

The free energy change is

$$\Delta F = -1629 - 3.31T \quad (4)$$

$$K_{622} = 20.1 \quad (4a)$$

The corresponding changes for II to III are

$$-27.997 + 26.633 = -1.664 \text{ kcal. and } -1.10 \text{ e. u.}$$

$$\Delta F = -1664 + 1.10T \quad (5)$$

$$K_{623} = 1.81 \quad (5a)$$

TABLE I

Assignment Compound.....	No.	Wave		Wave		
		no. I	No.	no. II	No.	Wave no. III
C—C—C	6	316	8	400	4	400
C—C=C	2	160	4	180	8	180
C—C—H	4	640	4	640		
C—C	4	950	4	900	4	900
At.....315°K.				345°K.		
<i>S</i> _{vib.}	14.88			21.30		
<i>S</i> _{int. rot.}	5.75			5.60		
<i>S</i> _{rot. trans.}	63.13			61.10		
Total <i>S</i>	83.76			88.00		
Obs. <i>S</i> ^a	83.92			88.00		
<i>C</i> _v (gas) ^a calcd.	34.7			32.3		
<i>C</i> _v (liq) ^b obs.	41.8			39.2		
At.....673°K.		673°K.		673°K.		
<i>S</i> _{vib.}	31.59	35.88		37.86		
<i>S</i> _{int. rot.}	4.65	5.18		4.4		
<i>S</i> _{trans.}	68.58	68.22		65.92		
Total <i>S</i>	104.87	109.28		108.18		

^a Observed entropies⁷ extrapolated to boiling point by continuing *C*_v curves from 298°K. and adding 29.6 e. u.

^b According to Kincaid and Eyring, *J. Chem. Phys.*, **6**, 620 (1938) the difference between *C*_v(liq.) and *C*_v(gas) is normally between 6 and 7 cal./mole deg. for complex materials. The differences observed here are 7.1 for I and 6.9 for III, which is quite reasonable. *C*_v(liq.) was found by using the value from entropy data⁷ and subtracting an approximate factor obtained from the Landolt-Börnstein "Tabellen" in the following manner:

$$C_p - C_v = T\alpha^2 V/\beta = 3 \text{ cal./mole deg.}$$

The constant for the same reaction at 350° as calculated from the data of Whitmore and co-workers⁵ was 20.3 for the ratio of III to I and 1.96 for the ratio of III to II. The results of Cramer and Glasebrook⁶ were 18 and 1.81, respectively.

Discussion.—The results obtained by these methods cannot be regarded as final inasmuch as the calculations involving the vibrational entropy are not exact. However, assuming that the internal potential barriers for rotation are those assigned, little change in the relative entropy would be observed when the vibrational frequencies are consistently changed. The agreement of the calculated and observed entropy and the reasonable approximation of the specific heat

of the perfect gas at the boiling point indicate that the assigned vibrations must be of the right order of magnitude.

Changes in the hindering potentials of the various groups by 500 cal. would change the difference in entropy by no more than 0.1 e. u. for I to III and even less for II to III.

The values for the vibrational frequencies were assigned by comparison of the molecules involved with similar olefins reported in Kohlrausch, "Der Smekal-Raman Effekt" and data in Hibben. The frequency assignments were made on the basis of similar work done on methylacetylene.¹⁰

Conclusion.—The rearrangement of these olefins using acidic materials as catalysts has been found to proceed in agreement with estimated thermodynamic values. The comparison of the dehydrations using acidic catalysts and those which do not furnish hydrogen ions indicates that the latter catalysts act merely in the removal of an equivalent of a water molecule with no effect upon the isomerization of the compounds formed. On the other hand, the catalytic action of hydrogen ion in the isomerization of olefins is definitely indicated.

The author wishes to thank Dr. F. C. Whitmore and Dr. J. G. Aston of the Pennsylvania State College and Dr. H. Eyring of this Laboratory for their assistance.

(10) Bryce Crawford, *J. Chem. Phys.*, **7**, 140, 555 (1939).

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The Utilization of Aliphatic Nitro Compounds. IV. Nitrodiols (Nitroglycols) Prepared from Simple Aldehydes¹

BY C. AUSTIN SPRANG² WITH ED. F. DEGERING

In a recent paper³ the authors discussed the condensation of nitroparaffins with aldehydes to form nitroalcohols. In a continuation of this work nitromethane has been condensed with aldehydes to form nitrodiols. Any primary nitroparaffin condenses with formaldehyde to form a nitrodiol,⁴ but only nitromethane condenses with

(1) Presented before the Division of Organic Chemistry at the Memphis meeting of the American Chemical Society, in April, 1942. Abstracted from a thesis presented to the Faculty of the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in June, 1941.

(2) Present address: Emery Industries, Inc., Cincinnati, Ohio.

(3) Sprang and Degering, *THIS JOURNAL*, **64**, 1063 (1942).

(4) Pauwels, *Rec. trav. chim.*, **17**, 27 (1898).

other aldehydes to form dihydric alcohols.^{5,6} Sodium hydroxide is a suitable catalyst for condensations with formaldehyde but for other condensations the only catalysts which have been used successfully have been mild alkalies⁷ such as calcium hydroxide or sodium or potassium carbonates. A large excess of the aldehyde is used to force the reaction as nearly to completion as possible and this is subsequently removed by low temperature distillation.

Procedure

4-Nitro-3,5-heptanediol.—The flask is charged with 61 g. (1 mole) of nitromethane, 50 ml. of 95% ethanol, and 3 g. of potassium carbonate. While stirring vigorously, 130 g. of propanal is added dropwise. External cooling is used to keep the temperature between 28–35°. A small amount of water is added to give a homogeneous solution which is left for four days at room temperature. The potassium carbonate is neutralized and the salt and aqueous layer removed. The solution is then stripped overnight with the water pump at room temperature to remove volatile substances. The salt, which precipitates, is removed by filtration and the stripping continued at room temperature at 1.5 mm. The residue is chilled to complete crystallization and then filtered (yield, about 50%) and finally recrystallized from a butanal-toluene mixture.

Unsymmetrical nitrodiols are prepared by first forming the nitroalcohol^{2,6} from nitromethane and the more complex of the aldehydes and then treating this product with the second aldehyde in the presence of potassium carbonate as described above.

Nitrodiols are white, crystalline substances, soluble in water or alcohol, but insoluble in hydrocarbon solvents. Some data for three nitrodiols are listed in the table.

Compound	Melting point, °C.	Empirical formula	Carbon or nitrogen, %	
			Calcd.	Found
4-Nitro-3,5-heptanediol	97	C ₇ H ₁₆ NO ₄	47.46	47.30 ^a
3-Nitro-2,4-hexanediol	94	C ₆ H ₁₄ NO ₄	8.58	8.47 ^b
8-Nitro-7,9-pentadecanediol	66-67	C ₁₅ H ₃₄ NO ₄	4.87	4.74 ^b

^a Percentage carbon by the "Wet Method," Pollard and Forsee, *Ind. Eng. Chem., Anal. Ed.*, **7**, 77 (1935).

^b Percentage nitrogen by "Kjeldahl," Harte, *ibid.*, **7**, 432-3 (1935).

Because of the presence of three functional groups, these compounds are quite reactive and have unusual possibilities in organic synthesis.

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(5) Schmidt and Wilkendorf, *Ber.*, **55**, 316 (1922).

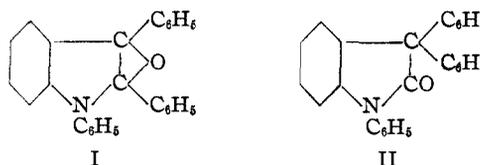
(6) Mousset, *Rec. trav. chim.*, **21**, 95 (1902).

(7) Hass and Vanderbilt, *Ind. Eng. Chem.*, **32**, 34 (1940).

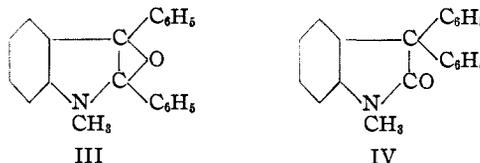
The Reaction of Phenylmagnesium Bromide with N-Phenylisatin

BY WARD C. SUMPTER

Stollé¹ obtained two products from the reaction of N-phenylisatin with excess phenylmagnesium bromide: a colorless compound melting at 161° and a yellow compound melting at 238°. Stollé described the colorless compound as 1,2,3-triphenylindole-oxide-2,3 (I). No formula was assigned to the yellow compound.



Myers and Lindwall² found that 2,3-diphenyl-1-methylindole-oxide-2,3 (III) is a yellow compound exhibiting greenish fluorescence and that a second colorless compound (IV) is obtained along with III when N-methylisatin reacts with excess phenylmagnesium bromide.



In the light of these facts it seemed likely that Stollé's characterization was in error and that the colorless compound (m. p. 161°) was compound II and that the yellow compound (m. p. 238°) was in reality compound I.

To test this conclusion the experimental work of Stollé has been repeated. Analyses of both compounds are in agreement with the formula C₂₆H₁₉ON. That the colorless compound (m. p. 161°) is in reality 1,3,3-triphenyloxindole (II) was confirmed by its synthesis from 3,3-dichloro-1-phenyloxindole, benzene and aluminum chloride. The yellow compound exhibits green fluorescence in solution and is analogous in color and fluorescence to compound III of Myers and Lindwall. Accordingly it seems reasonable to assign structure I to the yellow compound (m. p. 238°).

Treatment of compound II with phosphorus pentachloride yields 2,2-dichloro-1,3,3-triphenyl-di-hydroindole (V).

(1) Stollé, Hecht and Becker, *J. prakt. Chem.*, **135**, 358 (1932).

(2) Myers and Lindwall, *THIS JOURNAL*, **60**, 2153 (1938).