

THE USE OF DIETHYL PHOSPHONATE AS A SOLVENT AND CATALYST FOR THE PREPARATION OF ARYLHYDRAZONES*

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One of the difficulties in preparing arylhydrazones has sometimes been the lack of a suitable solvent for both the arylhydrazine and the carbonyl compound. Shine (1959) lists some of the methods available and reports that 2,5,8-trioxanonane (diglyme) is a convenient solvent in certain cases.

It has now been found that diethyl phosphonate (diethyl phosphite) is a good solvent for arylhydrazines and for many carbonyl compounds. Furthermore, addition of an acid catalyst to the mixture is unnecessary because traces of water hydrolyse the solvent giving the strong acid ethyl hydrogen phosphonate, HP(O)(OEt)(OH) , (Milobendzki and Sachnowski 1917) and more water is produced as the reaction proceeds. Under the conditions employed, side reactions between carbonyl compounds and the solvent do not compete seriously with hydrazone formation. Wild (1958) lists several 2,4-dinitrophenylhydrazones which are difficult to prepare by published methods, but when diethyl phosphonate was employed no difficulty was experienced in obtaining 2,4-dinitrophenylhydrazones of benzoin, di-n-butyl ketone, phenacyl bromide, or fenchone. 18-Pentatriacontanone (stearone) and 1-phenyloctadecan-1-one (stearophenone), selected because of their low solubility in hot ethanol, gave satisfactory yields of hydrazones, here described for the first time, but the hindered ketone 2-methyl-2-(1-hydroxy-1-methylethyl)cyclohexanone failed to react.

Experimental

To a solution of the carbonyl compound (1 mmole) in the minimum volume of diethyl phosphonate was added a solution of the arylhydrazine (1 mmole) in diethyl phosphonate (4 ml). In some instances, the hydrazone precipitated immediately or on keeping the solution for a few hours, but in others it was necessary to dilute the mixture with an equal volume of water in order

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to precipitate the product. Yields were sometimes improved by reducing the volume of solvent and by heating the mixture at 100 °C for 1 hr.

The arylhydrazones were recrystallized from methanol, ethanol, benzene, or acetone according to their solubilities. Melting points agreed with those in the literature except where stated and the yields ranged from 50–80%.

2,4-Dinitrophenylhydrazones.—Phenacyl bromide, m.p. 218–220 °C (lit. 220–220.5 °C); benzoin, m.p. 233–234 °C (234 °C); fenchone, 140–141 °C (140 °C); di-n-butyl ketone, 39–40 °C (40.5–41.0 °C); *p*-nitrobenzaldehyde, 331–333 °C (Wild 1958; 320 °C); benzophenone, 243–244 °C (Wild 1958; 239 °C); stearone, 57–59 °C (Found: N, 8.5%; Calc. for $C_{41}H_{74}N_4O_4$: N, 8.2%); stearophenone, 100–101 °C (Found: N, 10.5%. Calc. for $C_{30}H_{44}N_4O_4$: N, 10.7%).

Phenylhydrazones.—*p*-Nitrobenzaldehyde, 157 °C (159 °C); acetophenone 104–106 °C (105 °C).

p-Nitrophenylhydrazones.—Acetone, 147–148 °C (148 °C); benzophenone, 152–153 °C (154 °C).

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References

- MILOBENDZKI, T., and SACHNOWSKI, A. (1917).—*Roczn. Chem.* **15**: 48.
SHINE, H. J. (1959).—*J. Org. Chem.* **24**: 252.
WILD, F. (1958).—“Characterisation of Organic Compounds.” 2nd Ed. p. 114. (Cambridge Univ. Press.)