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DIMETHYL DIAZOMETHYLPHOSPHONATE: ITS PREPARATION AND REACTIONS

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Regitz and Anschütz[1] recently reported the preparation of diethyl diazomethylphosphonate. However, their procedure appeared to lack practical utility, giving only crude (34° boiling range) material in unspecified yield. Their product was characterized as the phosphazine, $(EtO)_2P(O)CH=N-N=PPh_3$, and no other chemical transformations were reported.

We have been investigating phosphorus-substituted diazoalkanes[2] and during the course of our studies have prepared dimethyl diazomethylphosphonate by a route different than that used by Regitz and Anschütz for the diethyl analog (Chart I). Our preparation afforded pure $N_2CHP(O)(OMe)_2$ as a distillable yellow liquid, bp 59° (0.42 mm), $n^{25}D$ 1.4585, ν^{film} (C=N=N) 2110(s), ν^{film} (P=O) 1250(s) cm^{-1}. Calcd. for $C_3H_7N_2O_3P$: C, 24.01; H, 4.70; found: C, 23.73; H, 4.85. Nmr (neat): δ 3.73 (d, 6, J = 11.5 Hz, P-OMe); 4.49 ppm (d,1, J = 10.7 Hz, P-C-H). This diazo compound was stable indefinitely when refrigerated. It reacted with triphenylphosphine in benzene to give $(MeO)_2P(O)CH=N-N=PPh_3$, m.p. 132-133°, and, as expected, with warm acetic acid to form $(MeO)_2P(O)-CH_2O_2CCH_3$, bp 63° (0.16), $n^{25}D$ 1.4295. Mercuration using mercury(II) acetylacetonate in dichloromethane gave $Hg[C(N_2)P(O)(OMe)_2]_2$, yellow needles with mp 106.5-107°, in 80% yield, and a surprisingly stable yellow silver salt which exploded at its mp of 125° also was prepared.

Of greater interest and preparative utility was the finding that dimethyl diazomethylphosphonate underwent carbenoid addition to the C=C bond when stirred at 0° with a large excess of an olefin in dichloromethane solution and in the presence of copper powder. When dichloromethane was not used, the yields were markedly reduced due to the low solubility of the diazo compound in the various olefins. In reactions with cyclohexene, copper powder was found to be the most effective catalyst, resulting in higher cyclopropane yields and less tar than in reactions employing copper(I) chloride or copper(II) acetylacetonate. Chart II summarizes the cyclopropanation reactions carried out. In addition to the cyclopropanes, all four reactions gave varying amounts of the carbene "dimer", $(MeO)_2P(O)CH=CHP(O)(OMe)_2$, a high boiling liquid which was identical to the product obtained by copper-catalyzed decomposition of the diazo compound in pure dichloromethane. Hydro-

genation and saponification of this compound gave the known[3] 1,2-ethanediphosphonic acid.

All new compounds were characterized spectroscopically and satisfactory (± 0.3%) combustion analyses were obtained for all. The infrared and nmr spectra of the olefin addition products were in agreement with their formulation as dimethylphosphono-substituted cyclopropanes.

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References

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CHART I

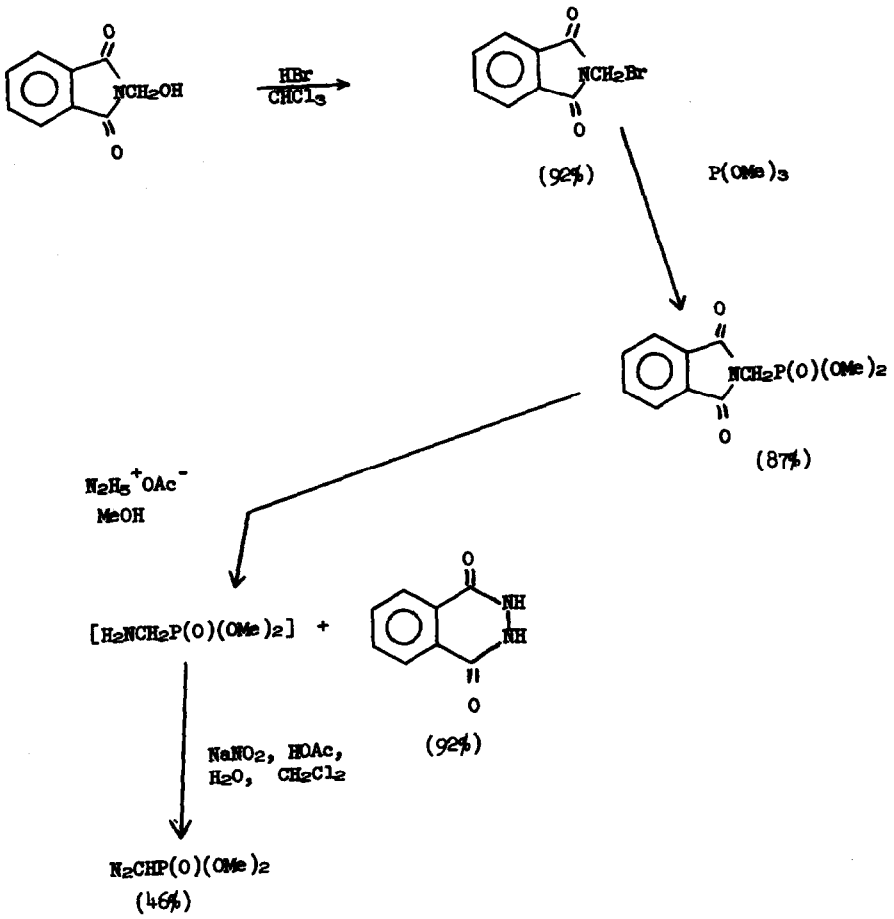
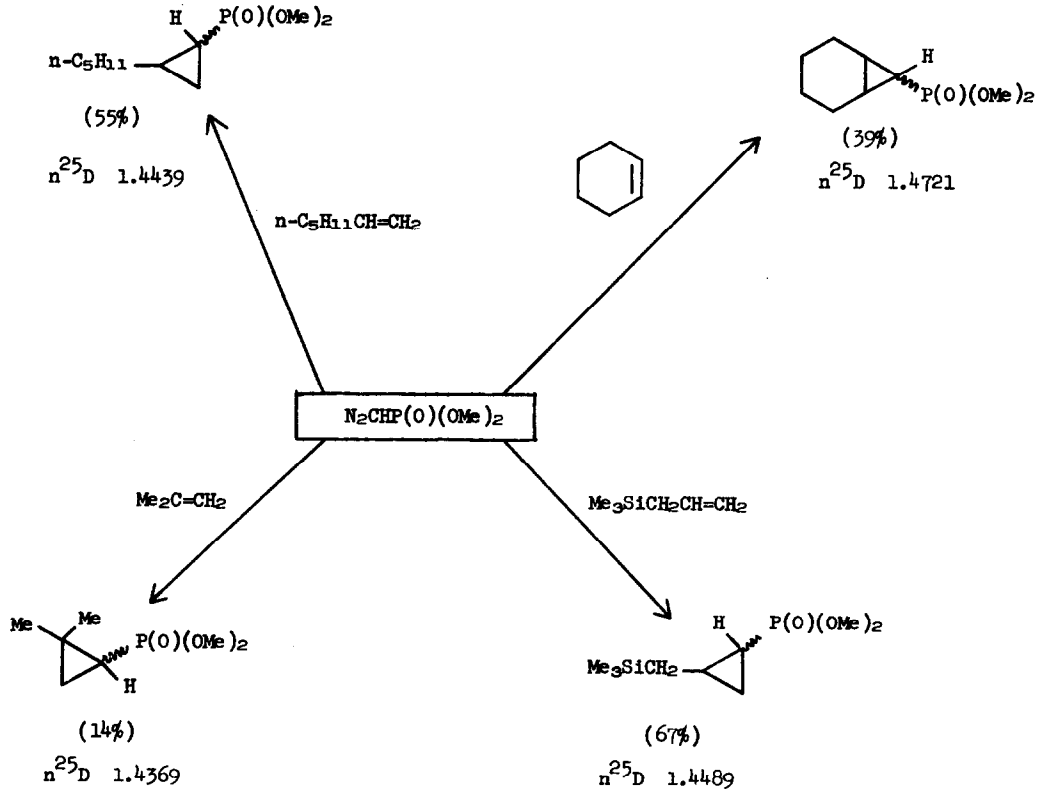

NCH2OH
HBr
CHCl3
NCH2Br
(92%)
P(OMe)3
NCH2P(O)(OMe)2
(87%)
N2H5+OAc-
MeOH
[H2NCH2P(O)(OMe)2] +
NH
NH
(92%)
NaNO2, HOAc,
H2O, CH2Cl2
N2CHP(O)(OMe)2
(46%)

CHART II


H
P(0)(OMe)2
n-C5H11
(55%)
n25D 1.4439
n-C5H11CH=CH2
H
P(0)(OMe)2
(39%)
n25D 1.4721
N2CHP(0)(OMe)2
Me2C=CH2
Me3SiCH2CH=CH2
Me
Me
P(0)(OMe)2
H
(14%)
n25D 1.4369
H
P(0)(OMe)2
Me3SiCH2
(67%)
n25D 1.4489