

may be calculated from the refractive index or the refractive index from the viscosity. When a less

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

precise result is desired and repeated calculations are necessary, one may utilize as auxiliary aids two nomographs designed by Davis.<sup>4</sup> With these,  $R$  and Souders'  $I$  may be found easily from the refractive index and the viscosity.

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).

DEPARTMENT OF PHYSICS  
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EMORY UNIVERSITY, GEORGIA

## Aromatic Cyclodehydrogenation. II. A New Synthesis of Fluorene<sup>1</sup>

BY MILTON ORCHIN<sup>2</sup>

We have recently reported<sup>3</sup> 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<sup>4</sup> 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<sup>5</sup>

2-Methylbiphenyl, I, was synthesized by the method of Sherwood, *et al.*<sup>4</sup> The yield of *o*-tolylcyclohexanol was

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(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.

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.<sup>3</sup> 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.

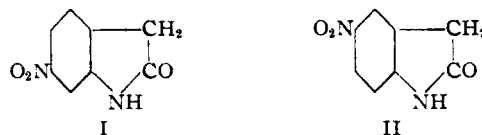
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RESEARCH AND DEVELOPMENT DIVISION  
BUREAU OF MINES, CENTRAL EXPERIMENT STATION  
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## The Structure of Baeyer's Nitro-oxindole

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

The first nitration of oxindole was carried out by Baeyer<sup>1</sup> 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<sup>2</sup> 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  $\beta$ -oxime of 5-nitroisatin. This supposed isatin oxime was called 6-nitroisatin oxime and the melting point reported as 238–239°.

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

(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).