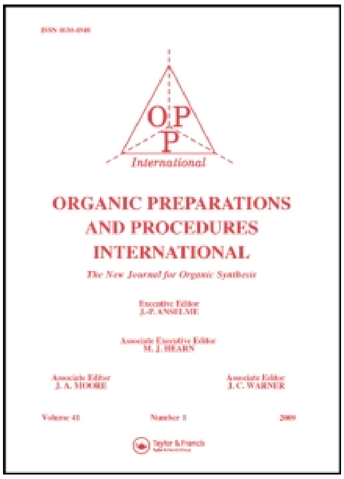

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AZIDOMETHYLDIPHENYLPHOSPHINE OXIDE

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AZIDOMETHYLDIPHENYLPHOSPHINE OXIDE

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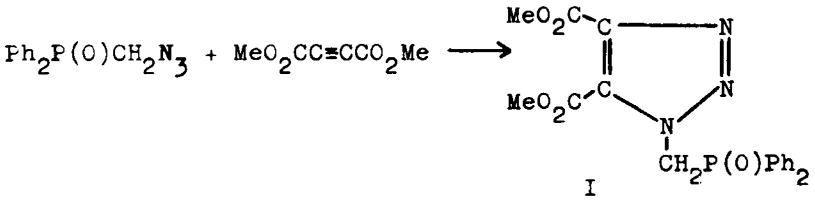
$$Ph_2P(O)CH_2Cl + NaN_3 \xrightarrow{DMF} Ph_2P(O)CH_2N_3 + NaCl$$



I

In connection with our studies concerning phosphorus-substituted diazoalkanes,[1-4] we had occasion to prepare the title compound by reaction of chloromethyldiphenylphosphine oxide with sodium azide. This azido derivative was characterized further via its reaction with the dimethyl ester of acetylenedicarboxylic acid to yield the triazole I.

Our studies of the chemistry of this phosphorus-substituted azide were not continued, and we report its preparation in view of its potential application as a precursor for the phosphorus-substituted nitrene, $Ph_2P(O)CH_2N$.

EXPERIMENTAL

To a solution of 2.5 g (10 mmol) of chloromethyldiphenylphosphine oxide[5] in 30 ml of DMF was added 2 g (30.8 mmol) of sodium azide. The resulting brown solution was stirred at 110° for 2 hr. The reaction mixture was allowed to cool to room temperature and 40 ml of chloroform was added. The resulting white emulsion was poured into 100 ml of water. The organic layer was separated and the aqueous phase was extracted with two 10 ml portions of chloroform. The combined chloroform solutions were dried ($MgSO_4$) and evaporated at reduced pressure to leave an oil. The latter was taken up in a small amount of chloroform and diethyl ether (40 ml) was added; white crystals deposited slowly. After their removal, the mother liquor was treated with hexane to precipitate more solid. The total yield was 51%; m.p. 109.5-111° (from cyclohexane/ethyl acetate). Anal. Calcd. for $C_{13}H_{12}ON_3P$: C, 60.69; H, 4.71. Found: C, 60.28; H, 4.87.

The nmr spectrum ($CDCl_3$; Varian A60) showed a doublet (J = 7.5 Hz) at δ 3.97 ($C\underline{H}_2$) and a multiplet at 7.3-8.0 ppm (aryl H). The ir spectrum (Nujol mull) showed the following bands: 2190(w), 2150(m), 2120(m), 2085(s), 1580 (w), 1460(s), 1435(s), 1375(m), 1315(w), 1280(m), 1245(s), 1190(m), 1175(s), 1125(s), 1100(m), 1070(w), 990(w), and 855(m) cm^{-1}.

The azidomethyldiphenylphosphine oxide thus prepared (2.57 g, 10 mmol) and dimethyl acetylenedicarboxylate (1.42 g, 10 mmol) were mixed and heated on the steam bath. A vigorous reaction commenced immediately. The resulting brown reaction mixture was cooled immediately. The solid which formed was crystallized from chloroform/cyclohexane to give 2.9 g (73%) of the 1,3-dipolar addition product I. Recrystallization from carbon tetrachloride/methanol resulted in fine white needles, m.p. 174.5-176°. Anal. Calcd. for $C_{19}H_{18}N_3O_5P$: C, 57.15; H, 4.54. Found: C, 57.33; H, 4.81.

The nmr spectrum of the product I (in $CDCl_3$) showed singlets at 3.91 and 3.97 (6H, $OC\underline{H}_3$), a doublet (J = 6.5 Hz) at 5.63 ($PC\underline{H}_2$) and a multiplet at 7.3-8.0 ppm (aryl H). The ir spectrum (Nujol mull) showed the following bands: 1745 (s), 1725(s), 1560(m), 1465(s), 1435(s), 1405(w), 1375(m), 1355(m), 1320(m), 1265(m), 1240(s), 1225(s), 1185(s), 1140 (m), 1120(m), 1095(w), 1060(m), 955(w), 820(w), 740(m), 730 (m), 710(w), and 690(m) cm^{-1}.[6]

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