

ments resulted in the formation of 93.5 g. of *n*-propyl nicotinate (b. p. (1 mm.) 80–82°). This represented a yield of 56.7%.

Nicotine and  $\beta$ -picoline behaved in a similar manner and gave yields of the esters in direct proportion to their ease of oxidation to nicotinic acid.<sup>3</sup>

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RECEIVED NOVEMBER 16, 1944

### Dehydration of Tetrahydrofurfuryl Alcohol<sup>1</sup>

By CHARLES HOWARD KLINE, JR.,<sup>2</sup> AND JOHN TURKEVICH

In the course of study of the catalytic synthesis of pyridine from furfural derivatives, the dehydration of tetrahydrofurfuryl alcohol was investigated. Paul<sup>3</sup> has found that the dehydration of tetrahydrofurfuryl alcohol over alumina results in the formation of 1,2-dihydropyrene, C<sub>8</sub>H<sub>8</sub>O, but did not investigate in detail the yields produced due to variation in temperature, contact body or lifetime of the catalyst.

The materials and experimental procedure were the same as those described by the authors in the publication of the catalytic synthesis of pyridine.<sup>4</sup>

Over alumina it was found that tetrahydrofurfuryl alcohol is unattacked at 250° but is readily dehydrated at 300 and 350°. The latter temperature is the optimum temperature for the dehydration and yields about 70% dihydropyrene. At 400° and above, high boiling material is chiefly formed and much of the feed alcohol is lost either as cracked gases (19% carbon dioxide, 57% unsaturates, 13% hydrogen and 11% saturated hydrocarbons) or catalyst deposit. Condensation of the tetrahydrofurfuryl alcohol residues appears to predominate at these temperatures. The alumina catalyst did not lose activity at 300° and at 350° the activity fell only moderately during four days of continuous operation. In all cases carbonaceous material was left on the surface of the catalyst. It is of further interest that at 300° the dehydration of tetrahydrofurfuryl alcohol poisoned the subsequent dehydration of absolute ethanol even though it did not poison further dehydration of the tetrahydrofurfuryl alcohol. Undoubtedly the tetrahydrofurfuryl alcohol poisons the catalyst for ethanol dehydration by being strongly adsorbed on the surface. This view is confirmed by the fact that only fifteen minutes after the start of the reaction, does the product come out of the catalyst exit tube. Further confirmation is the forty-degree rise in temperature of the catalyst bed on the introduction of the tetrahydrofurfuryl alcohol. This is to be contrasted with a nine degree rise when the ammonia is simultaneously introduced.

Over silica, tetrahydrofurfuryl alcohol is stable up to 400°, at which point some decomposition

sets in. Dihydropyrene was not the only product of the reaction but there was material boiling below and above this substance. At 450° about 20% water was formed and most of the non-aqueous product appeared as high boiling still residues.

Over thoria, tetrahydrofurfuryl alcohol was stable up to 450°. The low-boiling material collected during the 550° run polymerized on standing and had a sharp odor. These facts and its boiling point suggest that it may have consisted of pentenes and pentadienes. It should be pointed out that the recovery of tetrahydrofurfuryl alcohol was high. The inactivity of the thoria for the dehydration was not due to its general lack of catalytic activity. After revivification following the 450° run, the catalyst could be used to dehydrate anhydrous ethanol. One is thus faced with the interesting fact that on alumina the efficient dehydration of tetrahydrofurfuryl alcohol poisons the alumina for the dehydration of ethanol, while on thoria the inefficient dehydration of tetrahydrofurfuryl alcohol does not poison the dehydration of ethanol.

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PRINCETON, NEW JERSEY RECEIVED JANUARY 26, 1945

### A Relation between Viscosity and Refractive Index

By R. T. LAGEMANN

During an attempt to estimate the viscosity of higher members of some homologous series, it was noted that the viscosity and the refractive index for liquids are functionally related. A linear relation is found to hold for every homologous series if the molecular refraction  $R$  is plotted against the viscosity constant  $I$ , which is defined by Souders<sup>1</sup> as

$$I = \frac{M}{d} \{ \log_{10} (\log_{10} \eta) + 2.9 \}$$

where  $\eta$  is the viscosity in millipoises. For such a plot and for determining the constants of the equations, data for  $I$  may be obtained from Souders<sup>1</sup> and values of  $R$  from Eisenlohr,<sup>2</sup> Herz<sup>3</sup> and the Landolt-Börnstein tables.

In Table I are given the values of the constants  $a$  and  $b$  as calculated for several series by the method of least squares on the assumption that  $I = aR + b$ . From this table it may be seen that the slopes are very nearly identical for all the series examined, while the intercepts vary. That linear curves represent the relations very well may be deduced from the fact that use of the constants of Table I allows one to calculate values of  $I$  averaging within  $1/8$  of one per cent. of the experimental values. As a consequence, if the density and molecular weight of a liquid belonging to any of the series of Table I are known, the viscosity

(1) Original manuscript received July 19, 1944.

(2) Ensign, U. S. N. R.

(3) R. Paul, *Bull. soc. chim.*, [5] **2**, 2220–2227 (1935).

(4) Kline and Turkevich, *THIS JOURNAL*, **66**, 1710 (1944).

(1) M. Souders, Jr., *THIS JOURNAL*, **60**, 154 (1938).

(2) F. Eisenlohr, *Z. physik. Chem.*, **76**, 585 (1910).

(3) W. Herz, *Z. anorg. allgem. Chem.*, **179**, 211 (1929).

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).

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RECEIVED NOVEMBER 29, 1944

## 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

(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.

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.

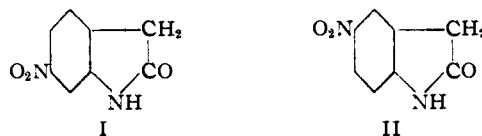
ORGANIC CHEMISTRY SECTION  
RESEARCH AND DEVELOPMENT DIVISION  
BUREAU OF MINES, CENTRAL EXPERIMENT STATION  
PITTSBURGH, PA. RECEIVED DECEMBER 12, 1944

## 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).