TABLE III

DEGREE OF CRYSTALLINITY OF NATURAL RUBBER ON STRETCHING (FROM BOONSTRA)[39]

$\Delta H_u = 15.3$ cal /g. of unit.

Elongation:	300%			400%			500%		
	ΔE, cal./g.	$\Delta E/\Delta H_u$	λ (X-ray)	ΔE, cal./g.	$\Delta E/\Delta H_u$	λ (X-ray)	ΔE, cal./g.	$\Delta E/\Delta H_u$	λ (X-ray)
Sample S	0.394	0.026	0.04	1.845	0.12	0.15	3.46	0.23	0.30
Sample T	.398	.026	.05	1.44	.095	.105	2.93	.19	0.19–0.22

mined by the X-ray method.[31] Quantitative agreement is obtained between $\Delta E/\Delta H_u$ and the degree of crystallinity, which strongly suggests that the crystallization process is the cause of the large internal energy changes that are observed. This conclusion is based solely on a thermodynamic analysis of the experimental facts without recourse to any molecular interpretation as to the nature of the retractive force. A quantitative molecular interpretation of the upsweep of the stress-strain curve which sets in at about $\alpha = 3$ naturally will have to take into account the phase change that is occurring. It cannot be explained solely on the basis of the entropy change that occurs in deforming a completely amorphous material.[40,41]

Acknowledgment.—The authors wish to acknowledge many interesting discussions on this subject with L. A. Wood and N. Bekkedahl and thank them for making available many of their original data.

[40] M. C. Wang and E. Guth, *J. Chem. Phys.*, **20**, 1144 (1952).

[41] A. Isihara, N. Hashitsume and M. Tatibana, *ibid.*, **19**, 1508 (1951).

WASHINGTON, D. C.

[CONTRIBUTION FROM THE RICHARDSON CHEMICAL LABORATORY, TULANE UNIVERSITY]

The Rate of Reaction of Ethyllithium and Anisole

BY T. F. FAGLEY AND ELIAS KLEIN

RECEIVED JUNE 18, 1954

The reaction of ethyllithium with anisole in benzene solutions was found to follow, at 30 and 40°, the rate law, $dV/dt = k(V_\infty - V)^2b^2/(V_\infty a)$, where V is the volume of ethane at time t, b and a are the initial concentrations of anisole and ethyllithium, respectively. The presence of the $(V_\infty a)$ term is interpreted. Dielectric constant measurements are correlated with the change in rate with anisole concentration.

In the extensive investigations of the reaction of alkyl and aryl alkali compounds with such compounds as anisole, thianaphthene and alkyl benzenes, hydrogen–alkali interchange has been interpreted to involve coördination of the organometallic reagent with the electronegative atom or with the pi electrons in the aromatic nucleus. Bryce-Smith[1] has suggested that the reactions are not nucleophilic, since the aromatic nucleus retains the electrons of the original carbon–hydrogen bond. He considered the reaction to involve a protophilic attack in which the alkali compound possibly functions as an ion-pair. Roberts and Curtin[2] stated that the predominantly *ortho* orientation observed with the substituents F, OCH_3, CF_3 in the benzene ring is best accounted for by assuming that the reaction involves an initial coördination of the metallic atom of the metalating agent with an unshared electron-pair of the substituent group followed by the removal of an *o*-hydrogen by the anion of the metalating agent.

In this Laboratory a kinetic study of the reaction of ethyllithium with anisole in benzene solutions has been made. The difficulty of preparing pure ethyllithium in peroxide-free ethers and the possibility of cleavage of the ether in concentrated solutions at and above room temperatures discouraged attempts at measurements in such media. The lithiation of thianaphthene in benzene was discarded because of precipitation of the product and evidence of catalytic effect of the solid. The reaction of ethyllithium, prepared in benzene, with benzene solutions of anisole was finally chosen for study. Considerable care was taken in the preparation of the reagents to eliminate ambiguities resulting from contamination by peroxides, ethoxides and colloidal lithium. The reaction was followed by measuring the volume of ethane collected over mercury, at constant pressure, as a function of time. The solubility of ethane in benzene–anisole mixtures necessitated using small volumes (5 milliliters) of relatively concentrated solutions. Further, since the reaction was extremely slow in solutions less concentrated than 1 molar in anisole (even in 1.667 *M* anisole the rate of evolution was 5 ml. per hour), and concentrated solutions of ethyllithium in benzene were not possible because of the limited solubility of ethyllithium in benzene, high concentrations of anisole were required. This presented the additional problem of "medium effect" on the kinetics. An attempt to evaluate this effect was made in terms of dielectric constant measurements of some anisole–benzene solutions.

Experimental

Materials.—The anisole was an Eastman White Label product. It was dried with metallic sodium and then fractionally distilled through a Vigreux column. The refractive index at 25° was 1.5144 for the sodium D-line. It was stored over sodium and a stream of oxygen-free dry nitrogen passed through it to displace any dissolved oxygen. The benzene used as solvent was Reagent Grade "Baker Analyzed"; it was fractionally crystallized, distilled and dried

[1] D. Bryce-Smith, *J. Chem. Soc.*, 1079 (1954).

[2] J. D. Roberts and P. Y. Curtin, THIS JOURNAL, **73**, 810 (1951).

with sodium. Its physical properties were the same as those given for benzene by Timmermans.[3]

The ethyllithium was prepared by treating metallic lithium sand with diethylmercury in a sealed reaction flask prepared as follows. A 150-ml. round-bottom flask was modified by drawing out the neck and sealing a six-inch test-tube to the bottom, and a three-inch piece of 10 mm. tubing to the shoulder. The flask was flame-dried and swept with nitrogen. The lithium sand, suspended in oxygen-free benzene, was then introduced and the neck of the flask sealed after freezing the benzene. The diethylmercury was introduced through the side-arm, the side-arm sealed off, and the flask allowed to stand for about three days. As the mercury was formed it amalgamated the smaller particles of lithium and the amalgam sank into the test-tube at the bottom of the flask. At the completion of the reaction, the flask was opened in a nitrogen-swept dry-box and the ethyllithium solution transferred to small glass ampoules with a calibrated 1-cc. syringe, introduced through the small-bore side-arm, which was broken off in the dry-box. The ampoules had previously been evacuated and filled with dry nitrogen. After they were filled, their contents were frozen and the necks sealed off in such a manner as to thin out the glass shoulders. The concentration of ethyllithium was determined by acid titration. The analyses agreed, within experimental error, with the volumetric measurement of the ethane evolved on hydrolysis. During every step of the preparation precautions were taken to exclude traces of moisture and oxygen. Those preparations which were not performed satisfactorily resulted in subsequent yellow colorations of the solutions in the ampoules, and in the extreme cases, in the precipitation of lithium ethoxide and lithium hydroxide. Only those ampoules which remained colorless and showed absence of a Tyndall cone were used in the experiments. The preparations showed no presence of mercury contaminants in tests with acidified H_2S solutions.

The nitrogen used to flush the reaction vessel was passed successively through an electrically heated column of copper, a silica-gel filled trap, a column of drierite, and a column of phosphorus pentoxide.

Apparatus.—The reaction chamber consisted of a 150-ml. erlenmeyer flask having a 24/40 standard taper fitting attached at the neck and a 19/32 one attached to a side-arm, which entered the erlenmeyer flask at a point about $^1/_4$" from the bottom. The 24/40 taper was attached to a capillary tubing leading to the water-jacketed buret through a three-way stopcock. The stopcock allowed the isolation of the three components of the system: reaction chamber, gas buret and a U-tube small-bore manometer filled with benzene saturated with ethane. The reaction flask was thermostatted by a two-liter beaker containing water pumped from a large constant temperature bath. Constant pressure was maintained by lowering or raising a leveling bulb filled with mercury until the levels of the benzene in the two arms of the U-tube were equal. Stirring was produced by a glass-enclosed bar magnet in the reaction flask, actuated by a Precision Scientific Mag-Mix motor-driven magnet.

The dielectric constant measurements were made with a onventional heterodyne-beat apparatus.

Results

The rate of the reaction of anisole with ethyllithium was, under the conditions of high anisole concentration as reported here, measurably rapid, the reaction usually reaching completion within 9–10 hours. The product of the metallation was confirmed by pouring the reaction mixture over a slurry of Dry Ice in ether. The ether solution was washed with 0.1 *N* NaOH and the aqueous layer separated. On neutralization of the aqueous layer and slow crystallization, transparent crystals of *o*-methoxybenzoic acid with a melting point of 102.0–102.2°, measured on a Hershberg melting point apparatus, were isolated.

The initial ethyllithium concentration was evaluated in three ways: by titration, with standard acid, of the hydrolyzed reaction mixture at the completion of a kinetic study; by breaking a duplicate ampoule in water and titrating the LiOH formed; and by measuring the volume of ethane released on hydrolysis of a separate sample. These methods agreed with one another to a precision of 0.8%. Since the hypodermic syringe used to fill the ampoules delivered 1.000 ± 0.007 ml. as determined by calibration with mercury, the precision was all that could be expected.

The quantity $(V_\infty - V)$ was taken as a measure of unreacted ethyllithium, since the anisole in all experiments was in such great excess that it was essentially constant. Plots of $1/(V_\infty - V)$ *versus* time were linear in all experiments, indicating that the reaction was second order in ethyllithium. It was found, however, that the half-lives of the reactions were directly proportional to the first power of the initial ethyllithium concentrations, a characteristic of zero-order reactions. Evaluation of the initial rates, by extrapolation of plots of log $(\mathrm{d}V/\mathrm{d}t)$ *versus* log $(V_\infty - V)$ revealed that over a twofold concentration range in initial ethyllithium the initial rates were independent of the initial ethyllithium concentration. Thus the data indicated that the rate of reaction was second order with respect to ethyllithium and inversely proportional to the square of the initial ethyllithium concentration. A differential plot (Fig. 2) of rate *versus* the square of the concentration of ethyllithium confirmed these relations. The rate equation suggested by these data is

$$\frac{-\mathrm{d}\,\{a(V_\infty - V)/V_\infty\}}{\mathrm{d}t} = \frac{k}{a^2}\left\{\frac{a(V_\infty - V)}{V_\infty}\right\}^2 b^n \qquad (1)$$

where a is the initial concentration of ethyllithium, b is the initial concentration of anisole, and $(V_\infty - V)/V_\infty$ represents the fraction of ethyllithium unreacted. This becomes, on simplification and integration

$$\mathrm{d}V/\mathrm{d}t = k\,\frac{(V_\infty - V)^2}{aV_\infty}\,b^n \qquad (2)$$

$$1/(V_\infty - V) = \frac{kb^nt}{V_\infty a} + 1/V_\infty \qquad (3)$$

Plots of $1/(V_\infty - V)$ *versus* t showed linearity, as indicated in Fig. 3. From these plots, by extrapolation to zero time, more accurate values of V_∞ could be obtained than from the experimental measurement after 10–12 hours, since equalization of pressure in the reaction chamber with atmospheric pressure on breaking the ampoule depended on opening the bleeding stopcock at the proper time. Too early or too late closing would lead to a constant error in the volume readings throughout the run and would give a spurious value for V_∞, although the difference $(V_\infty - V)$ would still be a true measure of unreacted ethyllithium.

The range of concentration of ethyllithium samples was limited by its solubility in benzene. Therefore, experiments in which ethyllithium was in excess of anisole were much too slow to measure with any precision, in view of the ambient temperature of the bath and fluctuations in barometric pressure over long intervals of time. The apparent order of the reaction with respect to the anisole was de-

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(3) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., New York, N. Y., 1950.

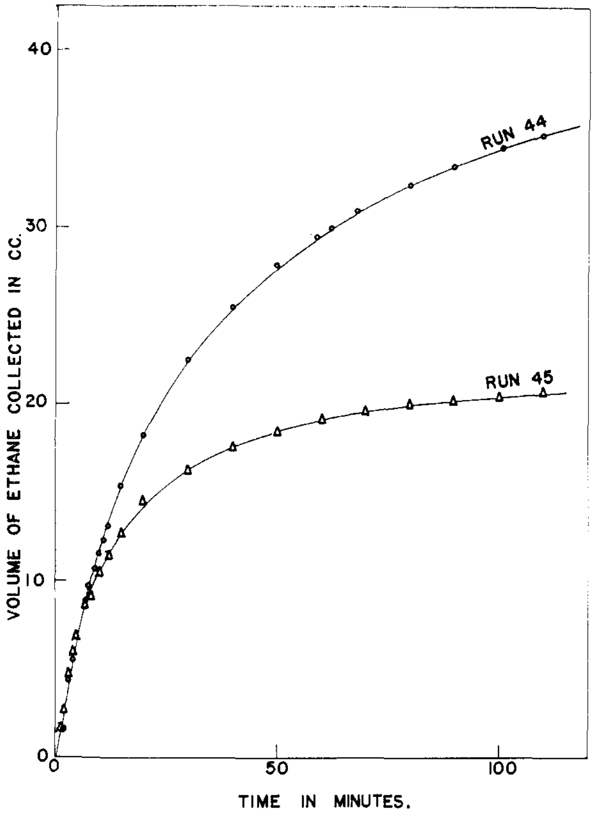

Fig. 1.

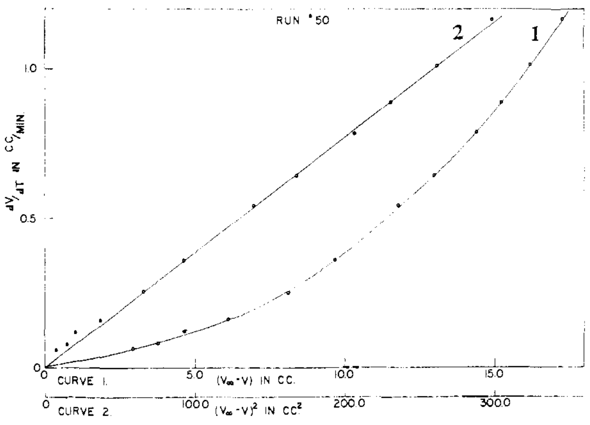

Fig. 2.

termined in experiments 53 and 54, in which the ethyllithium concentration was held constant and the anisole concentration, although still in large excess, was doubled. From equation 3 the half-life is given by

$$t_{1/2} = a/kb^n \qquad (4)$$

The half-lives of reactions 53 and 54 were inversely proportional to the square of the initial concentration of anisole. The over-all rate equation then becomes

$$\mathrm{d}V/\mathrm{d}t = \frac{k(V_\infty - V)^2 b^2}{V_\infty a} \qquad (5)$$

Table I gives a summary of the data for nine experiments involving samples of ethyllithium from five independent preparations. The V_∞ quantities were obtained from least squares analyses of the

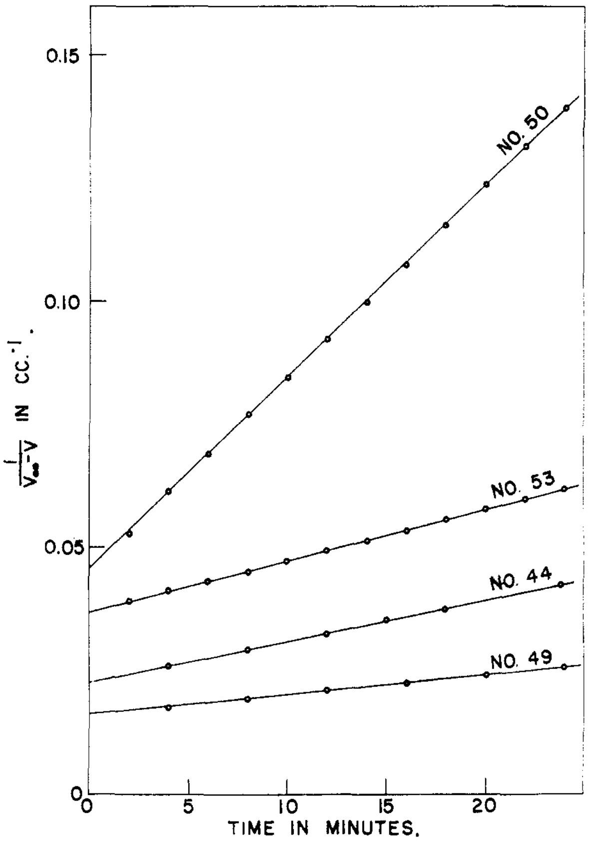

Fig. 3.

data fitted to equation 3, by evaluating the intercept of the regression line. The inverse of the intercept gave the value of V_∞. The column marked Slope gives the slope of the lines obtained from equation 3 by least squares. The half-lives listed in the last column were obtained, first, from the time corresponding to the instant at which the left hand side of equation 3 has the value $2/V_\infty$; and, second, from the experimental volume–time plot in which the volumes were corrected for the constant error incurred at the time of breaking the ampoule. The agreement of the values obtained by the two methods was within the limits of experimental error.

Discussion

The puzzling dependence of the half-life of the reaction on the first power of the initial concentration of ethyllithium and the apparent zero-order initial rates was at first thought to be indicative of an inhibition of the reaction by one of the products.[4] It is difficult, however, to see how ethane could inhibit the reaction chemically. The answer appears to lie in the fact that the rate of evolution of ethane at the beginning of the reaction depends on the difference between the rate of its formation and the rate of its solution. The solubility of ethane in benzene–anisole solutions is fairly large. If one considers the reaction to be truly second-order in ethyllithium then one can write

$$\mathrm{d}x/\mathrm{d}t = k_f(a - x)^2 b^n \qquad (6)$$

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[4] K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 17.

TABLE I

Expt.	Prep.	a = EtLi (mole l.$^{-1}$)	b = anisole (mole l.$^{-1}$)	Temp., °C.	D	V_∞	Slope, s × 10^4	$sV_\infty a$	$sV_\infty a/b$ × 10^4	$(sV_\infty a/b^2) = k$ × 10^4	$t^1/_2$ (min.)
30	1	0.2368	1.667	40.0	2.64	22.24	2.462	0.001295	7.785	4.67	123
44	2	.4772	6.136		3.60	43.64	8.243	.017160	27.98	4.56	27.8
45	2	.2386	7.363		3.85	20.89	49.096	.024072	33.28	4.52	9.9
47	3	.2699	7.363		3.85	20.57	45.007	.024098	33.94	4.61	11.1
49	3	.5630	5.454		3.44	61.44	4.079	.014109	25.69	4.71	39.1
50	4	.2754	7.363		3.85	21.59	38.481	.022090	31.15	4.23	11.5
									Av.	4.55 ± 0.11	
53	4	.2908	7.363	30.0	3.85	26.98	10.365	.008128	11.05	1.50	36.2
54	5	.2912	3.682		3.07	28.13	2.164	.001725	4.86	1.32	149
56	4	.2908	7.363		3.85	27.37	10.44	.008308	11.265	1.53	35.3

where a is the initial amount of ethyllithium, x the amount of ethane formed at time, t, and b the essentially constant concentration of anisole. Integration gives

$$x = \frac{a^2k_fb^nt}{1 + ak_fb^nt} \qquad (7)$$

The rate of formation, r_f, can then be written

$$r_f = k_f(a - x)^2b^n = k_f\frac{a^2b^n}{(1 + ak_fb^nt)^2} \qquad (8)$$

The rate of solution of ethane will depend on the difference between the amount, S, of ethane needed to saturate the solution and the amount x generated at any time t

$$r_s = k_s(S - x) = k_s\left(S - \frac{a^2k_fb^nt}{1 + ak_fb^nt}\right) \qquad (9)$$

The rate of escape of ethane will be the difference between these two

$$\begin{aligned} r_e &= r_f - r_s \\ &= k_f\frac{a^2b^n}{(ak_fb^nt + 1)^2} - k_s\left(S - \frac{a^2k_fb^nt}{1 + ak_fb^nt}\right) \qquad (10) \end{aligned}$$

At the time of saturation, t_s, the rate of escape should be equal to the rate of formation

$$r_s = 0$$

$$k_s\left(S - \frac{a^2k_fb^nt_s}{1 - ak_fb^nt^s}\right) = 0$$

$$S = \frac{a^2k_fb^nt_s}{ak_fb^nt_s + 1} = \text{constant for a given soln.} \qquad (11)$$

at $t = 0$, the rate of escape may or may not be zero, but one can say that the rate of solution is m times the rate of formation, where m may be a fraction or a whole number

$$\begin{aligned} k_sS &= mk_fa^2b^n \\ k_f &= k_sS/ma^2b^n \qquad (12) \end{aligned}$$

Substituting these values for S and k_f in the equation for the rate of escape at the time of saturation, one gets

$$\begin{aligned} r_f &= k_f(a - x)^2b^n \\ &= k_s/ma^2b^n(a - x)^2b^{2n} \quad [a^2k_ft_s/(ak_fb^nt_s + 1)] \\ &= (k/a^2b^n)(a - x)^2b^{2n} \qquad (13) \end{aligned}$$

since the quantity in brackets is a constant, proportional to the volume of ethane needed to saturate the solution.

It is seen from equation 13 that the rate at zero time ($x = 0$) will appear to be independent of the initial concentration of ethyllithium. Further, integration of 13 and the evaluation of $t_{1/2}$ will give for the latter an expression proportional to the first power of the initial ethyllithium concentration.

This was found to be the case empirically. For any one experiment the rate was, as shown by the linearity of plots of $1/(V_\infty - V)$ *versus* t, second order; but experiments involving different initial concentrations of ethyllithium gave widely different slopes (see table). From equation 3 it can be seen that the slope should be equal to $kb^n/(V_\infty a)$ and hence the specific reaction rate constant should be given by $sV_\infty a/b^n$, where s here is the slope. These values were constant within the precision of the measurements when n was set equal to 2, as can be seen in column 11 of the table.

The order of the reaction with respect to anisole may be questioned, since anisole in all experiments had to be in great excess to produce a measurable rate. In experiments 53 and 54 the mole fraction of anisole was about 0.7 and 0.35, respectively. Consequently the change in rate in these two runs (ethyllithium concentration being the same) may be the result of an electrostatic solvent effect. In the reaction between two dipolar molecules the dielectric constant of the solvent becomes important, particularly if the products are quite different in polarity from the reactants. The dipole moment of ethyllithium must be near that of n-butyllithium for which $\mu = 0.97$ debye. The dipole moment of anisole is 1.25 debyes and that of o-lithium anisole has been estimated by vector addition to be about 1.8 debyes. These lithium compounds do not behave like ionic compounds in solvents of low dielectric constant. The dielectric constant of pure benzene is 2.26; that of anisole, about 4.25.

To see whether the dielectric constant changed appreciably from one experimental run to another, measurements were made on some solutions of anisole and benzene with a conventional heterodyne-beat apparatus. A plot of these dielectric constants *versus* mole fraction of anisole was linear and extrapolated to the recorded values for benzene and anisole at mole fractions equal to 0 and 1, respectively. Density measurements and refractive indices were taken at the same time. Volume calculations from the density measurements showed that, within a precision of a few tenths of a per cent., the solutions were volume-ideal; and a plot of refractive index *versus* mole fraction was essentially linear. The values of the dielectric constants of the solutions, as read from the graph, are listed in Table I. In studies 53 and 54 the dielectric constant changed from 3.07 to 3.85 and $(sV_\infty a)$ changed by a factor 4.7. Plots of ($sV_\infty a/b$), the specific reaction rate constant one would expect if anisole enters into the rate equation to the first power, *versus* the dielectric constant D, and of ($sV_\infty a/b$) *versus* molarity of anisole, were linear. Plots of ($sV_\infty a$) *versus* D or *versus* molarity of anisole were definitely not linear, showing strong curvature. Furthermore, a plot of log ($sV_\infty a/b$) *versus* $(D - 1)/2D + 1$ was roughly linear. These suggest that the reaction is probably first order in anisole and that the extra order of unity in the observed kinetics arises from an electrostatic solvent effect.

Acknowledgment.—The authors are indebted to Mr. Roy Bennett for help in the dielectric constant measurements. One of them (E.K.) is indebted to American Cyanamid Co. for a fellowship held during this investigation. They are also indebted to Dr. D. A. Shirley for suggesting the original investigation.

NEW ORLEANS, LOUISIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF ILLINOIS]

The Synthesis of Unsymmetrically Disubstituted Hydrazines

BY H. ZIMMER, L. F. AUDRIETH, M. ZIMMER AND R. A. ROWE

RECEIVED MAY 17, 1954

Unsymmetrically disubstituted hydrazines, RRN·NH$_2$, can be prepared from the corresponding nitrosamines, RRN·NO, by use of the following reducing systems: (a) lithium aluminum hydride in ether, (b) sodium in alcohol and (c) sodium in liquid ammonia in the presence of substances which act as acids in ammonia. The following hydrazines have been prepared, where RR = $(C_2H_5)_2$, (n-$C_3H_7)_2$, (iso-$C_8H_7)_2$, (n-$C_4H_9)_2$, (iso-$C_4H_9)_2$, (n-$C_5H_{11})_2$, [$-CH_2(CH_2)_3CH_2-$] (N-aminopiperidine), $(CH_3)(C_6H_5)$ and ($-CH_2CH_2OCH_2CH_2-$) (N-aminomorpholine). Various identifying derivatives have been prepared such as the oxalate salt, 1,1-disubstituted semicarbazide, N-dialkylaminourethan, or the N,N-dialkylhydrazones.

Introduction

In connection with investigations which have had as their objective the extension of the Raschig synthesis to the preparation of N-substituted hydrazines[1] from the corresponding amines and chloramines it became necessary to have available for purposes of comparison a number of unsymmetrically N,N-disubstituted hydrazines of the aliphatic series. The two simplest members, N,N-dimethylhydrazine and N,N-diethylhydrazine, were first prepared by E. Fischer[2] from the corresponding nitrosamines by reduction with zinc and dilute acetic acid. Lithium aluminum hydride has been used more recently for the reduction of nitrosamines by Schueler and Hanna.[3] Although we too have found the lithium aluminum hydride method to be useful it has been our experience that the preparation of N,N-disubstituted hydrazines from the nitrosamines can be accomplished more easily if sodium is employed as the reducing agent either in alcoholic solution or in liquid ammonia in the presence of solutes that are acids in ammonia.

All three methods have been used in the present investigation to accomplish the preparation of a number of typical unsymmetrically disubstituted hydrazines. These are colorless liquids and possess a characteristic ammoniacal odor. All suffer autoxidation and deterioration on exposure to the atmosphere. Difficulties were experienced in attempting to analyze the free bases, even though formation of the desired substances was verified by determination of the neutral equivalents. For this reason all products were converted into appropriate derivatives.

The dimethyl and diethyl derivatives are very soluble in water; the di-n-propyl- and diisopropylhydrazines are only somewhat water soluble whereas both of the dibutylhydrazines and di-n-amylhydrazine are practically insoluble in water. Prolonged heating on the steam-bath is necessary to effect reduction of Fehling solution. Ethereal solutions react to precipitate salts when treated with anhydrous acids. The hydrochlorides and the sulfates are extremely hygroscopic. The oxalates represent well defined compounds. Crystalline compounds could not be obtained with picric acid and styphnic acid.

The hydrazines react with aldehydes and ketones, but most of the common carbonyl derivatives are liquids. Crystalline 1,1-disubstituted semicarbazides, $R_2NNHCONH_2$, are obtained with potassium cyanate in dilute aqueous acetic acid. No semicarbazide derivative of di-n-amylhydrazine could, however, be obtained. The methyl ester of chlorocarbonic acid reacts readily with diethylhydrazine to form N-diethylaminourethan methyl ester hydrochloride.

Acknowledgment.—The present investigation was carried out as one phase of a study of the fundamental chemistry of the Raschig synthesis for the preparation of hydrazine, sponsored by the Office of Ordnance Research, Contract DA-11-022-ORD-828. We wish to express our appreciation to Mrs. E. Fett, Mrs. L. Chang and Mr. J. Nemeth for carrying out microanalytical determinations.

Experimental

The nitrosamines were prepared by reaction of the secondary amine hydrochlorides with sodium nitrite. The preparation of di-n-amylnitrosamine is typical of the method employed and is given in detail since this particular compound had not previously been described in the literature.

The hydrazines were prepared by the reduction of the corresponding nitrosamines by use of three reducing systems: lithium aluminum hydride (method A), sodium in alcohol (method B) and sodium in liquid ammonia in the presence of an acidic solute (method C). Examples are presented below and are designed to be illustrative of the methods used specifically for the synthesis of compounds

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(1) L. F. Audrieth and L. H. Diamond, THIS JOURNAL, **76**, 4869 (1954).

(2) E. Fischer, *Ann.*, **199**, 281 (1879).

(3) F. W. Schueler and C. Hanna, THIS JOURNAL, **73**, 4996 (1951); **74**, 3693 (1952).