400 ml. of dry ether was added dropwise to a stirred mixture of 15.0 g. of lithium aluminum hydride in 400 ml. of ether over one hour. After stirring for an additional half-hour, the mixture was chilled and treated with water and dilute sulfuric acid. The product was isolated in the usual way as a crude red oil. Trituration with ether with chilling gave 29.1 g. (84%) of nearly colorless crystalline product. Recrystallization from water provided a colorless analytical sample, m.p. 100–102°.

*Anal.* Calcd. for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.64; H, 7.56.

The same diol was obtained in 38% yield by the lithium aluminum hydride reduction of the monoethyl ester of 1,2-dicarboxy-4,5-dimethoxyindan. To determine whether a different stereochemical configuration would result when a chemical reduction was carried out with 1,2-dicarbethoxy-4,5-dimethoxyindan, the following experiment was performed. A 5.0-g. quantity of IA was reduced with zinc dust in 20 ml. of aqueous acetic acid (2:1 aq.) at 95–100°. The neutral product, 4.4 g. of oil, was reduced with lithium aluminum hydride (2.0 g.) in 250 ml. of ether. The product was identical with that obtained from IIA; a mixed melting point was not depressed.

**1,2-Di-(hydroxymethyl)-6,7-dimethoxytetralin.**—The reduction of 4.0 g. of 1,2-dicarbethoxy-6,7-dimethoxytetralin with 2.1 g. of lithium aluminum hydride in dry ether yielded 2.3 g. (77%) of colorless crystalline product (by trituration with ether). An analytical sample was secured by recrystallization from water; m.p. 127–128.5°.

*Anal.* Calcd. for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.34; H, 7.82.

**6,7-Dimethoxy-3,3a,8,8a-tetrahydroindeno(1,2-c)furan** (*R.I. 1437*).—Treatment of 5.0 g. of 1,2-di-(hydroxymethyl)-4,5-dimethoxyindan with 20.5 g. of phosphorus tribromide in 75 ml. of dry benzene under reflux for 45 minutes gave a neutral oil (2.5 g.) as a product. This material gave an immediate precipitate with alcoholic silver nitrate solution. Numerous efforts were made to replace the halogen by reaction under standard conditions with sodium cyanide and with ethyl malonate. In each case the product was a colorless crystalline solid, m.p. 82–83.5° (from ether). This material was halogen-free; it did not react with bromine or potassium permanganate solutions, and was recovered unchanged after refluxing with 25% potassium hydroxide solution. From these properties and the analytical data, structure IV was assigned to this material.

*Anal.* Calcd. for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 70.51; H, 7.28.

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## Substitution in Polymethylbenzenes. III. A New Route to Isodurene Derivatives[1]

BY GABRIELLO ILLUMINATI AND GIANLORENZO MARINO

RECEIVED MAY 5, 1953

In connection with kinetic studies now in progress on hindered nitrohydrocarbons, we have found that 4-nitroisodurene[2] can be obtained by reduction of 4,6-dinitroisodurene and subsequent deamination of the resulting 4-nitro-6-aminoisodurene by the method previously described[3] for the preparation of 3-nitrodurene.

4,6-Dinitroisodurene has been reported by a number of early workers,[4] but the melting point given by Jannasch and Weiler, 180–181°, is different from the values ranging from 156 to 165°, given by the other authors, and appears never to have been duplicated. We have nitrated isodurene in chloroform solution with nitric acid in sulfuric acid under essentially the same conditions as for the nuclear nitration of durene.[1] Our results are in good agreement with those of Jannasch and Weiler.

Since pure isodurene is not a readily available compound,[5] we have also tried to prepare 4,6-dinitroisodurene from other sources. Smith and Cass[6] have shown that the tetramethylbenzene fraction obtained from the distillation of the product of methylation of xylene is a mixture of durene and isodurene, from which most of the durene can be frozen out. Thermal analysis of the system durene–isodurene[5a] shows that at the eutectic point, −28.1°, the system contains only 8% of durene. Smith and Taylor[7] have already used isodurene-rich mixtures for the preparation of isodurene compounds, by mercuration of the mixture and purification of the acetoxymercuriisodurene thus obtained by differential crystallization. We have found that on nitration of a durene–isodurene mixture with a composition close to the one corresponding to the eutectic point, a crude 4,6-dinitroisodurene is obtained which can be purified by only three crystallizations from ethanol. The yield of the dinitro compound, m.p. 181.5–183.5°, was 43% based on the isomeric starting material. Since preliminary experiments with identical samples of isodurene-rich isomeric mixtures indicated that nitration was a more reliable route than mercuration for the preparation of certain isodurene derivatives, 4,6-dinitroisodurene, rather than 4-acetoxymercuriisodurene, was chosen as the starting material for the preparation of 4-nitroisodurene.

On reduction of 4,6-dinitroisodurene by sodium disulfide we have obtained pure 4-nitro-6-aminoisodurene in quantitative yields. The latter compound, m.p. 139.5–140.5°, proved to be different from the product obtained by Noelting and Stoecklin,[8] m.p. 87–88°, on nitration of isoduridine and described as nitroaminoisodurene. Noelting and Stoecklin reported results of analyses but gave no proof of structure for their product. Since nitration of polymethylbenzenes often led to side-chain substitution depending on experimental conditions[9] and nitration of arylamines may give arylnitramines,[10] the compound of Noelting and Stoecklin could be either a ω-nitroisoduridine or isodurylnitramine. On the other hand, the structure of the compound described in this paper as 4-nitro-6-aminoisodurene appears to be conclusively established both by the specific method of preparation used here and by its deamination to 4-nitroisodurene.

Crude, low-melting 4-nitroisodurene was effectively decolorized and purified with the least loss

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[1] Part II of this series: G. Illuminati and M. Palmucci Illuminati, THIS JOURNAL, **75**, 2159 (1953).

[2] L. I. Smith and F. L. Taylor, *ibid.*, **57**, 2460 (1935).

[3] G. Illuminati, *ibid.*, **74**, 4951 (1952).

[4] E. Ador and A. Rilliet, *Ber.*, **12**, 329 (1879); O. Jacobsen, *ibid.*, **15**, 1853 (1882); W. R. Orndorff and Young, *Am. Chem. J.*, **15**, 267 (1890); P. Jannasch and M. Weiler, *Ber.*, **27**, 3441 (1894).

[5] (a) L. I. Smith and F. H. MacDougall, THIS JOURNAL, **51**, 3001 (1929); (b) S. F. Birch, R. A. Dean, F. A. Fidler and R. A. Lowry, *ibid.*, **71**, 1362 (1949); (c) C. D. Shacklett and H. A. Smith, *ibid.*, **73**, 766 (1951); (d) D. A. McCaulay and A. P. Lien, *ibid.*, **74**, 6246 (1952).

[6] L. I. Smith and O. W. Cass, *ibid.*, **54**, 1609 (1932).

[7] L. I. Smith and F. L. Taylor, *ibid.*, **57**, 2370 (1935).

[8] E. Noelting and L. Stoecklin, *Ber.*, **24**, 564 (1891).

[9] R. Willstätter and H. Kubli, *ibid.*, **42**, 4151 (1909).

[10] See, for example, W. J. Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Co., London, 1948, p. 320.

of material by chromatographic adsorption on alumina.

### Experimental[11]

**Materials.**—Pure isodurene was prepared according to Smith's method.[12] On careful fractionation of the product through a Fenske column, the middle fraction, b.p. 195.5–195.6°, $n^{20}\mathrm{D}$ 1.5130, was collected and used for nitration.

The isodurene-rich isomeric mixture used as a convenient starting material for the preparation of large amounts of 4,6-dinitroisodurene was obtained by submitting the tetramethylbenzene filtrate, after separation of durene in the usual manner[13] to a number of further freezing processes each followed by centrifugation with an International Equipment Co. refrigerated centrifuge at successively lower equilibrium temperatures down to −23°. After each centrifugation, the equilibrium liquid was separated from the solid (durene) by filtration, except for the last two processes at −20 and −23°, respectively, in which the equilibrium liquid was decanted. The clear liquid thus obtained was directly used for nitration. From 130 g. of starting tetramethylbenzene filtrate, 95 g. of such a liquid was obtained.

**Nitration Experiments.**—These experiments were carried out in essential accordance with the procedure described in Part II,[1] with the exception of the mode of addition of the nitrating reagent. In the present work, better results were obtained when a solution of nitric acid in 98% sulfuric acid was prepared first and then added to the chloroform solution of the hydrocarbon.

(a) **Nitration of Isodurene.**—On dinitration of 1.005 g. of isodurene (0.0075 mole) with a stoichiometric amount of nitric acid, 1.31 g. of crude 4,6-dinitroisodurene was obtained. After two crystallizations from ethanol, the yield was 0.95 g. (57.5%) of white needles, m.p. 181.5–183.5°. After two further crystallizations, a constant melting point value of 182.5–183.5° was observed.

Unlike durene[1] and prehnitene,[14] isodurene shows no sharp color change at the end of the reaction with a stoichiometric amount of nitric acid.

(b) **Nitration of the Isodurene-rich Isomeric Mixture.**—A four-batch dinitration of 20.0 g. of the isodurene-rich isomeric mixture, obtained at −23° as described above, was carried out with a stoichiometric amount of nitric acid in a straight-wall beaker of 15-cm. height and 4-cm. width, to give a combined yield of 25.9 g. of crude product, m.p. 160–175°. After three crystallizations from ethanol, the yield of 4,6-dinitroisodurene was 14.4 g. (43%), m.p. 181.5–183.5°.

**4-Nitro-6-aminoisodurene.**—To a boiling solution of 14.4 g. of 4,6-dinitroisodurene (0.064 mole) in 400 ml. of ethanol, a solution of sodium disulfide (prepared from 50 g. of crystalline sodium sulfide and 6.5 g. of sulfur in 145 ml. of water) was gradually added. The mixture was refluxed for an over-all time of five hours; then most of the alcohol was removed by distillation and the residue was poured into ice water. After filtration, the collected product was dissolved in hot 10% hydrochloric acid and the resulting solution was filtered, if necessary. This solution was made alkaline by gradual addition of concd. ammonia, and the product which separated was collected by filtration and dried. A beautiful yellow powder, m.p. 139.5–140.5°, was obtained; the yield was 12.1 g. (97.5%).

*Anal.* Calcd. for $C_{10}H_{14}N_2O_2$: C, 61.84; H, 7.26; N, 14.42. Found: C, 61.51; H, 7.65; N, 14.49.

**4-Nitroisodurene.**—4-Nitro-6-aminoisodurene was diazotized and the resulting diazo-salt was treated with 50% hypophosphorous acid according to the procedure previously described for the corresponding durene compound.[3] The reaction mixture was kept in ice water for a fortnight and, after filtration, the collected product was thoroughly mixed with chloroform. The chloroform solution thus obtained was filtered from any inorganic material left behind and then worked up in the usual manner.[3] From 7.77 g. of nitroamino compound (0.040 mole), 5.37 g. of a crude, brown-yellow product was obtained. For decolorization and purification, the latter was dissolved in 90 ml. of dry petroleum ether (b.p. 40–60°), and the resulting solution was applied on a column of 90 g. of alumina for adsorption. Elution was continued with a 5% solution of absolute ethanol in dry petroleum ether until a brown-yellow band due to impurities reached the bottom of the column. On evaporation of the combined elution liquids, a very pale-colored crystalline residue of 5.18 g. (72.2%) of 4-nitroisodurene, m.p. *ca.* 40°, was obtained. On recrystallization from methanol, the melting point raised to 41–42°.

With only a small percentage decrease in the final yield, the reduction of the diazo-salt can be made faster by keeping the reaction mixture at room temperature for two days or so.

**Acknowledgments.**—The authors are very grateful to Prof. V. Caglioti for encouragement. Thanks are also due to the Humble Oil and Refining Co., Baytown, Texas, for the generous gift of a large sample of tetramethylbenzene filtrate in a later part of the present work.

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[11] All melting points are uncorrected.

[12] L. I. Smith, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 360.

[13] Reference 12, p. 248.

[14] Unpublished studies.

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## Density and Refractive Index of Uranyl Fluoride Solutions[1]

BY JAMES S. JOHNSON AND KURT A. KRAUS

RECEIVED APRIL 8, 1953

In the course of an ultracentrifugal investigation of uranyl fluoride solutions, their densities and refractive indices were measured as a function of concentration.

The measurements were carried out near 25 and 30° and if necessary extrapolated to 25.0 and 30.0° from the observed temperature coefficients. Most density data were obtained pycnometrically (25-cc. samples) and a few with gradient tubes.[2] The refractive index measurements were carried out with a Bausch and Lomb dipping refractometer (calibrated with "known" solutions) using sodium-D light (reproducibility ±0.00004).

The materials used and the analytical procedures were described earlier.[3] Although the accuracy of the density measurements was approximately one part in 10,000, the accuracy of the determinations at high $UO_2F_2$ concentration is considerably less, in view of the uncertainty in the uranium analyses (±0.2% in the uranium concentration).

1. **Density.**—The density data, which are listed in Table I, could be fitted to the quadratic equation

$$1/d = 1/d_0 + aF_2 + bF_2^2 \qquad (1)$$

where $d$ is the density of the solution, $d_0$ the density of the pure solvent and $F_2$ the weight fraction of $UO_2F_2$. The empirical constants $a$ and $b$ were obtained from the intercept and slope of a plot of $(1/d - 1/d_0)/F_2$ *vs.* $F_2$, which is a straight line. At 25°, $a = -0.9120$ and $b = 0.0567$ and at 30°, $a = -0.9126$ and $b = 0.0569$ give satisfactory fit as shown in Table I. Dean[4] earlier measured densities of $UO_2F_2$ solutions in the range 13 to 66

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[1] This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] (a) K. Linderstrom-Lang and H. Lanz, *Compt. rend. trav. lab. Carlsberg*, **21**, 315 (1938); (b) C. Anfinsen, "Preparation and Measurement of Isotopic Tracers," J. Edwards, Ann Arbor, Michigan, 1947, p. 61.

[3] J. S. Johnson and K. A. Kraus, THIS JOURNAL, **74**, 4436 (1952).

[4] G. R. Dean, Report CC 2092, September, 1944.