g. (0.0167 mole) of IIIc, 10.0 g. of sodium hydroxide, 25 ml. of water and 100 ml. of alcohol was refluxed under nitrogen for 9 hr. The dark red reaction mixture was poured into 300 ml. of water, filtered and acidified to give 3.25 g. of a faint yellow solid melting at 185–187.5°. After six recrystallizations from 3:1 aqueous alcohol, 1.05 g. (28.9% yield) of diphenylphosphinic acid as long white needles was obtained melting at 188.5–189.0°. The literature[15] lists melting points of diphenylphosphinic acid ranging from 188–190° to 195–196°.

Anal. Calcd. for $(C_6H_5)_2P(O)OH$: P, 14.2; neut. equiv., 218. Found: P, 14.0; neut. equiv., 220.

2-Dibenzylphosphinyl-2-butanol.—A similar basic cleavage of 2-dibenzylphosphinyl-2-butanol resulted in a 59% yield of dibenzylphosphinic acid.

Reaction of Dibenzylphosphine Oxide and Benzaldehyde in Aqueous Alcoholic Base.—A mixture of 3.80 g. (0.0165 mole) of Ia, 1.80 g. (0.0169 mole) of benzaldehyde, 10.0 g. of sodium hydroxide, 20 ml. of water and 80 ml. of alcohol was refluxed for 12 hr. under nitrogen. After dilution with water, acidification and recrystallization, 2.45 g. (60.3% yield) of dibenzylphosphinic acid was obtained. Similar treatment of Ia in the absence of benzaldehyde resulted in the isolation of dibenzylphosphinic acid in 65.0% yield.

PITMAN, NEW JERSEY

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[14] R. Sauvage, *Compt. rend.*, **139**, 674 (1904).

[15] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 170.

[CONTRIBUTION FROM THE BOUND BROOK LABORATORIES, RESEARCH DIVISION, AMERICAN CYANAMID CO.]

The Use of Polyphosphoric Acid in the Synthesis of 2-Aryl- and 2-Alkyl-substituted Benzimidazoles, Benzoxazoles and Benzothiazoles[1]

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The formation of 2-aryl- and 2-alkyl-substituted benzimidazoles, benzoxazoles and benzothiazoles by the polyphosphoric acid-catalyzed condensation of a carboxylic acid, ester, amide or nitrile with an *o*-amino-, *o*-hydroxy- or *o*-mercapto-arylamine is described. The condensations proceed in good yield to give products which, in certain instances, are not readily attainable by conventional condensation techniques.

The utility of polyphosphoric acid as a remarkably effective condensing agent, particularly for intra- and intermolecular condensations, has been extensively demonstrated in recent years. Nothing has been reported, however, regarding its effectiveness in intermolecular condensations of the type found in the Phillips benzimidazole synthesis,[2] or in similar reactions leading to the benzoxazole and benzothiazole series (I). These condensations generally are carried out by thermal fusion, heating in solvents or in various concentrations of hydrochloric or sulfuric acid, or by heating under pressure in the presence of dilute hydrochloric acid.

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[1] Presented at the Delaware Valley Regional Meeting, Philadelphia, Pa., February 16, 1956.

[2] J. B. Wright, *Chem. Revs.*, **48**, 406 (1951).