1,10-Diphenyl-1,10-dioxodecane: mp 93–94° (lit.[8] mp 92–93°).

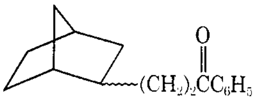
1,9-Diphenyl-1,9-dioxononane: mp 51–53° (lit.[9] mp 55–56°).

1,8-Diphenyl-1,8-dioxooctane: mp 85–87° (lit.[9] mp 91°).

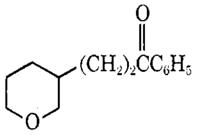
1,7-Diphenyl-1,7-dioxoheptane: mp 65.5–66.5° (lit.[10] mp 65–67°).

Products were identified by comparison of the nmr spectra and ir spectra with those of known samples.

Synthesis of ketonic precursors for terminal olefins was carried out by converting 0.3 mol of the appropriate cycloalkene to the trialkylborane.[3] This borane was partially hydrolyzed with 4.5 g (0.25 mol) of water whereupon 23.7 g (0.18 mol) of phenyl vinyl ketone[11] in 100 ml of THF was added. After 1 hr at 25° the THF was removed and the reaction mixture was held at 60° for 1 hr at 15 mm to remove volatile components. The irradiations were carried out with these crude mixtures. Samples of the respective ketones were isolated as their 2,4-dinitrophenylhydrazones (2,4-DNP): 3-cyclohexyl-1-phenylpropanone-1, mp (2,4-DNP) 179–180°; 3-cyclopentyl-1-phenylpropanone-1, mp (2,4-DNP) 157–159°; 3-cyclooctyl-1-phenylpropanone-1, mp (2,4-DNP) 151–152°; 3-(2-norbornyl)-1-phenylpropanone-1 (a), mp (2,4-DNP) 151–153°; 3-(3′-tetrahydropyranyl)-1-phenylpropanone (b) failed to yield an acceptable derivative; boron hydride is known, however, to add only to the 3 position of 4,5-dihydropyran.[12]



a



b

Methylenecyclohexane,[13] methylenecyclopentane,[13] methylenecyclooctane,[14] and 2-methylenenorbornane[15] had physical properties identical with those of authentic materials. 3-Methylenetetrahydropyran after purification by preparative glpc had n^{20}_{D} 1.4398; nmr (CCl_4) δ 1.70 (multiplet, 2,5 H), 2.28 (t, broadened, 2, J = 6.8 Hz, 4 H), 3.60 (t, 2, J = 5.0 Hz, 6 H), 3.92 (s, 2, 2 H), and 4.68 (s, 2, methylene OH); ir (neat) 3080, 1650, 1070, and 915 cm^{-1}. The mass spectrum had the parent peak at *m/e* 98.

Acknowledgment.—One of the authors (D. C. N.) thanks the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

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Ozonolysis of Unsaturated Phosphorus Compounds[1]

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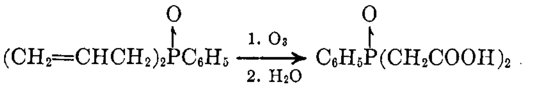
Received August 20, 1970

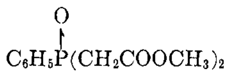
Ozonization has been used only rarely[2] as a synthetic reaction in organophosphorus chemistry except for the oxidation of phosphines to phosphine oxides.[3] Nevertheless, the technique is of general potential use in the high-yield oxidation of olefinic and acetylenic phosphine oxides to the related carboxylic acids.

Oxidation of diallylphenylphosphine oxide by ozone followed by decomposition in the presence of hydrogen peroxide and formic acid gave 2,2′-(phenylphosphinylidene)diacetic acid (**1**) in an 83% yield. Bromination of the methylene positions, formation of the corresponding anhydride, or decarboxylation *via* a Hunsdiecker reaction on **1** did not afford the desired products. The products of these reactions were not fully characterized. Esterification of **1** with methanol in the presence of sulfuric acid, with methanol and thionyl chloride, or with methyl iodide and base failed to yield the desired ester. However, when **1** was allowed to react with diazomethane, dimethyl-2,2′-(phenylphosphinylidene)diacetic acid (**2**) was obtained. The methylene position of **2** was also unreactive toward bromination.



$$(CH_2{=}CHCH_2)_2\overset{O}{\overset{\uparrow}{P}}C_6H_5 \xrightarrow[2.\ H_2O]{1.\ O_3} C_6H_5\overset{O}{\overset{\uparrow}{P}}(CH_2COOH)_2$$

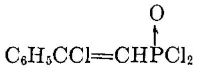
1



$$C_6H_5\overset{O}{\overset{\uparrow}{P}}(CH_2COOCH_3)_2$$

2

In the course of a related investigation, 2-chloro-2-phenylvinylphosphonic dichloride (**3**) was allowed to

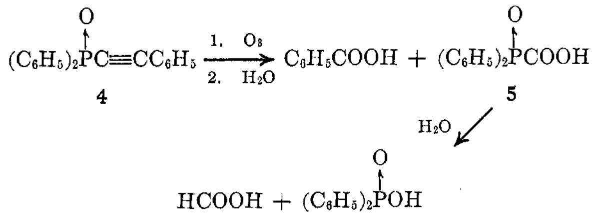


$$C_6H_5CCl{=}CH\overset{O}{\overset{\uparrow}{P}}Cl_2$$

3

react with phenylmagnesium bromide. The product obtained with 3 mol of Grignard reagent was phenylethynyldiphenylphosphine oxide (**4**). Characterization of **4** was based on the absence of a vinylic proton in the nmr spectrum, the distinct presence of the triple bond in the infrared spectrum, a melting point of a mixture of **4** and an authentic sample of **4**, and elemental analysis.

Ozonization of phenylethynyldiphenylphosphine oxide (**4**) gave benzoic acid, formic acid, and diphenylphosphinic acid. It has been shown[4] that the probable



$$\underset{\mathbf{4}}{(C_6H_5)_2\overset{O}{\overset{\uparrow}{P}}C{\equiv}CC_6H_5} \xrightarrow[2.\ \ H_2O]{1.\ \ O_3} C_6H_5COOH + \underset{\mathbf{5}}{(C_6H_5)_2\overset{O}{\overset{\uparrow}{P}}COOH}$$

$$\xrightarrow{H_2O} HCOOH + (C_6H_5)_2\overset{O}{\overset{\uparrow}{P}}OH$$

intermediate, diphenylphosphinylideneformic acid (**5**), is unstable under hydrolysis conditions. In a similar manner, ozonization of 1,2,3,4,5-pentaphenylphosphacyclopentadiene oxide with excess ozone caused complete decomposition of the ring structure to give phenylphosphonic acid and 4 equiv of benzoic acid.

[1] This work was supported by a grant, GP-5659, from the National Science Foundation.

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Experimental Section[5]

2,2′-(Phenylphosphinylidene)diacetic Acid (1).—Through a solution of 5.16 g (0.025 mol) of diallylphenylphosphine oxide[6] in 40 ml of methanol was passed ozonized oxygen at −78° until a blue color appeared (about 4 hr). The solvent was evaporated to give a clear, glassy, viscous material which was treated at −78° with 35 ml of 97% formic acid and 17 ml of 30% hydrogen peroxide and was stirred at room temperature overnight. The mixture was then heated to the reflux temperature for 2 hr, the solvents were evaporated, and the residue was triturated with ether to give a total of 5.0 g (83%) of **1**: mp 148–151° (lit.[7] 152–154°); nmr (D_2O) δ 7.6 (m, 5), 4.7 (HDO), 3.48 (d, 4, $J = 14.5$ Hz); ir (KBr) 3000, 1730 (C═O), 1440 (C_6H_5P), 1250 (P→O), 1120, 895, 748, 691, 662 cm^{-1}. *Anal.* Calcd for $C_{10}H_{11}O_5P$: C, 49.59; H, 4.59. Found: C, 49.44; H, 4.45.

The nmr of **1** in strong base (sodium hydroxide–deuterium oxide) showed a singlet in the methylene region. A multiplet of low intensity surrounded the base of this signal. When **1** was heated to 145° for 1.5 hr, bubbling occurred; the nmr spectrum of the resulting material had a doublet at 1.72 ($J = 13.5$ Hz), characteristic of the P-CH_3 group.

Dimethyl-2,2′-(phenylphosphinylidene)diacetic Acid (2).—To a mixture of 90 ml of 40% potassium hydroxide and 400 ml of ether at 0° was added 53.5 g (0.248 mol) of *N*-methyl-*N*-nitrosourea. The resulting yellow ether solution was decanted and the solids were washed five times with ether. To the combined ether fractions at 0° was added 30.0 g (0.1238 mol) of 2,2′-(phenylphosphinylidene)diacetic acid (**1**) in small portions. Considerable gas evolution occurred during addition. The resulting mixture was stirred for 2 hr at 0° and for 8 hr at room temperature. The white solid was filtered, recrystallized from ether, and dried to give 9.6 g (30%) of **2**: mp 102–103° (lit.[7] 102–104.5°); nmr ($CDCl_3$) δ 7.65 (m, 5), 3.67 (s, 6), 3.43 (d, 4, $J = 15.4$ Hz); ir (KBr) 2950, 1740 (C═O), 1440 (C_6H_5P), 1270 (P→O), 1180, 1105, 913, 738, 690 cm^{-1}. *Anal.* Calcd for $C_{12}H_{15}O_5P$: C, 53.37; H, 5.57. Found: C, 53.38; H, 5.23.

Attempts to esterify **1** with methanol in the presence of sulfuric acid with methyl iodide (on the salt of **1**) and by treatment of the acid with thionyl chloride followed by methanol did not yield the desired ester. The products of these reactions were not identified.

Phenylethynyldiphenylphosphine Oxide (4).—A mixture of 47 g (0.184 mol) of 2-chloro-2-phenylvinylphosphonic dichloride (**3**)[8,9] in 250 ml of dry ether was added to a solution of 0.552 mol of phenylmagnesium bromide in 700 ml of dry ether over a period of 1 hr. The mixture was then hydrolyzed with 10% sulfuric acid, washed with 10% sodium bicarbonate solution, dried, and distilled to give an orange, viscous material, bp 240° (0.1 mm). The distillate was recrystallized from ethanol and ether and washed successively with ether to afford **4**: mp 102° (lit.[10] 102°); ir (KBr) 3050, 2170 (C≡C), 1490, 1440 (C_6H_5P), 1195 (P→O), 1120, 998, 848, 756, 724, 704, 690 cm^{-1}. The nmr spectrum showed only aromatic and no vinyl signals. A melting point of a mixture of **4** and an authentic sample of **4**[10] was not depressed. *Anal.* Calcd for $C_{20}H_{15}OP$: C, 79.40; H, 4.97. Found: C, 79.34; H, 4.82.

Ozonization of Phenylethynyldiphenylphosphine Oxide (4).—Ozone was bubbled for 6.5 hr through a solution of 5 g (0.016 mol) of **4** in 200 ml of dry carbon tetrachloride at 0°. The resulting blue solution was combined with 150 ml of water and stirred overnight. A white solid precipitated and was filtered and dried to give 3.1 g (90%) of product. The melting point (189–192°) and infrared spectrum matched those of diphenylphosphinic acid.[11] The filtrate was reduced by evaporation to afford more solid. Filtration gave a small amount of material, mp 120–122°; a melting point of material mixed (50:50) with benzoic acid was 120–122°.

Ozonization of 1,2,3,4,5-Pentaphenylphosphacyclopentadiene Oxide.—Ozone was bubbled for 4 hr through a solution of 3 g (0.00624 mol) of 1,2,3,4,5-pentaphenylphosphacyclopentadiene oxide and 200 ml of dry chloroform at 0°. After 1 hr the yellow color had disappeared, but it returned by the end of the reaction. While the solution was still cold, 250 ml of water was added. The mixture was then stirred at room temperature overnight, the layers were separated, and the water layer was washed with chloroform. The organic portions were combined, and the chloroform was removed at reduced pressure. Sublimation of the residue gave >2.8 g (93%) of benzoic acid which was identified by its melting point (122°) and comparative infrared spectroscopy. The water layer was partially evaporated, filtered, and then evaporated to dryness to give 0.756 g (86%) of a solid. An infrared spectrum of this material was identical with that of phenylphosphonic acid.[11]

Registry No.—**1**, 17166-71-1; **2**, 17166-66-4; **4**, 7608-18-6; 1,2,3,4,5-pentaphenylphosphacyclopentadiene oxide, 1641-63-0.

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[5] Nmr spectra were taken on a Varian A-60 spectrophotometer with tetramethylsilane as an internal standard. Infrared spectra were taken on a Perkin-Elmer Model 21 double beam recording spectrophotometer. Melting points were taken on a Mel-Temp melting point block which was calibrated with known standards. Elemental analyses were performed by the University of Iowa Chemistry Department and by Micro-Tech Laboratories, Inc. Ozone was generated by a Welsbach, Model T-23 ozonator.

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The Synthesis of *N*-Alkylanilines *via* Aryne Reaction in Primary Aliphatic Amine Solvent[1a]

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Received December 11, 1970

Dehydrobenzene has so far found its widest area of synthetic application in the addition of ammonia and secondary amines.[2] Surprisingly, no detailed investigation concerning the addition of primary aliphatic, acyclic amines to aryne has been reported. One would expect that this reaction would yield readily isolable *N*-alkylanilines in a convenient one-step synthesis. This note reports the results (Table I) of the addition of various primary aliphatic amines to benzyne generated by the action of sodamide on bromobenzene.

TABLE I

REACTION OF BROMOBENZENE AND SODAMIDE IN VARIOUS PRIMARY ALIPHATIC AMINE SOLVENTS

Solvent, RNH_2, R	I, C_6H_5NHR, yield, %
n-C_3H_7	74
i-C_3H_7	71
n-C_4H_9	78
i-C_4H_9	72
sec-C_4H_9	72
tert-C_4H_9	72

$$C_6H_5Br + NaNH_2 + RNH_2 \longrightarrow \underset{\text{I}}{C_6H_5NHR}$$

It was found that this reaction is general and that good yields (71–78%) of corresponding *N*-alkylaniline I are obtained using a reaction time of 6 hr at room temperature and a sodamide–bromobenzene mole ratio

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[1] (a) Supported in part by Grant N-118 of the Robert A. Welch Foundation, Houston, Texas. (b) To whom correspondence should be addressed. (c) Robert A. Welch Undergraduate Fellow.

[2] For a comprehensive listing, see R. W. Hoffman, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967, p 115.