Oxidation with Nickel Peroxide.[1] The Preparation of Diazo-compounds from Hydrazones

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NICKEL PEROXIDE has been used as an oxidizing agent for many functional groups.[2] We have used nickel peroxide to oxidize some hydrazones to the corresponding diazo-compounds in good yields. The preparation of diphenyldiazomethane by the oxidation of benzophenone hydrazone has long been known. The oxidizing agents most frequently used have been mercuric oxide,[3] manganese dioxide,[4] and silver oxide.[5] Nickel peroxide oxidation of benzophenone hydrazone with a small excess of the theoretical amount of the oxidant resulted in a quantitative yield of diphenyldiazomethane in 1 hr. in contrast to the 6 hr. required with mercuric oxide. In the case of the oxidation with manganese dioxide, large excess of the oxidant was required for completion of the oxidation and the product obtained by this method was somewhat contaminated by diphenylketazine.

The oxidation of benzophenone hydrazone was carried out as follows. To a solution of benzophenone hydrazone in ether, nickel peroxide[2] (1·1 times the theoretical amount, determined by iodometry) was added while stirring on a magnetic stirrer, and the heterogeneous solution was allowed to react at 20° for 1 hr. The mixture was filtered, the solid was washed with the solvent, and the filtrate was evaporated to dryness under reduced pressure at room temperature. The residue gave a quantitative yield of the crude diazo-compound. The product at this stage was assayed by treatment with benzoic acid in ether solution and yielded the crude benzhydryl benzoate (97%), melting at 87·5°. This reaction was successfully applied to several kinds of monohydrazones as shown in the Table.

Phenylbenzoyldiazomethane, azibenzil, has been prepared in good yield by the oxidation of benzil monohydrazone with mercuric oxide at room temperature using ether as the solvent.[6] When nickel peroxide was substituted for mercuric oxide the reaction proceeded rapidly irrespective of the low temperature (0°) and yielded the crude α-diazoketone in a quantitative yield, but the product obtained by this method was contaminated with small amounts of impurities, as indicated by its infrared spectrum and by thin-layer chromatography. When the oxidation was performed at room temperature for 50 hr., we found that benzophenone was obtained from the reaction mixture in 30% yield and a small amount of diphenylketen was formed. The use of mercuric oxide has been found to be preferable to that of nickel peroxide for the preparation of phenylbenzoyldiazomethane. Oxidation of benzil dihydrazone with nickel peroxide was carried out in ether solution at 0°, and interrupted when the spot due to the hydrazone on a thin-layer chromatogram had disappeared (about 30 min.). The filtrate was evaporated under reduced pressure, the residue was distilled at 95—105°/0·2—0·3 mm. and yielded 60·8% of diphenylacetylene, m.p. 58—61°.

TABLE

Hydrazone of	Reaction Temp.	Reaction Hr.	Yield (%) of Diazo-compound
Acetophenone	0	1	55·7[a]
Acetone	0	1	16·7[b]
Benzaldehyde	0	1	68·4[c]
Fluorenone	20	1	92·2[d]
Diethyl mesoxalate	20	1	89·3[e]

[a] As *p*-nitrobenzoate (m.p. 45°)
[b] As *p*-nitrobenzoate (m.p. 108°)
[c] As *p*-nitrobenzoate (m.p. 84·5°)
[d] Recrystallized from petroleum (m.p. 98°)
[e] Rectified (b.p. 108·5°/11 mm.)

(*Received, September* 14*th*, 1966; *Com.* 687.)

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