tained 1.58 g (79%) of recovered salt **25** and cyclobutyldiphenylphosphine oxide (**29**) as the only product (shown by vpc).

Registry No.—**3**, 14799-82-7; **7a** (*cis*), 16958-34-2; **7a** (*trans*), 16958-35-3; **7b** (*cis*), 16958-36-4; **7b** (*trans*), 16958-37-5; **7c**, 16958-38-6; **7d**, 14799-59-8; **8**, 16958-40-0; **9**, 14799-61-2; **10**, 603-35-0; **11**, 791-28-6; **15**, 16540-56-0; **16**, 16958-42-2; **18**, 16958-43-3; **26**, 16958-45-5; **28**, 5244-75-7; **29**, 16958-47-7; **32**, 16958-48-8.

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Reactions of Carbamoyldiphenylphosphine

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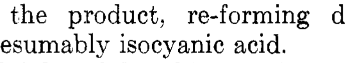
The preparation of carbamoyldiphenylphosphine (1) and the derivatives 2–7 is described. With p-toluenesulfonyl isocyanate a cycloaddition reaction gave the stable oxazetidone 9.

A recent publication by Papp and Buckler[1] described the preparation of carbamoyldiphenylphosphine (**1**) and its oxide (**2**). We also prepared these compounds as part of a program on the chemistry of isocyanic acid[2-4] and wish to report on several new derivatives.

Isocyanic acid reacted smoothly with diphenylphosphine in degassed benzene to give carbamoyldiphenylphosphine (**1**) in 75% yield. It was necessary to recrystallize the product from degassed benzene under nitrogen, since recrystallization in the presence of air led to phosphine oxide **2**. Attempted sublimation decomposed the product, re-forming diphenylphosphine and presumably isocyanic acid.

Carbamoyldiphenylphosphine underwent a variety of reactions characteristic of tertiary phosphines (Scheme I). Oxidation with hydrogen peroxide produced the phosphine oxide (**2**) in 53% yield. Treatment with sulfur in refluxing benzene gave an 81% yield of the phosphine sulfide (**3**). When 2 equiv of the phosphine were added to nickel carbonyl, carbon monoxide was readily displaced and a 91% yield of dicarbonylbis(carbamoyldiphenylphosphine)nickel (**4**) was obtained. Addition of benzyl iodide to a hot benzene solution of the phosphine resulted in a vigorous reaction and precipitation of the highly insoluble phosphonium iodide (**5**). A similar reaction with benzyl bromide produced the phosphonium bromide (**6**). Treatment of tetrachlorobis(ethylene)diplatinum with excess carbamoyldiphenylphosphine resulted in displacement of ethylene and a 46% yield of dichlorobis(carbamoyldiphenylphosphine)platinum (**7**).

When a benzene solution of the phosphine was treated with 1 equiv of p-toluenesulfonyl isocyanate, the expected urea **8** was not isolated. Instead, a 3% yield of



$(C_6H_5)_2\overset{O}{\overset{\|}{P}}\overset{O}{\overset{\|}{C}}NH\overset{O}{\overset{\|}{C}}NHSO_2C_6H_4CH_3$

8

a product tentatively identified as 4-amino-4-diphenylphosphinyl-3-p-tolylsulfonyl-1,3-oxazetidone (**9**) was obtained. The cycloadduct **9** was favored over the urea structure **8** by both infrared and mass spectral evidence. A doublet carbonyl band at 1750 and 1780 cm^{-1} is consistent with the four-membered ring in **9**, but not with either of the carbonyl groups in the urea **8**.[5] A major carbon dioxide peak in the mass spectrum of the compound is also easily explained by structure **9**, but not by **8**.

Compounds similar to **9** have been suggested as intermediates in the reaction of isocyanates with disubstituted amides.[6,7] In these cases, loss of carbon dioxide occurred spontaneously and amidines were the sole product. The thermal stability of our product (mp 170° dec) is surprising in view of these results, although stable oxazetidones have recently been prepared from alkyl isocyanates and electronegatively substituted ketones.[8] A doublet carbonyl band was observed in these compounds, but occurred at much higher frequency (1890 and 1935 cm^{-1} for the product of hexafluoroacetone and methyl isocyanate) than that observed for **9**. This increase is probably due to the presence of two electronegative trifluoromethyl groups. The compounds also had an intense CO_2 peak at m/e 44 in the mass spectrum, as does **9**.

Experimental Section[9]

Carbamoyldiphenylphosphine (1).—A solution of 5.3 g (0.123 mol) of isocyanic acid in 25 ml of degassed benzene was added dropwise to 16.4 g (0.088 mol) of diphenylphosphine. A water bath surrounding the reaction flask kept the temperature below 30°. After the addition was complete, the solution was allowed to stand at room temperature for 2 hr. The precipitated solid (12.0 g., 60% yield) was filtered under nitrogen and recrystallized from degassed benzene under nitrogen. After drying, the sample had mp 118–120° (lit.[1] mp 115–116°).

Anal. Calcd for $C_{13}H_{12}NOP$: C, 68.11; H, 5.28; N, 6.11; P, 13.52. Found: C, 68.12; H, 5.47; N, 6.04; P, 13.79.

The nmr spectrum (acetone-d_6) of the compound showed a series of complex peaks from 7.1 to 7.7 ppm. After addition of deuterium oxide, a DOH peak appeared at 4.0 ppm. The ratio of the aromatic signals to this signal was approximately 5:1.

A second preparation under similar conditions furnished 75% yield of product.

Attempted sublimation of the product resulted in its decomposition. The liquid that formed on the cold finger had an infrared spectrum identical with that of diphenylphosphine.

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[1] G. P. Papp and S. A. Buckler, *J. Org. Chem.*, **31**, 588 (1966).

[2] F. W. Hoover, H. B. Stevenson, and H. S. Rothrock, *ibid.*, **28**, 1825 (1963).

[3] F. W. Hoover and H. S. Rothrock, *ibid.*, **28**, 2082 (1963).

[4] F. W. Hoover and H. S. Rothrock, *ibid.*, **29**, 143 (1964).

[5] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 214.

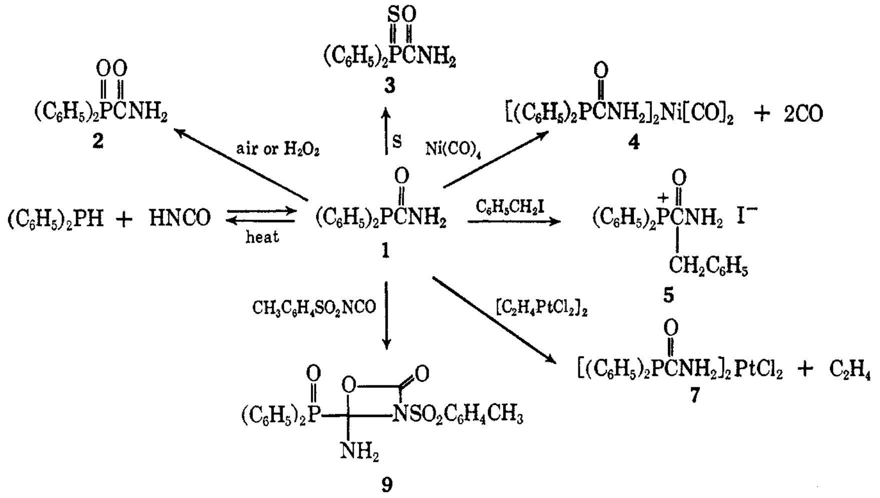
[6] H. Ulrich, *Chem. Rev.*, **65**, 369 (1965).

[7] C. King, *J. Org. Chem.*, **25**, 352 (1960).

[8] R. J. Shozda, *ibid.*, **32**, 2960 (1967).

[9] All melting points (Fisher-Johns apparatus) are uncorrected. Proton nmr spectra were obtained with Varian A-60 spectrometer.

SCHEME I



Diphenylcarbamoylphosphine Oxide (2).—When an attempt was made to recrystallize carbamoyldiphenylphosphine from benzene in the presence of air, the phospine oxide slowly precipitated, mp 197–200° dec (lit.[1] mp 190–191°). This compound had a strong P═O infrared band at 1180 cm^{-1} which was absent in the spectrum of the parent phosphine.

Anal. Calcd for $C_{13}H_{12}NO_2P$: C, 63.67; H, 4.94; N, 5.71; P, 12.63. Found: C, 64.04; H, 4.93; N, 5.77; P, 12.73.

In the nmr spectrum (DMSO-d_6) of this compound the amide protons appeared as three broad bands at 8.50, 8.75, and 8.93 ppm. The aromatic protons appeared as a series of complex signals between 7.4 and 8.1 ppm. The intensities of these signals were in the expected ratio of 1:5. The amide signals disappeared completely when the sample was shaken with deuterium oxide.

The oxide was prepared more conveniently by addition of 30% hydrogen peroxide (0.6 g of H_2O_2, 17.6 mmol) to a solution of 3.2 g (14 mmol) of carbamoyldiphenylphosphine in 40 ml of acetone. The solution refluxed vigorously for 30 sec and a solid immediately precipitated. After recrystallization from toluene, 2.4 g of product was obtained (53% yield, mp 197° dec) This product had an infrared spectrum identical with that of a sample previously prepared by air oxidation of the phosphine.

Carbamoyldiphenylphosphine Sulfide (3).—To a solution of 5.0 g (21.8 mmol) of carbamoyldiphenylphosphine in 25 ml of benzene was added 2.0 g (62.5 mmol) of sulfur. After the mixture was refluxed for 4 hr, the benzene was removed under vacuum. The residue was washed with 10 ml of carbon disulfide and recrystallized from benzene, furnishing 4.0 g of product, mp 143°. The mother liquor was chromatographed on Florisil to obtain an additional 0.6 g. The total yield of product was 4.6 g (81% yield).

Anal. Calcd for $C_{13}H_{12}NOPS$: C, 59.76; H, 4.63; N, 5.36; P. 11.86; S, 12.27. Found: C, 60.02; H, 4.97; N, 5.31; P, 12.38; S, 12.01.

In the nmr spectrum ($CDCl_3$), the amide protons appeared as a broad band between 7.2 and 7.5 ppm. The aromatic protons appeared as complex signals between 7.6 and 8.1 ppm. On addition of deuterium oxide the amide signal slowly disappeared.

Dicarbonylbis(carbamoyldiphenylphosphine)nickel (4).—To a solution of 1.5 g (6.5 mmol) of carbamoyldiphenylphosphine in 40 ml of benzene was added 0.555 g (3.25 mmol) of nickel carbonyl. As the mixture was heated the phosphine dissolved and a solid began to precipitate as the benzene started to reflux. The heat was then removed, and the solution was stirred for 1 hr while cooling to room temperature. Filtration gave 1.7 g of product (91% yield), mp 171–172° dec.

Anal. Calcd for $C_{28}H_{24}N_2NiO_4P_2$: C, 58.67; H, 4.22; N, 4.90; Ni, 10.24. Found: C, 58.78; H, 4.12; N, 5.03; Ni, 10.23.

The compound could be recrystallized from nitromethane, but developed a pale green color (probably due to Ni^{2+}) when heated in this solvent.

Benzylcarbamoyldiphenylphosphonium Iodide (5).—To a solution of 3.0 g (13.1 mmol) of carbamoyldiphenylphosphine in 70 ml of hot degassed benzene was added 5.2 g (24 mmol) of benzyl iodide. An exothermic reaction caused the benzene solution to reflux for 5 min. The mixture was stirred at room temperature overnight, then filtered to give 4.0 g of the phosphonium salt. The filtrate was refluxed for 2 hr and furnished an additional 1.5 g of the salt. Total yield of product was 5.5 g (94% yield), mp 222° dec.

Anal. Calcd for $C_{20}H_{19}INOP$: C, 53.71; H, 4.28; N, 3.13. Found: C, 53.84; H, 4.67; N, 1.95.

This salt was insoluble in all common organic solvents.

Benzylcarbamoyldiphenylphosphonium Bromide (6).—A procedure similar to that used for the corresponding iodide was followed. From 2.0 g (8.75 mmol) of carbamoyldiphenylphosphine and 5 ml of benzyl bromide, 2.6 g (74% yield) of product was obtained, mp 202° dec.

Anal. Calcd for $C_{20}H_{19}BrNOP$: C, 60.01: H, 4.78; N, 3.50. Found: C, 60.20; H, 4.83; N, 2.61.

Dichlorobis(carbamoyldiphenylphosphine)platinum (7).—A slurry of 0.61 g (1.035 mmol) of tetrachlorobis(ethylene)diplatinum and 1.2 g (5.24 mmol) of carbamoyldiphenylphosphine in 20 ml of benzene was refluxed for 10 min, then stirred at room temperature overnight. The precipitated solid was filtered and recrystallized from a mixture of ethyl acetate and methanol. The product had mp 252–254° dec; a yield of 0.7 g (46.5%) was obtained.

Anal. Calcd for $C_{26}H_{24}Cl_2N_2O_2P_2Pt$: C, 43.10; H, 3.34; N, 3.86; Pt, 26.94. Found: C, 44.00; H, 3.75; N, 2.15; Pt, 27.54.

4-Amino-4-diphenylphosphinyl-3-*p*-tolylsulfonyl-1,3-oxazetidone (9).—To a solution of 3.0 g (13.0 mmol) of carbamoyldiphenylphosphine in 50 ml of benzene was added a solution of 3.84 g (19.5 mmol) of *p*-toluenesulfonyl isocyanate in 20 ml of benzene. No temperature rise was observed during the addition, but the phosphine partially dissolved. The solution was heated to 78° for 5 min and allowed to cool. The benzene was removed under vacuum, and the oily residue was dissolved in absolute ethanol, treated with charcoal, and filtered. On cooling, a solid formed (175 mg, 3% yield) which, after two recrystallizations from ethanol, had mp 170° dec.

Anal. Calcd for $C_{21}H_{19}N_2O_5PS$: C, 57.01; H, 4.33; N, 6.33; P, 7.00. Found: C, 56.92; H, 4.28; N, 6.39; P, 6.81.

The nmr spectrum of this product (pyridine-d_5) had peaks at 9.0 (broad singlet), 6.0–8.8 (complex multiplets), and 2.12 ppm (sharp singlet) in an approximate ratio of 2:14:3. On addition of D_2O the peak at 9.0 ppm exchanged completely.

Registry No.—**1,** 3659-43-6; **2,** 3659-45-8; **3,** 16790-96-8; **4,** 16799-84-1; **5,** 16790-97-9; **6,** 16790-98-0; **7,** 16799-83-0; **9,** 16790-99-1.