of *p*-toluidine and 0.45 g. of *p*-tolylazo-β-naphthol. A quantitative recovery of azo dye was made assuming one mole of dye was produced from 1 mole of triazene. Furthermore, 79% of the expected toluidine and 80% of the excess β-naphthol was obtained. This experiment carried out in toluene rather than methanol resulted in a net absorption of one mole of nitric oxide; only a small yield of azo dye resulted, however. The principal product was an intractable tar. No apparent reaction occurred between ditolyltriazene and nitric oxide in methanol in the absence of passive coupler.

Fate of the Unstable Coupling Component Produced in an Inert Solvent.—Diphenyltriazene (5.0 g.) in 100 ml. of anhydrous thiophene-free benzene was treated at room temperature with nitric oxide in the usual way. When reaction had ceased, the solution was filtered to give 3.2 g. of dry solid. The dark solution was distilled to remove benzene, then steam distilled to give 1.9 g. (49%) of biphenyl, m.p. 69°. The residue was a dark tar, identical in appearance and odor to the usual "diazo resins" produced during typical biaryl syntheses by the Gomberg–Bachmann reaction.

The Reaction of Nitric Oxide with 1,3-Di-*p*-tolyl-1-methyltriazene.—In an attempt to isolate N-nitroso-N-methyltoluidine, the N-methyltriazene (8.80 g.) was treated with nitric oxide at 0°. The usual precipitate was obtained, which was identical to that from 1,3-di-*p*-tolytriazene. However, no N-nitrosoamine could be isolated. The absorption of nitric oxide, however, followed a somewhat different course. It was autocatalytic, but leveled off at a net absorption of about 2 moles.

Reaction of 1,3-Bis-(4-chlorophenyl)-triazene with Nitric Oxide.—One gram of this triazene in a mixture of 25 ml. of cyclohexane and 25 ml. of benzene was treated with nitric oxide at room temperature. (The reaction was too slow at 0°.) As above, a white solid was isolated (440 mg.) which contained 17.1% chlorine (Dumas) without further purification. A recrystallization from isopropyl alcohol–ether as described above gave *p*-chlorophenyldiazonium nitrate.

Anal. Calcd. for $C_6H_4N_3O_3Cl$: Cl, 17.6. Found: Cl, 17.4. Calcd. for $C_6H_4N_3O_3Cl\cdot H_2O$: C, 32.9. Found[6]: 32.1, 32.9, 31.9, 32.3, 32.3.

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[6] Wet carbon method. These samples were analyzed "as received" without additional drying, whereas the samples for Dumas halogen were dried *in vacuo* overnight over anhydrone.

[7] An earlier version of this manuscript was received on March 23, 1949.

Synthesis of 2,4-Dihydroxybenzohydrazide

BY BERNARD CAMBER[1] AND DOMINIC D. DZIEWIATKOWSKI

A new color test for aldehydes and ketones was introduced in 1949[2] based on the coupling of a diazonium salt with the naphtholic hydrazide derivative of an aldehyde or ketone to form a stable, intensely colored azo dye. The application of one reagent of this group, 2-hydroxy-3-naphthoic hydrazide, to histochemistry,[2–4] to the qualitative and quantitative study of urinary ketosteroids,[5] and to the isolation of estrone[6] has been reported. The usefulness of a phenolic hydrazide, 2,4-dihydroxybenzohydrazide, in the histochemical differentiation of active carbonyl groups and in the characterization of ketosteroids is now under study. No reference to the synthesis of 2,4-dihydroxybenzohydrazide has been found in the literature.

2,4-Dihydroxybenzohydrazide.—In a 100-ml. round-bottom flask with a ground glass joint 18.2 g. (0.1 mole) of ethyl 2,4-dihydroxybenzoate was dissolved in 10 ml. of absolute ethanol by warming. To the warm solution 8 ml. of 100% hydrazine hydrate was added slowly with mixing. Most of the ethanol was removed by distillation. The flask was attached to a reflux condenser and the reaction mixture refluxed for two hours. At the end of one hour an additional 4 ml. of hydrazine hydrate was added through the condenser. On cooling to room temperature the reaction mixture solidified. The flask with the reaction mixture was placed over anhydrous calcium chloride in an evacuated desiccator and kept therein for three days at room temperature to further remove the ethanol and thereby drive the reaction nearer completion. The solid was dissolved in a minimum volume, about 200 ml., of boiling 95% ethanol. A light tan crystalline precipitate was deposited on cooling to room temperature. The amount of precipitate increased further by placing the mixture at 0° for three hours. The precipitate was then isolated by filtration and washed repeatedly with small volumes of cold 95% ethanol. It was redissolved in slightly more than the required minimum volume of 95% ethanol and the solution was decolorized with activated carbon (Darco, Grade G-60). After 12 hours at 0° a nearly white crystalline product was isolated. It was dried briefly in air and then for 24 hours *in vacuo* over calcium chloride at room temperature. The yield was 5.7 g. (34%), m.p. 240–241° (uncor.). Two more recrystallizations from 95% ethanol gave colorless lath-like needles, m.p. 245–246° (uncor.).

Anal.[7] Calcd. for $C_7H_8O_3N_2$: C, 50.00; H, 4.76; N, 16.66. Found: C, 50.04; H, 4.82; N, 16.70.

Benzaldehyde 2,4-Dihydroxybenzoylhydrazone.—To 10 ml. of a saturated 95% ethanol solution of the hydrazide 0.1 ml. of freshly distilled benzaldehyde was added followed by 0.1 ml. of glacial acetic acid. The mixture was kept hot, short of boiling, for 20 minutes. After it had cooled, 10 ml. of distilled water was added and the reaction mixture was set aside at 0° for 24 hours. The resultant solid was isolated by filtration, washed with water and then with ether. One recrystallization from alcohol–water gave yellow needles in large part as burrs, m.p. 239° (uncor.).

Anal. Calcd. for $C_{14}H_{12}O_3N_2$: C, 65.62; H, 4.69; N, 10.93. Found: C, 65.61; H, 4.86; N, 11.08.

Cyclopentanone 2,4-Dihydroxybenzoylhydrazone.—The conditions of synthesis were as those for the benzaldehyde hydrazone. One recrystallization from alcohol–water gave colorless needles, m.p. 265° (uncor.) with decomposition.

Anal. Calcd. for $C_{12}H_{14}O_3N_2$: C, 61.53; H, 5.98; N, 11.96. Found: C, 61.62; H, 5.99; N, 12.36.

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[1] Advanced Medical Fellow of the Commonwealth Fund, 1949–1950.

[2] B. Camber, *Nature*, **163**, **285** (1949).

[3] R. Ashbel and A. M. Seligman, *Endrocrinology*, **44**, 565 (1949).

[4] R. S. Benua and E. Howard, *Bull. Johns Hopkins Hosp.*, **86**, 200 (1950).

[5] B. Camber, *Fed. Proc.*, **9**, 158 (1950).

[6] J. A. Ledogar and N. W. Jones, Jr., *Science*, **112**, **586** **(1950)**.

[7] All analyses were performed by Mr. T. Bella, Rockefeller Institute for Medical Research, New York, N. Y.

Evidence that 1-Isopropyl-3-*t*-butylbenzene from Aluminum Chloride Alkylation of Benzene with Isobutene is Really 1,3-Di-*t*-butylbenzene

BY FRANCIS E. CONDON AND EDWARD E. BURGOYNE

That 20% of the product of aluminum chloride alkylation of benzene with isobutene was 1-isopropyl-3-*t*-butylbenzene,[1] or that this compound was formed by sulfuric acid or aluminum chloride "rearrangement" of 1,4-di-*t*-butylbenzene,[2] seems questionable because (1) treatment of the compound with aluminum chloride and benzene gave *t*-butyl-

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[1] Legge, THIS JOURNAL, **69**, 2079 (1947).

[2] Legge, *ibid.*, **69**, 2086 (1947).