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.

Acknowledgment.—We wish to thank Mr. L. M. White and Miss Marian Simone for the analyses reported.

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LOS ANGELES, CALIF. RECEIVED MARCH 21, 1951[7]

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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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NEW YORK, N. Y. RECEIVED MARCH 14, 1951

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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**, 536 (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).

benzene but no isopropylbenzene and (2) the dinitro derivative melted 16–17° higher than the literature value.

That the compound was really 1,3-di-*t*-butylbenzene is suggested by the formation of considerable 1,3-dialkylbenzene in other alkylations.[3] This compound, which was first described only recently, has been obtained by aluminum chloride rearrangement of 1,4-di-*t*-butylbenzene,[4] under conditions similar to those producing the so-called 1-isopropyl-3-*t*-butylbenzene,[2] and by synthesis from 2,4-di-*t*-butylphenol.[5] The physical properties of 1,3-di-*t*-butylbenzene correlate well with those of the so-called 1-isopropyl-*t*-butylbenzene, as shown in the following compilation:

	d^t_4	n^t_D	B.p., °C., at	*P*, mm.
1,3-Di-*t*-butylbenzene[4]	.....	1.4870^{20}	106.5	18.2
	.....	......	78.5	4.4
1,3-Di-*t*-butylbenzene[5]	0.8589^{20}	1.4879^{20a}	101	11.2
	$.8547^{25}$	1.4874^{25a}	89.5	6.6
	.....	......	73	2.5
"1-Isopropyl-3-*t*-butylbenzene"[1]	0.8512^{30}	1.4832^{30}	221–222	760

[a] One of these appears in error, perhaps typographically.

The synthesis of 1,3-di-*t*-butylbenzene from 2,4-di-*t*-butylphenol has been repeated. Acetylation of the 1,3-di-*t*-butylbenzene yielded a ketone that gave a 2,4-dinitrophenylhydrazone melting at 211–212° (cor.), in comparison with 208–210° reported.[5] Nitration[6] of the 1,3-di-*t*-butylbenzene gave a dinitro derivative that, twice recrystallized from ether, had a melting point of 164.5–166.0° (cor.), which is practically identical with that of 165.4–166.3° (cor.) reported for the dinitro derivative of the so-called 1-isopropyl-3-*t*-butylbenzene.[1]

Anal.[7] Calcd. for $C_{14}H_{20}N_2O_4$: C, 59.98; H, 7.19. Found: C, 59.93, 60.01; H, 7.39, 7.27.

Reduction of the dinitro derivative with tin and hydrochloric acid[6] gave a diamino derivative that, once recrystallized from isoöctane, had a melting point of 153–154° (cor.), in comparison with 159.1–160.6° (cor.) for the diamino derivative of the so-called 1-isopropyl-3-*t*-butylbenzene.[1]

Anal.[7] Calcd. for $C_{14}H_{24}N_2$: C, 76.31; H, 10.98. Found: C, 75.09, 74.53, 74.14; H, 10.98, 10.90, 10.49. (There was insufficient sample for further purification and analysis.)

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[3] Berry and Reid, THIS JOURNAL, **49**, 3142 (1927); Newton, *ibid.*, **65**, 320 (1943); Simons and Hart, *ibid.*, **69**, 979 (1947).

[4] Johnson and Adams, U. S. Patent 2,429,691 (1947).

[5] Pines, Czajkowski and Ipatieff, THIS JOURNAL, **71**, 3798 (1949).

[6] Ipatieff and Schmerling, *ibid.*, **59**, 1056 (1937).

[7] By Mr. J. E. Puckett.

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BARTLESVILLE, OKLA.
RECEIVED NOVEMBER 30, 1950

The Aqueous Solubility of Hafnium Oxide by the Radioactive Isotope Technique

BY R. A. COOLEY AND H. O. BANKS

Except for thorium oxide whose solubility in water is given[1] as less than 2 × 10^{-5} g. per liter at 25°, little information is available on the solubility of the oxides of group IVa of the periodic table. Since a knowledge of the solubility of the group IVa oxides may be of some value in geochemical, metallurgical and other considerations, we investigated briefly the solubility of hafnium oxide in water by utilizing hafnium 181, a beta and gamma emitter with a half-life of 46 days. Fortunately 99.99% of hafnium 181 decays to stable tantalum 181 so that complications due to radioactive daughter isotopes are not troublesome.

Experimental

The radioactive hafnium oxide was purchased from the Atomic Energy Commission and had been prepared by neutron irradiation of hafnium oxide in a pile. According to the supplier's spectrographic analysis of the sample it contained not more than 0.75% ZrO_2.

The hafnium oxide was placed in contact with distilled water agitated and thermostated to ±0.3° at various temperatures. After 24 to 72 hours it was assumed that equilibrium had been reached and a 200-, 300- or 500-ml. amount of the liquid phase was removed by a previously warmed pipet equipped with a cotton filter. This solution was then usually evaporated in a beaker for radioactivity measurement of the remaining HfO_2. However, another method which may be novel was examined briefly and might prove particularly valuable in cases where a large amount of solution must be evaporated without loss of salt, however small, by deposition on the walls of the container. In this method the container is lined with a thin sheet of polythene before being filled. The solution is then evaporated to dryness under reduced pressure and at a temperature of less than 90°. The polythene sheet is then folded to occupy a minimum of surface on a counting planchet. Toluene, which dissolves polythene, is then added and the toluene–polythene mixture is stirred and finally ignited to leave a uniform layer of the active oxide on the planchet without any layer of unnecessary absorbing material. The substitution of cellophane and acetone for polythene and toluene in the above method did not prove satisfactory since the cellophane was not sufficiently water-proof.

Results

Table I shows the average solubility indicated by duplicate runs at different temperatures. The duplicates agreed within a range of 1.5 to 10%.

Equilibrium was not approached from both sides of the temperatures chosen.

TABLE I

SOLUBILITY OF HfO_2 IN H_2O AT VARIOUS TEMPERATURES

Temp., °C.	Micrograms HfO_2 100 g. H_2O
34.6 ± 0.3	2.3
49.7 ± .3	2.8
60.0 ± .3	2.9
70.3 ± .3	3.2
89.7 ± .3	4.7

The experimental points do not obey the van't Hoff equation well, but by the method of least squares the heat of solution was estimated as about 3 kcal./mole.

A few determinations were made in which sodium sulfate or ammonium nitrate were added to the water–HfO_2 mixture and it was found that the solubility of HfO_2 increased as would be predicted by the Debye–Hückel theory.

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[1] A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Vol. I, 3rd ed., D. Van Nostrand Co., New York, N. Y., 1940, p. 1533.

UNIVERSITY OF MISSOURI
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ROLLA, MISSOURI
RECEIVED NOVEMBER 3, 1950