REACTION OF TRIMETHYL PHOSPHITE AND TRI(DIMETHYLAMINO)PHOSPHINE WITH C,N-DIPHENYLNITRONE AND 2,5-DIPHENYL-3,4-DIAZACYCLOPENTADIEN-1-ONE-3,4-DIOXIDE

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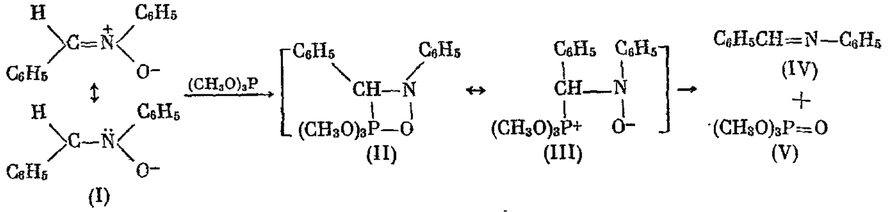
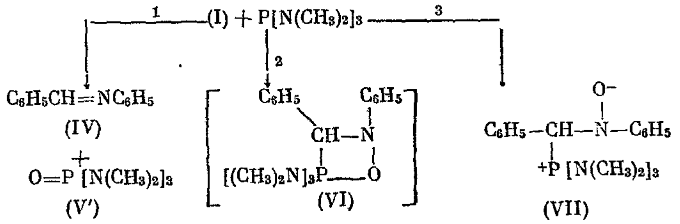
C,N-Diphenylnitrone (I) reacts with trimethyl phosphite the same as does 2,5-diphenyl-3,4-diazacyclopentadien-1-one-3,4-dioxide [1], with a transfer of oxygen from (I) to the $(CH_3O)_3P$ to give trimethyl phosphate and benzalaniline.



The formation of phosphorane (II) as an intermediate product, and also of adduct (III), is not excluded if the reaction proceeds by the 1,3-dipolar mechanism [2-4].

The reaction of tri(dimethylamino)phosphine with nitrone (I) can proceed in the following directions: 1) with the transfer of oxygen from nitrone (I) to the tri(dimethylamino)phosphine to give tri(dimethylamino)-phosphine oxide, 2) with the formation of phosphorane (VI) [5], and 3) with the formation of the bipolar ion (VII)



The reaction of nitrone (I) with tri(dimethylamino)phosphine in CH_2Cl_2 solution at ~20°C gives a mixture of benzalaniline (IV), tri(dimethylamino)phosphine oxide (V') (δ_{31P} −24 ppm), and the bipolar ion (VII) (δ_{31P} −48 ppm), which were isolated by chromatographing on silica gel.

2,5-Diphenyl-3,4-diazacyclopentadien-1-one-3,4-dioxide reacts with tri(dimethylamino)phosphine in the same manner as nitrone (I) to give tri(dimethylamino)phosphine oxide and the bipolar ion (IX). The bipolar adducts (VII) and (IX) were isolated in the analytically pure form via the salts (VIII) and (X) with sodium tetraphenylboronate

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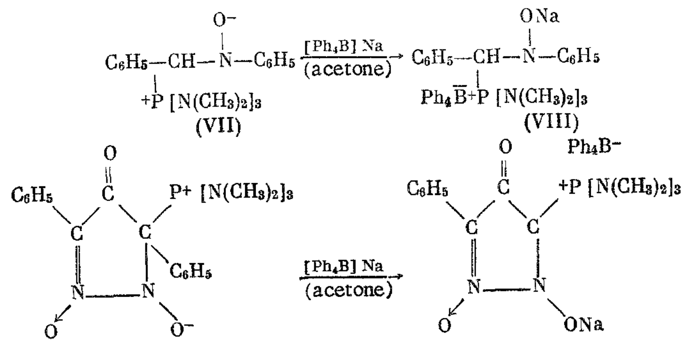

(IX) (X)

The formation of a similar salt was not observed when the C,N-diphenylnitrone was reacted with trimethyl phosphite in the presence of sodium tetraphenylboronate. Via special experiments it was shown that neither C,N-diphenylnitrone nor trimethyl phosphite form complexes with sodium tetraphenylboronate.

EXPERIMENTAL METHOD

Reaction of C,N-Diphenylnitrone (I) with Trimethyl Phosphite. An equimolar mixture of 2 g of nitrone (I) [6], mp 113-114°, and 1.3 g of trimethyl phosphite was heated in a sealed tube at 140-150° for 24 h. Distillation gave 1 g of trimethyl phosphite, bp 79-80° (14 mm), n_D^{20} 1.4020 (IR spectrum (in a capillary film, ν, cm^{-1}): 1045 v.s (P–O–C), 1188 m (P–O–CH_3), 1280 s (P=O) etc.), and 1.2 g of benzalaniline with bp 92-93° (2.10^{-4} mm), mp 50-51°. The mixed melting point with an authentic specimen [7] was 50-51°. Found: N 7.95; 8.05%. $C_{13}H_{11}N$. Calculated: N 7.73%. The IR spectrum has the $\nu_{C=N}$ band at 1625 cm^{-1}, characteristic for benzalanilines [8], and lacks the band at 1559 cm^{-1}, which is characteristic for the $\nu_{\underset{\wedge}{C}=\overset{+}{N}-\overset{-}{O}}$ of nitrones [9].

Reaction of C,N-Diphenylnitrone (I) with Tri(dimethylamino)phosphine. To a solution of 0.5 g of nitrone (I) in absolute CH_2Cl_2 in a Dry Box was added 0.4 g of tri(dimethylamino)phosphine. The solution gradually assumed an intense yellow color over a period of 30 min. After removal of the solvent in vacuo the thick dark liquid, with δ_{31P} –48, –23, and –12 ppm, was chromatographed on KSK silica gel (0.25 mesh, 10 g). The following products were isolated: 1) benzalaniline with mp 50-51°; eluted with a 4:1 petroleum ether–benzene mixture; the mixed melting point with an authentic specimen was not depressed; 2) a mixture of benzalaniline and benzaldehyde; the latter was identified by the IR spectrum ($\nu_{C=O}$ 1700 cm^{-1}); eluted with petroleum ether; 3) a mixture of nitrone (I) and benzalaniline (C_6H_6); identified by the IR spectrum; 4) tri(dimethylamino)phosphine oxide (CH_2Cl_2 : CH_3OH = 10 : 1) with n_D^{20} 1.4590; δ_{31P} –24 ppm; identified by the IR spectrum; 5) a dark liquid was eluted with a 10 : 1 CH_2Cl_2 : CH_3OH mixture, whose IR spectrum corresponds to the structure of bipolar ion (VII) (ν, cm^{-1}): 710, 765, 782 w, 1008 v.s, 1045, 1070 m, 1180 s, 1305 s, 1460, 1485 m, 1590 w, 1620 v.w.

Reaction of C,N-Diphenylnitrone (I) and Tri(dimethylamino)phosphine with Sodium Tetraphenylboronate. A solution of 0.5 g of nitrone (I), 0.1 g of tri(dimethylamino)phosphine, and 0.9 g of sodium tetraphenylboronate in acetone was let stand at ~20° for 15 days. After removal of the acetone the residual thick mass was treated with water to give salt (VIII) (1.5 g, 88%) as a fine colorless powder with mp 100-102°. Found: N 7.83; 7.97; P 4.23; 4.13%. $C_{43}H_{49}N_4OPBNa$. Calculated: N 7.97; P 4.41%. Infrared spectrum (as a Nujol mull, ν, cm^{-1}): 615 m, 713, 745, 1000 s, 1070 m, 1150, 1220, 1380, 1460 s.

Reaction of 2,5-Diphenyl-3,4-diazacyclopentadien-1-one-3,4-dioxide with Tri(dimethyamino)phosphine. To a solution of 0.5 g of 2,5-diphenyl-3,4-diazacyclopentadien-1-one-3,4-dioxide in CH_2Cl_2 in a Dry Box was added 0.3 g of tri(dimethylamino)phosphine. The color of the solution changed from dark cherry-red to brown. After 7 days the CH_2Cl_2 was removed in vacuo; δ_{31P} –38 and –26 ppm; IR spectrum (ν, cm^{-1}): 709 m, 750 s, 773 m, 1000 v.s, 1072 m, 1185, 1205 s, 1245 m, 1305 s, 1460, 1486, 1640 m.

The obtained thick mass was treated with an acetone solution of 0.6 g of [Ph_4B]Na. After 13 days the acetone was removed and the residue was treated with water to give salt (X) with mp 71-73°. Found: N 8.79; 8.92; P 3.87; 4.13%. $C_{45}H_{48}N_5O_3PBNa$. Calculated: N 9.07; P 4.01%. Infrared spectrum (as a Nujol mull, ν, cm^{-1}): 615 m, 711, 740 s, 775 m, 851 w, 920 m, 1015 s (sn 1000), 1070, 1150, 1180, 1245 m, 1320, 1382, 1465 s, 1585, 1645 w.

CONCLUSIONS

1. C,N-Diphenylnitrone reacts with trimethyl phosphite to give trimethyl phosphate and benzalaniline.

2. C,N-Diphenylnitrone and 2,5-diphenyl-3,4-diazacyclopentadien-1-one-3,4-dioxide react with tri(dimethylamino)phosphine in two directions: with the transfer of oxygen from the nitrone to the tri(dimethylamino)phosphine, and with the formation of bipolar ions, which were isolated as the sodium salts by reaction with sodium tetraphenylboronate.

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