(0.00229 mole) of IV in contact with 10.0 g. (0.153 g.-atom) of powdered zinc. The suspension was filtered. The filtrate was neutralized with aqueous sodium carbonate and dried over solid sodium carbonate. A black tar left by evaporation of the benzene was dissolved in petroleum ether (b.p. 77–115°) and cooled. A black oil formed which was removed by filtration and discarded. The clear filtrate was seeded with III and set aside in the cold. The slow-forming crystals weighed 0.1 g. (10%), m.p. 179–182°. A mixed melting point with III was not depressed, and the infrared spectra were practically indistinguishable.

Alternate synthesis of 10-methyl-9-(triphenylsilyl)acridan (II). To a solution of 0.4 g. (0.00205 mole) of 10-methylacridan in 20 ml. of ether was added 2.5 ml. of an ethereal solution containing 0.0025 mole of *n*-butyllithium.[11] The solution became bright red in color. To this solution was added, all at once, 0.71 g. (0.0025 mole) of chlorotriphenylsilane. The red color was discharged. Ether was added to increase the volume of the reaction mixture, and hydrolysis was effected with water. The ether layer was dried over sodium sulfate and evaporated. The solid was recrystallized from ethanol to give 0.75 g. (81%) of II, m.p. 179–181°. A mixed melting point with a sample of II prepared by the first procedure was not depressed. The infrared spectra were identical.

10-Methyl-9-(triphenylsilyl)acridan(II) *from 9-(triphenylsilyl)acridan*(III). Five ml. of an ethereal solution containing 0.005 mole of *n*-butyllithium[11] was added to a solution of 1.5 g. (0.00342 mole) of III in 20 ml. of ether, followed by an excess of methyl sulfate. Ether was added to increase the volume of the reaction mixture, which was then hydrolyzed with water. The organic layer was dried over sodium sulfate and evaporated. Recrystallization of the solid from ethanol gave 0.92 g. (59%) of II, m.p. 179–181°. A mixed melting point with a sample of II prepared by the first method described was not depressed. The infrared spectra were identical.

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Base Strengths of Some Alkylhydrazines[1]

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In connection with studies on the acylation[3] and alkylation of hydrazine and some of its derivatives the base strengths of a number of alkylhydrazines were needed. A survey of the literature revealed that aside from that of hydrazine itself,[4] only the values of trimethyl- and tetramethyl hydrazine have been reported.[5] Accordingly, the apparent dissociation constants of the remaining members of the methylhydrazine series and of a number of ethylhydrazines were determined by potentiometric titration in water at 30°.

EXPERIMENTAL

Methylhydrazine and 1,1-dimethylhydrazine were purchased. The other alkylhydrazines were prepared by known methods (see Table I for references). Each hydrazine was carefully purified before use by drying over calcium sulfate and then over freshly cut sodium. The sample was finally distilled through a short Vigreux column in an atmosphere of nitrogen. A middle fraction with a boiling range of not more than one degree was collected for use in the determinations of base strengths.

Since hydrazines of low molecular weight are volatile, hygroscopic, easily oxidized compounds, the freshly distilled materials were sealed in weighed glass ampoules. The neutralization equivalent was used as a check on the purity of the sample, and in general agreed to within 2% of the calculated value. Ethylhydrazine, 1,2-dimethylhydrazine, and 1,2-diethylhydrazine were obtained as the dihydrochlorides and were titrated in this form. In these cases the neutralization equivalents were 5–6% low, which may be accounted for by the fact that hydrazine dihydrochlorides tend to lose hydrogen chloride on standing or during recrystallization.[6]

The base strength of each hydrazine, measured and recorded in Table I as pK_a', was taken as the half-neutralization point of the titration curve of the hydrazine (*p*H *vs.* volume of standard hydrochloric acid added). The ampoules of hydrazines, containing samples weighing from 0.1 g. to 0.4 g., were crushed below the surface of the water just before beginning the titration. Sufficient water was used to give an initial concentration of from 0.02*M* to 0.05*M*. The surface of the solution was bathed in nitrogen throughout the titration. The temperature of the reaction mixture was maintained at 30 ± 0.1°. The titration was followed with a Beckman *p*H Meter, Model F, equipped with glass and calomel electrodes, and standardized before use with a buffer solution of *p*H 7.00. The pK_a''s in Table I are the averages of the several titrations in each case. The average deviation of the pK_a' was no larger than ±0.05 in any case.

In some cases the hydrochlorides of the hydrazines were used for the determination of the pK_a'. With dihydrochlorides, like those of the 1,2-dialkylhydrazines, two breaks were observed in the curve, of which the second break was not sharp. In the latter case calculation of the second derivative in the region of the curve's steepest slope (*i.e.*, near the end point) gave reproducible results.[7] As a check on this method the pK_a' values of methylhydrazine and of 1,1-dimethylhydrazine were determined by titration of their hydrochlorides with base. The results agreed within 0.1 *p*K unit of those obtained by titration of the free hydrazine with acid.

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TABLE I

pK_a' VALUES OF ALKYLHYDRAZINES at 30°

Hydrazine	Method of Preparation	pK_a'[a]	$\Delta pK_a'$[b]
NH_2NH_2	[c]	8.07[d]	
CH_3NHNH_2	[c]	7.87	−0.20
$(CH_3)_2NNH_2$	[c]	7.21	−0.66
$CH_3NHNHCH_3$	[e]	7.52[f]	−0.35
$(CH_3)_2NNHCH_3$	Ref. 5	6.56	−0.65
$(CH_3)_2NN(CH_3)_2$	Ref. 5	6.30[g]	−0.26
$C_2H_5NHNH_2$	[h]	7.99[f]	−0.08
$(C_2H_5)_2NNH_2$	[i]	7.71	−0.28
$C_2H_5NHNHC_2H_5$	[j]	7.78[f]	−0.21

[a] Average deviation = ±0.05. [b] Difference of two adjacent members of the same series. [c] Purchased. [d] Reported value: 7.95 (at 25°) (ref. 4). [e] R. L. Hinman, *J. Am. Chem. Soc.*, **78**, 1645 (1956). [f] From titration of dihydrochloride. [g] This value taken from ref. 5. [h] G. Gever and K. Hayes, *J. Org. Chem.*, **14**, 813 (1949). [i] H. Zimmer, L. F. Audrieth, M. Zimmer, and R. A. Rowe, *J. Am. Chem. Soc.*, **77**, 790 (1955). [j] R. Renaud and L. C. Leitch, *Can. J. Chem.*, **32**, 545 (1954).

DISCUSSION

The most striking fact about the results recorded in Table I is that substitution of an alkyl group for a hydrogen of the hydrazine molecule is accompanied by a *decrease* in base strength, and that further decreases accompany the introduction of additional alkyl groups. It is also apparent that each member of the ethylhydrazine series is more basic than its methyl homolog.

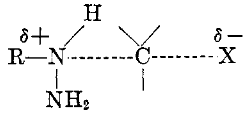
Although the latter effect parallels that in the amine series, the general base-weakening effect of alkyl groups in the hydrazine series is the opposite of what one would expect on the basis of the base strengths of the corresponding amines, or on the basis of the usual electron-donating character of alkyl groups. Thus, the methylamines fall in the following sequence[8] with respect to their base strengths:

$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3.$$

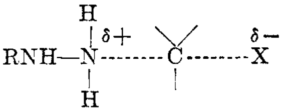
The ethylamines fall in a similar order.[8]

The results reported in this note contradict the assumption occasionally found in the literature[9,10] that the alkylhydrazines are more basic than hydrazine itself, just as the methylamines are more basic than ammonia. The results are also pertinent to the theory which holds that successive alkylations of a hydrazine take place on the same nitrogen because the nitrogen which bears the more alkyl groups is always the more basic.[10] The term basic, as used in the reference cited, does not refer to the measured affinity of the nitrogen for a proton or other acid, but rather to an idealized electronic state of the nitrogen, predicted on the basis of the usual inductive or conjugative effects of the attached groups. In this sense, which is one frequently used today, the explanation is not incompatible with the present finding that the over-all basicity of the molecule decreases as alkyl groups are introduced.[11] When applied to phenylhydrazine, however, this theory predicts that alkylation should take place on the nitrogen which does not bear the phenyl group because of the greater predicted "basicity" of that nitrogen. Although it has been claimed that alkylation does in fact occur on the predicted nitrogen (Ref. 10, p. 382), the evidence in the literature shows that alkylation occurs mainly on the nitrogen which bears the phenyl group.[12]

A more refined and potentially useful explanation of the phenomenon of alkylation of hydrazines can probably be reached by application of the concept of nucleophilicity.[13] It should also be noted that the positive charge which develops in the transition state will be better stabilized on that nitrogen which bears the larger number of alkyl groups (I).



I



II

Similar considerations may explain the fact that the ease of alkylation increases as successive alkyl groups are introduced. Previous explanations have been based on the assumption that basicity in the alkylhydrazine series increases as the number of alkyl groups is increased.[9,10]

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(11) The measured base strength of an alkylhydrazine may actually be a measure of the average of the proton affinities of the two nitrogens.

(12) See for example: G. Minunni, *Gazz. chim. ital.*, **22**, II, 218 (1892); M. Busch and K. Lange, *J. prakt. chem.*, **144**, 291 (1935). Results confirming that alkylation of phenylhydrazine occurs on the phenyl-bearing nitrogen have been obtained by Mr. B. E. Hoogenboom in this laboratory. These results will be published in the near future.

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Formation of 1,3-Dimethyl-5,5-diphenylhydantoin and Related Reactions

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The reaction of benzil with urea in the presence of alkoxide ion gives a mixture of 5,5-diphenyl-