steam cone, the residue was fractionated in a Podbielniak-type column. A yield of 30 g. of the alcohol distilling at 152–155°, $n_D^{11.4}$ 1.4250 (lit.,[1] b.p. 152–154°, $n_D^{11.4}$ 1.42428) was obtained.

2-Chloro-2,5-dimethylhexane. 2,5-Dimethyl-2-hexanol (13 g., 0.10 mole) was shaken intermittently with 42 ml. of concentrated hydrochloric acid over a 1-hr. period. Fresh acid was charged into the separatory funnel and this process was repeated. The organic layer was dried over anhydrous sodium sulfate and then distilled under reduced pressure. The yield of 2-chloro-2,5-dimethylhexane, b.p.$_{20 \text{ mm.}}$ 58°, n_D^{15} 1.4255; (lit.,[8] b.p.$_{14 \text{ mm.}}$ 44–45°, n_D^{15} 1.42495) amounted to approximately 50%.

Alkylations. (*1*) *p-Di-tert-butylbenzene.* A solution of 2-chloro-2,5-dimethylhexane (3 g., 0.02 mole) and *p*-di-*tert*-butylbenzene (1.90 g., 0.01 mole) in 5 ml. of carbon bisulfide was cooled below 0° in an ice salt bath. Powdered anhydrous aluminum chloride (2.66 g., 0.02 mole) was added in small portions to the stirred reaction mixture over a period of 2 hr. During this time there was copious evolution of hydrogen chloride and a brown complex formed at the bottom of the reaction mixture. After a total of 4 hr. reaction time, the complex was decomposed in water and allowed to stand overnight. The semisolid organic layer was extracted with ether and the ether solution concentrated to yield colorless needles, 1.20 g., yield 40%. This product softened above 200° and melted at 220°. A sample recrystallized from ethanol-benzene proved to be identical (by mixed melting point and ultraviolet spectra) to the octahydrooctamethylanthracene (m.p. 220°) reported earlier.

(*2*) *Benzene.* A mixture of benzene (3.1 g.) and 2-chloro-2,5-dimethylhexane (3.0 g.) was treated with catalytic amounts of anhydrous aluminum chloride (0.1 g.) below 0°. No observable reaction took place in the cold. The reaction mixture was then left at room temperature for two days. However, working up of the product yielded only volatile liquids and no trace of solid hydrocarbon.

In a second experiment a mixture of 2-chloro-2,5-dimethylhexane (3.0 g., 0.02 mole) and benzene (0.78 g., 0.01 mole) was cooled below 0°. Anhydrous aluminum chloride (2.66 g., 0.02 mole) was added in small portions over a 3-hr. period to the reaction mixture kept below 0°. After about 3 hr. reaction time a few milliliters of carbon bisulfide was added to facilitate stirring of the semisolid mass. The reaction was continued for a total of 8 hr. after which time the temperature had risen to 20°. The complex was decomposed in water and after standing overnight a crystalline crust formed in the hydrocarbon layer. Extraction with ether and concentration of the ether yielded 0.31 g. of colorless needles. This product proved to be identical with octamethyloctahydroanthracene by mixed melting point and ultraviolet spectrum.

Acknowledgments. The authors express their thanks to the National Research Council of Canada for financial assistance. We are indebted to G. A. Harrington of the Indoil Chemical Company, Chicago, for a generous sample of *p*-di-*tert*-butylbenzene.

SACKVILLE, N. B.
CANADA

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[8] *Beilstein*, I, 422.

[CONTRIBUTION FROM E. I. DU PONT DE NEMOURS & CO., INC., EASTERN LABORATORY]

Reaction of Nitric Oxide with Nitrosocyclohexane Dimer

L. G. DONARUMA AND D. J. CARMODY

Received October 29, 1956

The reaction of nitric oxide with bisnitrosocyclohexane has been studied. The possibility that an adduct of nitric oxide with the nitroso compound is formed and rearranges to cyclohexyldiazonium nitrate is discussed. A rationalization for the formation of the products, cyclohexyl nitrate, cyclohexyl nitrite, and nitrocyclohexane, by decomposition of the diazo nitrate is presented.

The reaction of nitric oxide with hydrocarbons (I) has been studied by other investigators.[1] The major products of this reaction are the nitrate (II), the nitroparaffin (III), and the nitrite (IV). We have studied the reaction of nitric oxide with cyclohexane in the presence of various dehydrogenation catalysts and obtained similar products.

$$\underset{\text{(I)}}{\mathrm{RH}} \xrightarrow{\overset{\Delta}{\mathrm{NO}}} \underset{\text{(II)}}{\mathrm{RONO_2}} + \underset{\text{(III)}}{\mathrm{RNO_2}} + \underset{\text{(IV)}}{\mathrm{RONO}}$$

(Subscript "a" indicates that R = cyclohexyl.)

$$\mathrm{I_a} \xrightarrow[\mathrm{NO}]{\overset{\Delta}{\text{Catalyst}}} \mathrm{II_a} + \mathrm{III_a} + \mathrm{IV_a} + \mathrm{C_6H_{11}OH} + \text{traces of nitroolefins and carbonyl compounds}$$

Catalyst = Pt, Pd, S, NO_2

Brown[2] suggested that nitroso compounds (V) are intermediates in the reaction of nitric oxide with hydrocarbons. We allowed nitrosocyclohexane to react (V_a) with nitric oxide and obtained cyclohexyl nitrate (II_a), nitrocyclohexane (III_a), and cyclohexyl nitrite (IV_a) as the major products. Brown[2] suggested that diazo nitrates (VII) are formed by the reaction of nitric oxide with nitroso compounds (V) and that the isolable products are formed by the decomposition of the diazo nitrate followed by reaction of the decomposition products with oxides of nitrogen present in the reaction mixture.[2,3]

$$1/2(\mathrm{C_6H_{11}NO})_2 \rightarrow \underset{\mathrm{V_a}}{\mathrm{C_6H_{11}NO}} \xrightarrow[\substack{25°\text{–}50° \\ \text{1–6 atm.}}]{\mathrm{NO}} \mathrm{II_a} + \mathrm{III_a} + \mathrm{IV_a} + \text{traces of carbonyl compounds and other nitrated products}$$

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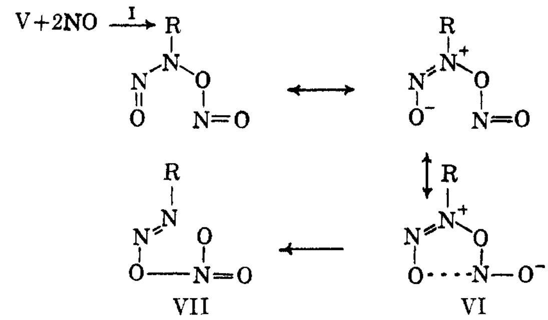
[1] Burkhard, Brown, Herrick, Myers, and Hurd, paper presented at the 126th Meeting, American Chemical Society, New York, N. Y., September 1954.

[2] Brown, paper presented at the 126th Meeting, American Chemical Society, New York, N. Y., September 1954.

[3] Gray and Yoffe, *Quart. Revs.*, 362 (1955).



$$\mathrm{VII} \longrightarrow \mathrm{R\cdot} + \mathrm{N_2} + \mathrm{\cdot NO_3}$$
$$\hookrightarrow \mathrm{R^+} + \mathrm{N_2} + \mathrm{{}^-NO_3}$$

$$\mathrm{R\cdot} + \mathrm{I} + \mathrm{\cdot NO_3} \longrightarrow \mathrm{RONO_2{}^*} \xrightarrow{\mathrm{I}} \mathrm{RONO_2} + \mathrm{I^*}$$
$$\mathrm{R^+} + \mathrm{{}^-NO_3} \longrightarrow \mathrm{RONO_2}$$
$$\mathrm{RO\cdot} + \mathrm{\cdot NO_2} \longrightarrow \mathrm{RONO_2}$$
$$\mathrm{\cdot NO_3} + \mathrm{\cdot NO} \longrightarrow 2\mathrm{\cdot NO_2}$$
$$\mathrm{R\cdot} + \mathrm{\cdot NO_2} \longrightarrow \mathrm{RNO_2{}^*} + \mathrm{RONO^*} \xrightarrow{\mathrm{I}} \mathrm{RNO_2} + \mathrm{RONO} + \mathrm{I^*}$$
$$\mathrm{RONO^*} \longrightarrow \mathrm{RO\cdot} + \mathrm{\cdot NO}$$
$$\mathrm{I^*} \xrightarrow[\text{or wall}]{\text{solvent (I)}} \mathrm{I}$$

In order to investigate the reaction further, a study was made of the rate of reaction of nitrosocyclohexane with nitric oxide in cyclohexane solution at temperatures of 25°–51° and pressures of 0.5–6 atmospheres. Table I shows the results of the kinetic measurements.

TABLE I

Reaction of Bisnitrosocyclohexane with Nitric Oxide at Various Temperatures and Pressures in Cyclohexane

T°C.	Pressure (p.s.i. ga.)	10^3k (min.$^{-1}$)	$\Delta S\ddagger$ (e.u.)
25°	21.5	1.15	—
25°	69	1.17	—
25°	50	1.14	77.9
33.5°	50	10.4	77.9
51°	50	462.	76.9

E_A = 47,700 cal./mole
$\Delta H\ddagger$ = 47,085 cal./mole

The rate constants indicate that the rate may be independent of nitric oxide pressure. Even at pressures as low as 0.5 atmospheres the rate did not drop off.[4] At the low pressures, the rate constants drifted somewhat during the initial stages of the reaction. This may have been due to diffusion effects.

When nitric oxide was admitted to a solution of bisnitrosocyclohexane in cyclohexane, a temperature rise occurred. This observation and the apparent zero order dependence of the rate on nitric oxide suggested that perhaps nitric oxide was reacting initially with nitrosocyclohexane to form a complex of some nature. Figure 1 shows the infrared spectrum of bisnitrosocyclohexane in cyclohexane (concentration 0.1 g./100 ml.). Infrared spectra also were taken of cyclohexane solutions of bisnitrosocyclohexane which had been in contact with nitric oxide (Figure 2). Figure 2 shows that the usual nitroso band at 8.28 μ has broadened and been modified by the contact with nitric oxide, a new band has appeared at 5.5 μ, and at 6.10 μ and 6.44 μ where the nitrate and nitro bands, respectively, appear, the products are beginning to form (dotted line

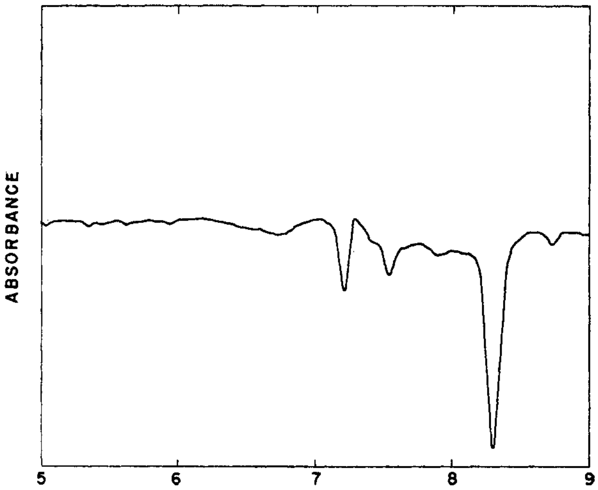


Fig. 1.—Infrared Spectrum of a Cyclohexane Solution of Bisnitrosocyclohexane

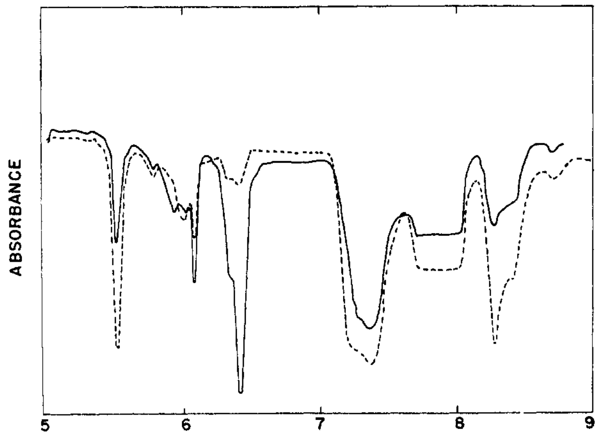


Fig. 2.—Infrared Spectra of a Cyclohexane Solution of Nitric Oxide and Nitrosocyclohexane

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[4] Actually, rate measurements were made at pressures as low as 20 mm. ga. in an apparatus consisting of a gas filled nitrometer tube connected to a sealed reaction flask. Agitation was supplied with a magnetic stirrer. The reactions in this apparatus were run over shorter periods of time at higher bisnitrosocyclohexane concentrations (0.1 g./100 ml.). The rates were affected by diffusion during the initial stages of the reaction. However, after contact with nitric oxide for 1 hr., the reaction rate constants were never smaller than those obtained at higher pressures. For example, the rate constant obtained at 25° and 20 mm. ga. pressure over a period of 1 hr. was 1.32 × 10^{-3} (min.$^{-1}$). Constant pressure over longer periods of time could not be maintained in the apparatus. Checks at 0.5 atm. ga. in the shaker gave similar results.

spectrum). Furthermore, it can also be seen that upon standing (solid line spectrum), the intensity of the modified nitroso band at 8.28 μ diminished and the intensities of the nitrate and nitro bands increased. The new band at 5.5 μ also exhibits similar behavior. Figure 3 shows that the spectrum of bisnitrosocyclohexane at 8.28 μ returned to its usual shape (Figure 1) after washing with water to regenerate bisnitrosocyclohexane from the complex, and that the intensities of the nitro and nitrate bands were not affected by the water wash. Since nitric oxide is very insoluble in cyclohexane at atmospheric pressure and no bands characteristic of nitric oxide[5] appear in the spectra in Figure 2, the spectral data might be interpreted as indicating that a complex is formed from nitric oxide and nitrosocyclohexane.

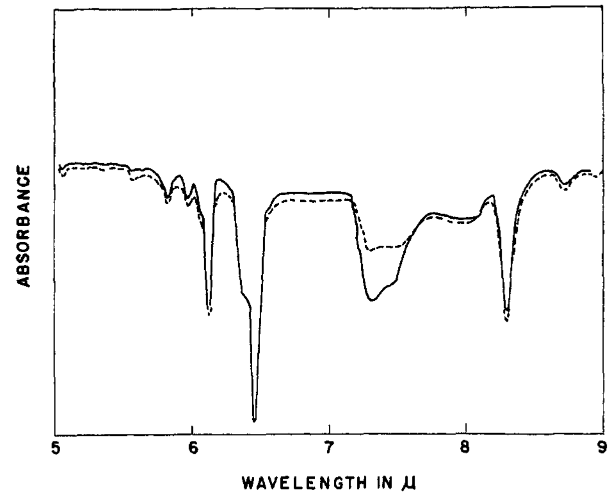
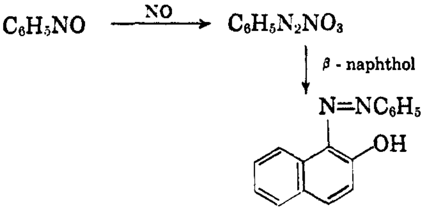


FIG. 3.—INFRARED SPECTRA OF A WATER WASHED CYCLOHEXANE SOLUTION OF NITRIC OXIDE AND NITROSOCYCLOHEXANE.

The high positive entropy of activation shown in Table I was interpreted to indicate that any transitory species formed by the action of nitric oxide on nitrosocyclohexane has a greater number of degrees of freedom than the initial reactants.[6] If a complex such as VI_a was formed by reaction of nitric oxide with nitrosocyclohexane, the complex (VI_a) should isomerize to the diazo nitrate (VII_a) if the postulated mechanism is creditable. To do this, the binding forces in the complex should weaken and the resulting loosening of the structure should be accompanied by a large increase in entropy.[6] Such changes in the structure of an activated state should give a large entropy of activation as was found experimentally. Moreover, the high entropy increase can help compensate for the high activation energy. The rapid reaction rates observed, despite the high activation energy, at the moderately low temperatures employed in this study are consistent with a large entropy increase.[6] Such a relationship of reaction rate to activation entropy is well known in the denaturation of proteins.[6]

Positive entropies of activation also are characteristic of reactions which yield several products from a single species[6] and if a diazo nitrate (VII_a) is an intermediate in the reaction and does decompose to yield a nitrate (II_a), a nitroparaffin (III_a), and a nitrite, the presence of a diazonium nitrate as an intermediate would be expected to contribute markedly to a high positive activation entropy. Moreover, Bamberger[7,8] has shown that nitrosobenzene reacts with nitric oxide to yield benzene diazonium nitrate.



These observations and the fact that Brown[2] found that nitrogen was the only gas formed in the reaction of hydrocarbons with nitric oxide make it appear possible that a diazo nitrate is an intermediate in this reaction. It seems likely that the changed spectrum (Figure 2) of the nitroso compound (V_a) after exposure to nitric oxide is not characteristic of a diazonium nitrate. Diazonium salts absorb strongly at 4.3–4.7 μ.[9] No absorption was noticeable in this region of the spectrum.

The kinetic data, the spectral data, and the work of Brown[2] and Bamberger[7,8] indicate that the reaction of nitric oxide with nitrosocyclohexane might involve the rapid formation of an adduct (VI_a) of nitric oxide with all or most of the nitroso compound (V_a). This adduct may or may not have the structure (VI_a) which Brown has postulated. The adduct might then rearrange to cyclohexyldiazonium nitrate (VII_a) and decompose homolytically and/or heterolytically to yield species which can react with oxides of nitrogen present in the system to yield cyclohexyl nitrate (II_a), nitrocyclohexane (III_a), and cyclohexyl nitrite (IV_a).

$$V_a + 2NO \longrightarrow VI_a \longrightarrow VII_a \longrightarrow II_a + III_a + IV_a + N_2$$

The apparent zero order of the reaction in nitric oxide and the temperature rise upon the addition of nitric oxide to the system make it seem likely that the formation of the complex (VI_a) is fairly rapid and complete with little or no tendency of the complex (VI_a) to revert back to nitric oxide and nitrosocyclohexane (V_a). Stable aliphatic diazonium salts appear to be unknown. Therefore, it would be expected that if a diazo nitrate (VII_a) were formed

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(5) Pearson, Fletcher, and Gantz, *Anal. Chem.*, **28**, 1218 (1956).

(6) Glasstone, Laidler, and Eyring, *The Theory of Rate Processes*, pp. 21-27, 196, 296, 407, 442-446. McGraw-Hill, Inc., New York, 1941.

(7) Bamberger, *Ber.*, **51**, 634 (1918).

(8) Bamberger, *Ber.*, **30**, 508 (1897).

(9) Whetsel, Hawkins, and Johnson, *J. Am. Chem. Soc.*, **78**, 3360 (1956).

in the reaction it would decompose rapidly to yield the observed reaction products (II$_a$, III$_a$, IV$_a$). The dissociation of bisnitrosocyclohexane (V$_a$) to the monomeric state must also be a fast change because of the observed nitric oxide order. This line of reasoning seems to indicate that the rate-determining step in the overall reaction is the isomerization of the adduct (VI$_a$) to the diazo nitrate (VII$_a$). However, if this is true then no contribution to the high positive entropy of activation from the decomposition of the diazonium nitrate is possible. Therefore, another plausible explanation of the data is that after the complex (VI$_a$) is formed it acquires energy, becomes activated, and rearranges to the diazo nitrate (VII$_a$) accompanied by an increase in entropy. The diazo nitrate (VII$_a$) might then become activated and decompose with another increase in entropy to yield the intermediates which are necessary to form the observed products (II$_a$, III$_a$, IV$_a$). Since no known bands[9] characteristic of diazonium salts appear in the infrared spectrum of the reaction mixture, it would seem likely that the energy of activation of this process is lower than that necessary to activate the complex (VI$_a$) and only very small quantities would be present at any given time. The contribution of this process to the activation entropy of the overall reaction would probably be smaller than that of the isomerization of the complex (VI$_a$) to the diazo nitrate (VII$_a$).[10]

EXPERIMENTAL

Materials. Bisnitrosocyclohexane was prepared by the oxidation of *N*-cyclohexylhydroxylamine.[11] Cyclohexyl nitrate and cyclohexyl nitrite were prepared by the esterification of cyclohexanol.[12] Nitrocyclohexane was purified by repeated distillation under reduced pressure. The cyclohexane used as a solvent was distilled through an 18 in. Vigreux column.

Apparatus. The apparatus employed was a Parr low pressure shaker bomb. An electrically heated insulated bottle with a thermocouple attached to read the inside temperature was used to contain the reaction mixture. In this equipment, it was possible to maintain the temperature within three-tenths degree of the desired reading.

Analytical method. Because the concentration of reaction products was less than 0.2% a 1.0 mm. infrared cell was employed. The following instrumental conditions were used on the Perkin Elmer Model 21 spectrophotometer.

Resolution, 9.84
Response, 1
Gain, 6
Speed, 3
Suppression, 0

The absorption bands used to measure the concentration of each major product as well as the concentration range covered in preparing the working curves are given below.

Component	Band	Base Point	Concn. Range
Nitrosocyclohexane	8.28	8.60	0–0.2 g./100 ml.
Nitrocyclohexane	6.44	5.50	0–0.2 g./100 ml.
Cyclohexyl nitrate	6.10	5.50	0–0.06 g./100 ml.

Distilled cyclohexane was used as solvent and as blank in each case. The working curves of concentration versus absorbance gave excellent agreement with Beer's Law.

Synthetic samples were prepared and analyzed with the following results.

	Concn. in G./100 Ml.		
	Bisnitrosocyclohexane	Nitrocyclohexane	Cyclohexyl Nitrate
Present	0.136	0.0025	0.0017
Found	0.135	0.0030	0.0017
Present	0.107	0.0617	0.0168
Found	0.107	0.0625	0.0168
Present	0.0450	0.0247	0.0420
Found	0.0455	0.0260	0.0423

In order to analyze actual samples taken in the rate study, oxides of nitrogen had to be removed from the solution. This was accomplished by washing 100 ml. of the cyclohexane solution twice with 50 ml. of distilled water. The major products were not affected significantly.

Bisnitrosocyclohexane (G./100 Ml.)	
Before Wash	After Wash
0.0500	0.0490
0.0515	0.0515
0.0420	0.0415

In reactions of nitric oxide with the nitroso dimer at 25°, 90–100% of the products were accounted for as cyclohexyl nitrate and nitrocyclohexane during the first hour of reaction. After 2 hr. of reaction 70–80% of the products consisted of the same two compounds. At this point, cyclohexyl nitrite and carbonyl compounds which probably were formed as a result of the build up of nitrogen dioxide in the system[2,13] began to appear as products. After 17 hr., 65–70% of the products were still accounted for as nitrocyclohexane and cyclohexyl nitrate. Nitrogen dioxide is known to oxidize cyclohexyl nitrite to mixtures of dibasic acids.[13] This might account for the presence of the carbonyl compounds. The infrared absorption of the nitrite ester can be seen as a shoulder on the nitrate band in Figure 3. Other products present were polynitrocyclohexanes which absorb at lower wavelengths in the infrared than nitrocyclohexane (6.35–6.40 μ) and appear in Figures 2 and 3 as a shoulder on the nitro band in Figures 2 and 3.

Cyclohexyl nitrate was always the major product. The ratio of the nitrate to nitrocyclohexane varied with the reaction time and temperature. The ratio of nitrate to nitroparaffin for 70% consumption of the nitroso dimer was always near 3:1 regardless of time or temperature.

Although all solutions were analyzed within 15 min. after being taken from the constant temperature bath and washed, a check was made on their stability at room temperature. The following results indicated that the washed solutions were relatively stable.

Time (hr.)	0.25	4.0	6.0	24
	Concn. in G./100 Ml.			
Bisnitrosocyclohexane	0.081	0.078	0.076	0.072
Nitrocyclohexane	0.005	0.007	0.008	0.015
Cyclohexyl nitrate	0.010	0.010	0.010	0.010

Procedure. The samples were prepared by dissolving approximately 0.5 g. of bisnitrosocyclohexane in distilled cyclohexane and diluting the solution to 1 l. One hundred milliliters of this solution was placed in the pressure bottle. The bottle was sealed and brought to the desired temperature. Nitric oxide was then admitted to the bottle at the pressure desired. Agitation was started and the sample al-

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[10] De Tar and Kwong, *J. Am. Chem. Soc.*, **78**, 3921 (1956).

[11] Muller and Metzger, *Chem. Ber.*, **88**, 165 (1955).

[12] Kornblum and Teitelbaum, *J. Am. Chem. Soc.*, **74**, 3076 (1952).

[13] Doumani, Coe, and Attane (To Union Oil Co.), U. S. Patent **2,465,984** (1949).

lowed to shake for the required time period. The sample was then removed, washed with two 50 ml. portions of distilled water, passed through a filter paper to remove traces of water, and analyzed for bisnitrosocyclohexane, nitrocyclohexane, and cyclohexyl nitrate. These operations were repeated at various intervals of time under identical conditions of temperature and pressure until sufficient data were obtained to make the necessary calculations for the desired pressure and temperature. All reactions were carried to at least 70% consumption of the nitroso dimer.

Handling of data. The rate constants were calculated by integration of the first order rate expression using two widely separated time limits[14] and from the slope of the plot of the logarithm of the concentration of bisnitrosocyclohexane *vs.* time. The slope was determined statistically by the method of least mean squares.[15,16] The agreement between the two methods was excellent. The rate constant at 51° was determined by measuring the half-life of bisnitrosocyclohexane under the usual reaction conditions and calculating the rate constant from the half-life.[14]

The activation energy (E_a) was determined from the slope of the curve obtained by plotting the logarithm of the rate constant at various temperatures *vs.* the reciprocal of the absolute temperature[14] and determining the slope of the curve by the method of least mean squares.[15,16] $\Delta H\ddagger$ was determined from the relationship.[6]

$$\Delta H\ddagger = E_A - RT$$

The entropies of activation were calculated from the Eyring equation.[6]

Acknowledgments. The services of Mr. J. L. Swyler and Mr. G. Gesty who carried out the experimental work are deeply appreciated.

The advice and consultation of Dr. G. R. Coraor, Dr. J. D. Roberts, and Dr. C. Gardner Swain were invaluable in carrying out this investigation.

WILMINGTON, DEL.

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[14] Getman and Daniels, *Outlines of Physical Chemistry*, p. 342–386, John Wiley and Sons, Inc., New York, 1947.

[15] Roseveare, *J. Am. Chem. Soc.*, **53**, 1651 (1931).

[16] Reed and Theriault, *J. Phys. Chem.*, **35**, 673 (1931)

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL CORPORATION]

ortho-Alkylation of Aromatic Amines[1]

GEORGE G. ECKE, JOHN P. NAPOLITANO, ALLEN H. FILBEY, AND ALFRED J. KOLKA[2]

Received November 5, 1956

Primary and secondary aromatic amines react with olefins in the presence of aluminum anilide type catalysts to yield products alkylated in the *ortho* positions. No *para* alkylated products were detected.

The nuclear alkylation of aromatic amines by aluminum halide catalyzed reactions has not found wide application because of complications arising from the characteristics of the amino group. It was recently found in these laboratories that primary and secondary aromatic amines could be alkylated with olefins using the corresponding aluminum anilide as the catalyst to give products from which only *ortho*-alkylated amines could be isolated.

TABLE I

REACTIONS OF AROMATIC AMINES WITH OLEFINS USING N-ALUMINO CATALYSTS

Reactants		Temperature, °C	Operating Pressure Range, psi	Reaction Time, Hours	Recovered Amine, Mole %	2-Alkyl-Amine Mole %	2,6-Di-Alkylamine Mole %
Olefin	Amine						
Ethylene	Aniline	330	450–500	24	29	33	20
Ethylene[a]	Aniline[a]	330	600–800	9	1	2	90[b]
Ethylene	*N*-Methylaniline	205	600–800	3	—	86	—
Ethylene	*N*-Ethylaniline	205	600–800	2.5	2	86	—
Ethylene	*o*-Toluidine	325	600–800	8	—	—	90
Ethylene	α-Naphthylamine	300	600–800	3	55	30	—
Ethylene	*N*-Ethyl-*m*-chloroaniline	255	600–800	3	3	85[c]	—
Propylene	Aniline	330	600–800	5	81	4	—
Propylene	*N*-Methylaniline	235	500–700	4	32	54	—
Isobutylene	Aniline	330	720–730	3	92	2	—
Decene	*N*-Methylaniline	300	90–100	0.5	—	35	—
Cyclohexene	*N*-Methylaniline	300	280–300 (vapor pressure)	0.5	89	2	—

[a] This reaction was carried out using 6.7 mole % of aluminum anilide as compared with 3–4 mole % of catalyst in the other experiments. [b] The dialkylated product consisted of 86% of 2,6-diethylaniline and 4% of 2-ethyl-6-*sec*-butylaniline. [c] Approximately equal amounts of *N*-ethyl-2-ethyl-3-chloroaniline and *N*-ethyl-2-ethyl-5-chloroaniline were produced.

An investigation of the process has made several generalizations possible in regard to the reactivities of the reactants (Table I) and the structures of

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[1] Presented in part before the Division of Organic Chemistry at the 130th meeting of the AMERICAN CHEMICAL SOCIETY, Atlantic City, N. J., Sept., 1956 and in a preliminary communication, *J. Org. Chem.*, **21**, 711 (1956).

[2] Present address, Koppers Co., Inc., Koppers Bldg., Pittsburgh, Pa.