

## SECTION C, PHYSICAL SCIENCES

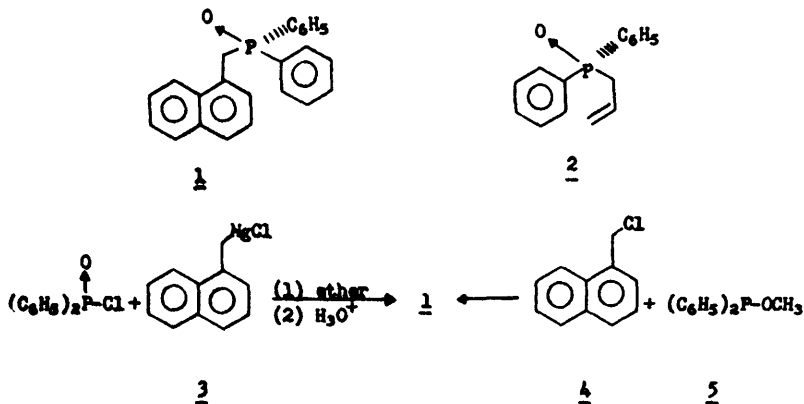
**Diphenyl-(1-naphthylmethyl)phosphine Oxide and  
Allyldiphenylphosphine Oxide. Unsymmetrical  
Tertiary Phosphine Oxides.<sup>1</sup>**

**K. DARRELL BERLIN and JACK F. CALVERT<sup>2</sup>**

Department of Chemistry, Oklahoma State University, Stillwater

Studies in progress on the synthesis of unsymmetrical tertiary phosphine oxides (Sasse, 1963; Berlin and Nagabhushanam, 1964) have necessitated the preparation of diphenyl-(1-naphthylmethyl)phosphine oxide (1) and allyldiphenylphosphine oxide (2) previously unknown. Unsymmetrical phosphine oxides of the type  $Ar_2P(O)R'$  appear important in view of the significant discovery that triphenylphosphine oxide can be cleaved by alkyllithium reagents to give useful lithium-containing organophosphorus intermediates (Seyferth, Welch and Heeren, 1964).

Condensation of diphenylphosphinic chloride and the Grignard reagent 3 gave 1 in yields which averaged about 15%. Nucleophilic displacements on phosphinic halides by Grignard reagents are well documented (Berlin, Austin, Peterson, and Nagabhushanam, 1964) but apparently coupling of the Grignard reagent 3 is a serious side reaction since 1,2-di-(1-naphthyl)ethane could be isolated from the mixture. Application of the Michaelis-Arbuzov rearrangement (Harvey and De Sombre, 1964; Aksnes and Aknes, 1964) to the synthesis of 1 proved more satisfactory and served as an alternative route for structure confirmation. An exothermic reaction occurred above 100 C when 4 was slowly added to methyl diphenylphosphinite (5) under nitrogen. Completion of the condensation was effected by holding the temperature at 140-5 C for one hour. Elemental and infrared analyses support the structure for 1 as does the nuclear magnetic resonance (N.M.R.) spectrum (in  $CDCl_3$ ). Absorption for aromatic protons was centered at  $\delta$  7.5 (multiplet) and for the methylene hydrogen at  $\delta$  4.08 (doublet,  $J_{P-CH_2} = 13.7$  cps). Isolation of product (54%) was more



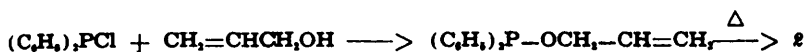
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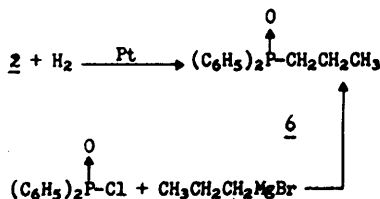
facile by this second method and is to be recommended in preference to the Grignard experiment.

Although Arbuzov and Nikonorov (1948) reported a compound they considered to be **2**, we were unable to duplicate the product. In an attempt to obtain **2** via the Michaelis-Arbuzov reaction of **5** with allyl chloride, a complex mixture was obtained, one component of which was diphenylmethylphosphine oxide. This appears analogous to the observation of Harwood and Grisley (1960), who observed that dimethyl phenylphosphonite was isomerized extremely rapidly to methyl methylphenylphosphinate by methyl bromide, a by-product in the reaction of  $\beta$ -bromoethyl acetate with the phosphonite.

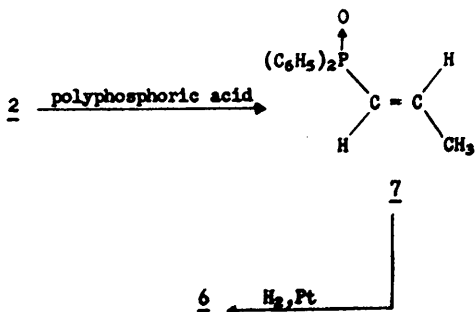
Allyl alcohol and diphenylphosphinous chloride reacted in ether in the presence of pyridine to give



presumably the phosphinite which, as reported (Arbuzov and Nikonorov, 1948), should give **2**. The compound previously recorded (Arbuzov and Nikonorov, 1948) melted at 94-5 C while the product of our distillation melted at 109-10.5 C. Infrared adsorption at 1640 (C=C, weak), 1178 (P  $\rightarrow$  O), 1441 (C<sub>6</sub>H<sub>5</sub>-P), and 921 cm<sup>-1</sup> (C=CH<sub>2</sub>) supports the structure of our tertiary phosphine oxide. Examination of the N.M.R. spectrum (in CDCl<sub>3</sub>) shows a quartet centered at  $\delta$  3.18 (CH<sub>2</sub> adjacent to the phosphoryl group) with each signal of nearly equal area and separated by 7 cps. The center of a complex multiplet was located near  $\delta$  5.28; this multiplet was apparently due to the terminal methylene hydrogen and internal vinyl protons. Confirmation of structure **2** was achieved by reduction to the known diphenylpropylphosphine oxide (**6**), which was prepared by the alternative route shown.



Migration of the double bond into conjugation with the phosphoryl group was a conceivable explanation of the product obtained by Arbuzov and Nikonorov (1948). However, treatment of **2** with polyphosphoric acid



gave a low yield of 7, the structure of which was confirmed by reduction to 6. Since 7 melted at 124 C, it was presumably not the compound isolated by Arbuzov and Nikonorov (1948). N.M.R. analysis (in  $\text{CHCl}_3$ ) of 7 was complicated by solubility limitations in most solvents and by P-H and H-H coupling. Complex multiplets were centered at approximately  $\delta$  7.5 (aromatic protons) and  $\delta$  6.5 (vinyl protons). A doublet at  $\delta$  1.69 ( $J = 6$  cps) was to be expected and was assigned to the terminal methyl group. It is tentatively assumed that 7 has the *trans*-arrangement of the vinyl protons which would be expected from the rearrangement of 2 to 7 under acidic conditions.

#### EXPERIMENTAL

**Analytical methods**—All melting points and boiling points are uncorrected. The microanalyses were performed by Galbraith Labs., Inc., Knoxville, Tenn. The N.M.R. spectra were recorded on a Varian A-60 high-resolution spectrometer with tetramethylsilane as the internal standard. The infrared spectra were recorded on a Beckman IR-5A as films or KBr pellets. Gas-liquid chromatography (g.l.c.) analyses were performed with an Aerograph A-550 Hy F1 Unit with hydrogen flame detection cell. We thank Dr. W. Ebert, Victor Chemical Company, for generous samples of diphenylphosphinic chloride.

**Preparation of methyl diphenylphosphinite (3)**—This phosphinite was prepared using a slightly modified method of Arbuzov and Nikonorov (1948). Methanol (21.89 g, 0.682 mole) and triethylamine (68.88 g, 0.682 mole) were dissolved in 400 ml of anhydrous ether under nitrogen. Diphenylphosphinic chloride (150.0 g, 0.682 mole) in 100 ml of anhydrous ether was added dropwise to the solution at 10-15 C (ice bath). After the addition was complete (1.5 hours), the reaction mixture was boiled 1 hour. Triethylamine hydrochloride was filtered off under nitrogen and the filtrate was concentrated. Distillation of the residue yielded a clear viscous liquid, bp 118-120 C/4 mm; yield, 100.2 g (68.2%);  $n_D^{20}$  1.6012, reported  $n_D^{20}$  1.6030 (Arbuzov and Nikonorov, 1948), absorption maxima 1436  $\text{cm}^{-1}$  ( $\text{C}_6\text{H}_5$ -P), 1020  $\text{cm}^{-1}$  (P-O-C).

**Preparation of diphenyl-(1-naphthylmethyl)phosphine oxide (1) via a Michaelis-Arbuzov rearrangement**—To freshly prepared 3 (45.0 g, 0.207 mole) under nitrogen was added dropwise 1-naphthylmethyl chloride (37.16 g, 0.207 mole) at room temperature. Since no apparent reaction had occurred when approximately one-third of the halide had been added, the flask was heated slowly to 100-115 C. A very exothermic reaction ensued and a gas was evolved with a sharp rise in temperature to approximately 180 C. When the initial, vigorous evolution of gas had subsided, the remainder of the halide was added dropwise (1 hour). When the addition was complete, the reaction mixture was heated at 140-5 C for an additional hour. When allowed to cool below 130 C, the mixture solidified. Recrystallization of the solid (benzene-ether) gave a feathery material, 42.4 g (54.1%), mp 162-3.5; absorption maxima 1431  $\text{cm}^{-1}$  ( $\text{C}_6\text{H}_5$ -P), 1181  $\text{cm}^{-1}$  (P  $\rightarrow$  O).

Analysis:  $\text{C}_{22}\text{H}_{18}\text{O}$ ; Calculated: C, 80.59; H, 5.50; P, 9.04  
 Found C, 80.53; H, 5.45; P, 8.91.

**Preparation of 1 via a Grignard reaction**—Diphenylphosphinic chloride (47.31 g, 0.20 mole) in 80 ml of dry ether was added dropwise to 0.271 mole of 1-naphthylmethylmagnesium chloride prepared from 8.2 g (0.34 g atom) of magnesium, 50 g (0.283 mole) of 1-naphthylmethyl chloride and 400 ml of dry ether. When the addition was complete (1.5 hour) the mixture was heated at reflux for 2 hours. A gummy solid formed in the orange-colored mixture. Hydrolysis was effected with 20% aqueous ammonium chloride at room temperature. The resulting heterogeneous mixture was stirred 14 hours at room temperature during which time the mixture became chalky white in appearance. The solid was filtered off and the organic layer was separated. A combination of benzene-ether

extracts and the original organic layer was washed with 10% aqueous sodium bicarbonate and dried ( $\text{Na}_2\text{SO}_4$ ). When the organic layer was concentrated, a dark yellow oil resulted which deposited white crystals (mp 162-3 C) identified by infrared analysis as 1,2-di-(1-naphthyl)ethane, reported mp 160-1 C (Khaletskii and Kaplan, 1956).

Treatment of the filtered, white solid from the original reaction mixture with boiling benzene gave an organic solution and an insoluble fraction which was filtered off. When concentrated the filtrate deposited a white feather-like material. The compound (from benzene-ether) weighed 10.0 g (14.6%), mp 162-3 C. The infrared spectrum was identical to that of the previously prepared phosphine oxide 1. The above yield was the average from three runs although in a separate isolated experiment a higher return (35.5%) was realized. Dilution effects are probably critical here to minimize coupling of the Grignard reagent. Nevertheless, with comparable reaction times the average yield of 1 obtained from the Grignard reaction was inferior to that from the rearrangement process.

*Synthesis and proof of structure for allyldiphenylphosphine oxide (2)*

—Allyl diphenylphosphinite was prepared using the same general method described by Arbuzov and Nikonov (1948). Vacuum distillation gave several fractions of which the major component distilled at 135-49 C/0.15 mm. The heavy oil solidified upon cooling and the resulting solid was recrystallized three times (benzene/low-boiling petroleum ether), mp 109-10.5 C; yield 7.8 g (30.4%). Thin-layer chromatography (alumina with  $\text{CHCl}_3$ -acetone) and g.l.c. (5% silicone rubber on 80/100 Chromosorb G) showed the compound to be pure.

Analysis:  $\text{C}_{15}\text{H}_{15}\text{OP}$ ; Calculated: C, 74.35; H, 6.24; P, 12.81  
Found C, 74.38; H, 6.28; P, 12.74.

By means of a Parr apparatus, 2 (2.0 g, 0.01 mole) was hydrogenated at 3 atm in the presence of 80 ml of benzene and platinum oxide (0.025 g). Concentration of the filtrate left an oil which deposited white crystals of diphenylpropylphosphine oxide (6), mp 100-1.5 C, reported mp 100-1 C (Trippett, 1961); absorption maxima, 1439  $\text{cm}^{-1}$  ( $\text{P}-\text{C}_2\text{H}_5$ ), 1180  $\text{cm}^{-1}$  ( $\text{P} \rightarrow \text{O}$ ). The N.M.R. spectrum (in  $\text{CHCl}_3$ ) showed a multiplet centered at approximately  $\delta$  7.62 (aromatic hydrogen) and a triplet centered at  $\delta$  1.0 ( $J = 7$  cps; methyl protons).

*Preparation of 2 (Grignard reaction)*—The allyl Grignard reagent was prepared by the method of Grummitt, Budewitz and Chudd (1963). Diphenylphosphinic chloride (23.64 g, 0.1 mole) was added slowly to allylmagnesium chloride (0.74 mole) with stirring under nitrogen at 0-5 C. When the addition was complete, the reaction mixture was stirred an additional 2 hours and allowed to come to room temperature. Decomposition was effected with 20% aqueous ammonium chloride and the pasty mass obtained was filtered. Extracts (benzene-ether) of the water layer and the organic phase were combined and dried ( $\text{Na}_2\text{SO}_4$ ). When the solution was evaporated to approximately 100 ml, white crystals of 2 began to form, 15.2 g (80.9%); mp 109-10.5 C (benzene-ether). The compound was identical to that previously synthesized.

*Preparation of diphenylpropylphosphine oxide (6)*—Since an authentic sample of 6 was not available, it was synthesized by adding dropwise diphenylphosphinic chloride (10.0 g, 0.042 mole) to *n*-propylmagnesium bromide (0.06 mole) at room temperature. The addition required 30 minutes after which time the reaction mixture was boiled 1 hour. Decomposition and workup was essentially the same as that described for the previous experiment in the synthesis of 2. The yield of 6 was 7.5 g (93.7%); mp 98.5-100 C. The infrared spectrum was identical to that displayed by the phosphine oxide cited earlier.

*Rearrangement of 8; synthesis of 7*—Allyldiphenylphosphine oxide (3.0 g, 0.016 mole) and commercial polyphosphoric acid (30.0 g; 105%) were stirred at room temperature. Since a color change was not observed, the mixture was heated to a maximum of 210 C for 1.5 hour (the mixture became reddish brown). The reaction mixture was then poured into ice water and neutralized (10% sodium bicarbonate) and extracted three times (benzene-ether). The organic layer was washed (NaHCO<sub>3</sub>), dried (Na<sub>2</sub>SO<sub>4</sub>), and then evaporated to approximately 30 ml. When it was chilled, white crystals of 7 formed which were recrystallized (benzene/low-boiling petroleum ether), yield 0.6 g (20%); mp 124.5-26 C; absorption maxima, 1640 cm<sup>-1</sup> (C=C), 1440 cm<sup>-1</sup> (C<sub>6</sub>H<sub>4</sub>-P), 1178 cm<sup>-1</sup> (P → O).

Analysis: C<sub>16</sub>H<sub>14</sub>OP; Calculated: C, 74.35; H, 6.24; P, 12.81  
 Found C, 74.25; H, 6.14; P, 12.78.

Diphenylvinylphosphine oxide, a close model for 7, displays a peak for the P → group at 1177 cm<sup>-1</sup> [inadvertently given as 1190 cm<sup>-1</sup> (Berlin and Butler, 1961)]. Reduction of this  $\alpha,\beta$ -unsaturated phosphine oxide gives the ethyl analog, which shows a band at 1180 cm<sup>-1</sup> for the P → O group. Consequently, infrared absorption for the P → O function is not greatly affected by an attached simple alkenyl group.

Reduction of 7 over platinum in a Parr apparatus at room temperature for 1 hour at 3 atm gave 6.

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