may be calculated from the refractive index or the refractive index from the viscosity. When a less precise result is desired and repeated calculations are necessary, one may utilize as auxiliary aids two nomographs designed by Davis.[4] With these, R and Souders' I may be found easily from the refractive index and the viscosity.

TABLE I

CONSTANTS OF THE EQUATION $I = aR + b$

Series	Number of members	a	b
Monohydric alcohols	4	12.0	16
Monocarboxylic acids	5	11.9	11
Esters of acetic acid	3	11.8	3
Aliphatic ketones	3	10.5	23
Ethyl esters	3	11.1	18
Paraffins	8	12.0	−20
Alkyl iodides	3	11.2	−47

For series of related compounds such as the ethylene halides, Souders' I and the molecular refraction are also linearly related, with slopes different, however, from those of homologous series. Other liquids than those listed in Table I also yield points close to the curves represented in Table I. Therefore, for liquids in general a rough rule states that Souders' I is about twelve times the molecular refraction.

[4] D. S. Davis, *Ind. Eng. Chem.*, **33**, 1537 (1941); **34**, 258 (1942).

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RECEIVED NOVEMBER 29, 1944

Aromatic Cyclodehydrogenation. II. A New Synthesis of Fluorene[1]

BY MILTON ORCHIN[2]

We have recently reported[3] the conversion of 2,2′-dimethylbiphenyl to 4-methylfluorene by passing the former over palladium-charcoal-asbestos at 450°. We now find that the same treatment readily converts 2-methylbiphenyl, I, to fluorene.

The steps in the synthesis of I[4] consisted of the condensation of *o*-tolylmagnesium bromide with cyclohexanone, dehydration of the resulting carbinol to 2-methyl-1′,2′,3′,4′-tetrahydrobiphenyl, II, and dehydrogenation of II to I. We have found that II can also be converted directly to fluorene, thus making synthetic fluorene available by a three-step process.

Experimental[5]

2-Methylbiphenyl, I, was synthesized by the method of Sherwood, *et al.*[4] The yield of *o*-tolylcyclohexanol was raised to 65% by refluxing the Grignard reaction mixture for twenty-four hours prior to decomposition with ice. Dehydration of the carbinol with formic acid gave II in 95% yield.

Cyclodehydrogenations to Fluorene.—The apparatus, catalyst and procedure used were the same as previously described.[3] During a period of three hours, 9.8 g. of I was passed once over the catalyst. The mixture of oil and solid in the receiver was taken up in alcohol, the mixture chilled and filtered, whereupon 2.80 g. of material, melting point 104–110°, was obtained. One recrystallization gave pure fluorene, m. p. 115.0–115.8°. The material in the original mother liquor was chromatographed on alumina and the more strongly adsorbed fraction gave 0.54 g. additional fluorene. When 9.0 g. of II was treated as above 2.06 g. of pure fluorene was obtained. In this experiment a portion of the oil which came through was recycled. There was no diminution in the activity of the catalyst, and it is apparent that the conversion to fluorene can be made quantitative by increasing the time of contact. When *o*-tolylcyclohexanol was passed over the catalyst, a small quantity of fluorene was formed, but the catalyst was rapidly poisoned and the conversion soon stopped completely.

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RECEIVED DECEMBER 12, 1944

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[1] Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Patent applied for. Article not copyrighted.

[2] Organic chemist, Central Experiment Station, Bureau of Mines, Pittsburgh, Pa.

[3] Orchin and Woolfolk, THIS JOURNAL, **67**, 212 (1945).

[4] Sherwood, Short and Stansfield, *J. Chem. Soc.*, 1832 (1932).

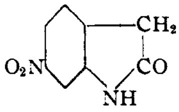
[5] The author wishes to thank Mr. E. O. Woolfolk for valuable assistance with a portion of the experimental work.

The Structure of Baeyer's Nitro-oxindole

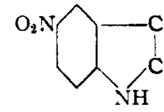
BY WARD C. SUMPTER, MARION MILLER AND MARY EDITH MAGAN

The first nitration of oxindole was carried out by Baeyer[1] through the action of potassium nitrate on a solution of oxindole in concentrated sulfuric acid. Baeyer reported that the substance did not possess a definite melting point but that it decomposed at about 175°. The position taken by the nitro group was not determined by Baeyer.

Subsequently Borsche, Weussmann and Fritzsche[2] reported that Baeyer's compound was 6-nitrooxindole (I) and while failing to present proof for this structure did present evidence which on its face seemed to establish the fact that the compound was not the expected 5-nitro-oxindole (II) but an isomer. These workers reported that treatment of a solution of the nitro-oxindole in alcohol with nitrous acid gave a nitroisatin oxime which was not identical with the β-oxime of 5-nitroisatin. This supposed isatin oxime was called 6-nitroisatin oxime and the melting point reported as 238–239°.



I



II

In view of the fact that substitution in this series takes place normally in position 5[3,4,5] it seemed quite likely that Borsche, Weussmann and

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[1] Baeyer, *Ber.*, **12**, 1312 (1879).

[2] Borsche, Weussmann and Fritzsche, *ibid.*, **57B**, 1149 (1924).

[3] Brunner, *Monatsh.*, **58**, 369 (1931).

[4] Stollé, Bergdoll, Auerhahn and Wacker, *J. prakt. Chem.*, [2] **128**, 1 (1930).

[5] Sumpter and Jones, THIS JOURNAL, **65**, 1802 (1943).

Fritzsche were incorrect in their characterization of Baeyer's product as 6-nitro-oxindole. Accordingly the nitration of oxindole by Baeyer's procedure was repeated. Instead of decomposing at about 175° as reported by Baeyer the product was found to melt at 240–241°. The same product was obtained when oxindole was nitrated through the agency of fuming nitric acid rather than potassium nitrate. Treatment of a solution of this compound in ethyl alcohol with nitrous acid in accordance with the procedure of Borsche, Weussmann and Fritzsche failed to yield an isatin oxime but resulted only in the recovery of unchanged nitro-oxindole; m. p. 240–241°.

On the other hand, treatment of a solution of the nitro-oxindole in glacial acetic acid with sodium nitrite yielded 5-nitroisatin-β-oxime, identical with an authentic sample prepared from 5-nitroisatin of known structure.[5,6] It follows from this fact that Baeyer's nitro-oxindole is 5-nitro-oxindole and not 6-nitro-oxindole[7] as stated by Borsche and his co-workers.

To further support the conclusion that the compound in question was 5-nitro-oxindole a sample was coupled with benzenediazonium chloride. The β-phenylhydrazone of 5-nitroisatin which resulted was identified by comparison with an authentic sample.[5]

5-Nitro-oxindole (II).—A. The nitration was accomplished as directed by Baeyer.[1] The crude product was purified by crystallization from 50% acetic acid from which it separated as nearly colorless needles; m. p. 240–241°.

B. Oxindole (0.05 mole) was dissolved in 25 ml. of concentrated sulfuric acid and the mixture maintained at 0° while 2.1 ml. of fuming nitric acid (sp. gr. 1.5) was added dropwise. After the addition of the nitric acid the reaction mixture was allowed to stand at 0° for thirty minutes and poured over cracked ice. The precipitate was collected, washed with water and crystallized from 50% acetic acid from which it separated as nearly colorless needles; m. p. 240–241°. The yield was 7.35 g. or 82% of the theoretical. The identity of the product with that obtained by Baeyer's procedure was established by melting point methods.

Anal. Calcd. for $C_8H_6N_2O_3$: N, 15.73. Found: N, 15.57.

5-Nitroisatin-β-oxime.—Nitro-oxindole (0.01 mole) was dissolved in 100 ml. of glacial acetic acid and 1.73 g. (0.025 moles) of sodium nitrite added in small portions. The yellow precipitate which soon separated was collected and purified by crystallization from ethyl alcohol from which it separated as light yellow needles; m. p. 228–229°. The melting point was unchanged when the substance was mixed with a sample of 5-nitroisatin-β-oxime (m. p. 228–229°) prepared from 5-nitroisatin.[5,6]

5-Nitroisatin-β-phenylhydrazone.—Nitro-oxindole (1.34 g.) was dissolved in 75 ml. of ethyl alcohol and a solution of 10 g. of sodium acetate in 25 ml. of water added. The mixture was cooled to 0° and a solution of benzenediazonium chloride (from 0.75 g. aniline) added. The reddish yellow precipitate which soon formed was collected and purified by crystallization from glacial acetic acid. The melting point of the substance was 295° both alone and when mixed with an authentic sample of 5-nitroisatin-β-phenylhydrazone.[5]

This work has been supported by a research grant (A. A. A. S.) received through the Kentucky Academy of Science.

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RECEIVED JANUARY 4, 1945

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[6] Calvery, Noller and Adams, THIS JOURNAL, **47**, 3059 (1925).

[7] A compound designated as 6-nitro-oxindole was employed by Parks and Aldis (*J. Chem. Soc.*, 1845 (1938)). Due to the fact that these authors gave erroneous literature references it is impossible to determine from an examination of their paper the origin of the substance they designated as 6-nitro-oxindole.

The Identification of Aldose Sugars by their Mercaptal Acetates

BY M. L. WOLFROM AND J. V. KARABINOS[1]

E. Fischer[2] has stated that the ease of crystallization of most aldose thioacetals (mercaptals) should lend itself to the preparative isolation of sugars from their solutions. Application of this principle has been made in the case of a number of aldoses, as for example, with 6-bromo-D-glucose,[3] 5-desoxy-L-arabinose,[4] D-altrose[5] and 2,3,6-O-trimethyl-D-glucose.[6]

The mercaptals of the aldoses have occasionally been employed for identification purposes.[7] It is our purpose herein to describe a general procedure of wide applicability for the identification of aldomonosaccharides as their acetylated diethyl mercaptals. The ease of isolation of these substances and their high yield of formation make them excellent characterizing derivatives. They are optically active and their rotations in chloroform solution can readily be ascertained. Furthermore, these derivatives are characteristic of one particular sugar and not of three, as is the case with the osazones. The presently known acetylated diethyl mercaptals of the aldomonosaccharides are listed in Table I. If desired, the acetylated mercaptal can readily be deacetylated to the parent mercaptal and the latter used as a confirmatory derivative.

Since concentrated acid is employed in their formation, the acetylated diethyl mercaptals of the aldoses are best limited to the characterization of the aldomonosaccharides, although the low temperature employed does keep the hydrolysis at a minimum and the acetylated diethyl mercaptal of maltose has indeed been isolated in crystalline form.[8] Ketoses[2] and 2-desoxyaldoses[9] are very sensitive to acidity and are destroyed by the high acidity employed in the mercaptalation

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[1] Hoffmann-La Roche Fellow of The Ohio State University Research Foundation.

[2] E. Fischer, *Ber.*, **27**, 673 (1894).

[3] E. Fischer, B. Helferich and P. Ostmann, *ibid.*, **53**, 873 (1920).

[4] D. R. Swan and W. L. Evans, THIS JOURNAL, **57**, 200 (1935).

[5] N. K. Richtmyer and C. S. Hudson, *ibid.*, **57**, 1716 (1935). R. C. Hockett and L. B. Chandler, *ibid.*, **66**, 627 (1944).

[6] M. L. Wolfrom and L. W. Georges, *ibid.*, **59**, 601 (1937).

[7] C. Neuberg, *Ber.*, **33**, 2243 (1900); M. L. Wolfrom, W. J. Burke, K. R. Brown and R. S. Rose, Jr., THIS JOURNAL, **60**, 571 (1938); M. L. Wolfrom and T. S. Gardner, *ibid.*, **62**, 2553 (1940); *ibid.*, **65**, 750 (1943); M. L. Wolfrom and D. E. Pletcher, *ibid.*, **63**, 1050 (1941).

[8] M. L. Wolfrom, Mildred R. Newlin and E. E. Stahly, *ibid.*, **53**, 4379 (1931).

[9] Private communication from Dr. J. Compton