pounds is further illustrated by their apparent dissociation constants.[5]

	pK'_a	
	66% DMF	Water
11-Membered ring (Id)	7.8	9.1
9-Membered ring (Ib)	10.6	9.2

The increment in pK'_a observed for Ib in changing solvent from 66% dimethylformamide to water is reversed in sign from that usually observed for tertiary amine-H^+ (compare Id, which is normal), but is typical for enols and acid types, wherein hydrogen is being removed from neutral oxygen, and is therefore evidence of the existence of the transannular quaternary form, $R-\overset{|}{\underset{|}{N}}{}^{+}-\overset{|}{\underset{|}{C}}-OH$, of the base conjugate acid in dimethylformamide.

The 8-membered ring[6] aminoketone, 1-methyl-1-azacycloöctan-5-one (If), exhibits carbonyl absorption at 1683 cm.$^{-1}$ and no absorption above 3000 cm.$^{-1}$; the perchlorate is transparent in the 6 μ region; pK'_a 9.75 in 66% DMF, 8.75 in water.

Formulations involving interaction of 3° amine and ketone functions are thus indicated for 8-, 9- and 10-membered rings in which a full transannular bond between N and Cco can create a 5- or 6-membered ring within the larger cycle.

Diethyl γ,γ'-methylimino-bis-butyrate was treated with sodium in xylene under acyloin ring-closure conditions to give (53%) 1-methyl-1-azacyclononan-5-ol-6-one (Ib), m.p. 95–97° (Calcd. for $C_9H_{17}NO_2$: C, 63.12; H, 10.01; N, 8.18. Found: C, 63.74; H, 9.98; N, 7.90); perchlorate[7] (Calcd. for $C_9H_{18}ClNO_6$: C, 39.97; H, 6.63. Found: C, 39.70; H, 6.93). Similarly, from diethyl γ,γ'-ethylimino-bis-butyrate was obtained (60%) 1-ethyl-1-azacyclononan-5-ol-6-one (Ic), b.p. 64–65° (0.15 mm.), $n^{20}D$ 1.4999 (Calcd. for $C_{10}H_{19}NO_2$: C, 64.83; H, 10.33; N, 7.56. Found: C, 65.12; H, 10.49; N, 7.69); perchlorate[7] (Calcd. for $C_{10}H_{20}ClNO_6$: C, 42.08; H, 7.08. Found: C 41.78; H, 7.13). From diethyl δ,δ'-methyl-imino-bis-valerate was obtained (47%) 1-methyl-1-azacyclohendecan-6-ol-7-one (Id), b.p. 85–86° (0.2 mm.), $n^{20}D$ 1.4926 (Calcd. for $C_{11}H_{21}NO_2$: C, 66.29; H, 10.62; N, 7.03. Found: C, 66.52, H, 10.70; N, 7.21); perchlorate[7] (Calcd. for $C_{11}H_{22}ClNO_6$: C, 44.04; H, 7.39. Found: C, 44.40; H, 7.67). Diethyl δ,δ'-ethylimino-bis-valerate yielded (64%) 1-ethyl-1-azacyclohendecan-6-ol-7-one (Ie), b.p. 65° (0.02 mm.), $n^{20}D$ 1.4907 (Calcd. for $C_{12}H_{23}NO_2$: C, 67.56; H, 10.87; N, 6.57. Found: C, 67.39; H, 10.67; N, 6.45). Dieckmann ring closure of diethyl γ,γ'-methylimino-bis-butyrate at high dilution in xylene using potassium *t*-butoxide,[8] followed by hydrolysis and decarboxylation, yielded (20%) 1-methyl-1-azacycloöctan-5-one, purified through the picrate, m.p. *ca.* 300° dec. (Calcd. for $C_{14}H_{18}N_4O_8$: C, 45.40; H, 4.90; N, 15.13. Found: C, 45.56; H, 4.86; N, 15.13); perchlorate, m.p. 260–261° dec. (Calcd. for $C_8H_{16}ClNO_5$: C, 39.75; H, 6.67; N, 5.79. Found: C, 39.85; H, 6.51; N, 5.66).

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[5] We are indebted to Mr. Donald O. Woolf, Jr., and Dr. Harold E. Boaz of Eli Lilly and Company, Indianapolis, Ind., for the electrometric titrations and for aid in their interpretation.

[6] H. C. Brown and E. A. Fletcher, THIS JOURNAL, **73**, 2808 (1951), have demonstrated the coördination of $>N:$ with $B{<}\begin{matrix}O-\\O-\\O-\end{matrix}$ across an 8-membered ring in triethanolamine borate.

[7] Hygroscopic glass.

[8] N. J. Leonard and R. C. Sentz, *ibid.*, **74**, 1704 (1952).

SELECTIVE REDUCTIONS OF AROMATIC SYSTEMS TO MONOÖLEFINS

Sir:

In an earlier publication from this Laboratory[1] we announced the surprisingly large uptake of lithium metal by aromatic ring systems in a solvent of ethylamine. Thus, in some instances, six equivalents of metal were absorbed per benzene nucleus. This clearly indicated that far more extensive reduction of the aromatic rings was occurring than had been observed previously in the sodium–ammonia system.

We now wish to announce the application of this discovery to practical organic syntheses. Thus, employing the lithium–ethylamine reducing medium, we have succeeded in reducing naphthalene, in a one-step operation, directly to $\Delta^{9,10}$-octalin in 52% yield. The nitrosyl chloride of our product melted at the same point as an authentic specimen,[2] and a mixed m.p. was not depressed. A 2,4-dinitrobenzenesulfenyl chloride derivative melted at 142–142.5°. *Anal.* Calcd. for $C_{16}H_{19}O_4N_2SCl$: C, 51.82; H, 5.14; N, 7.56. Found: C, 51.57; H, 5.46; N, 7.65.

Likewise we have shown that tetralin is reduced in 68% yield to $\Delta^{9,10}$-octalin by lithium in ethylamine, thus indicating that naphthalene may pass through this intermediate in its reduction to $\Delta^{9,10}$-octalin. Certainly the above reactions appear to be the method of choice at the moment for the preparation of this olefin. It is noteworthy that sodium in liquid ammonia is reported[3] to reduce naphthalene to tetralin. We have found that lithium in ammonia acts similarly. The greater basicity of ethylamine compared to liquid ammonia may be one of the factors causing more extensive reduction in these cases, although we have not as yet proved this point.

In another case we reduced biphenyl to 1-cyclohexylcyclohexene in 66% yield, the nitrosyl chloride derivative giving an undepressed mixed m.p. with an authentic sample.[4] Sodium in liquid ammonia is reported[5] to reduce biphenyl to 1-phenyl-1-cyclohexene, again indicating a marked difference in the two systems.

Similarly benzene is reduced by lithium–ethylamine to cyclohexene, showing again a tendency for the reagent to leave one unreduced double bond.

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[1] R. A. Benkeser, R. E. Robinson and H. Landesman, THIS JOURNAL, **74**, 5699 (1952).

[2] P. D. Bartlett, F. E. Condon and A. Schneider, *ibid.*, **66**, 1538 (1944).

[3] P. Lebeau and M. Picon, *Compt. rend.*, **158**, 1514 (1914). See also C. B. Wooster and F. B. Smith, THIS JOURNAL, **53**, 179 (1931).

[4] R. Criegee, E. Vogel and H. Hoger, *Ber.*, **85**, 144 (1952).

[5] W. Huckel and H. Bretschneider, *Ann.*, **540**, 157 (1939).

In this regard it seems to bear some resemblance to the calcium–ammonia reducing system, but differs from it in being far more convenient to handle on a laboratory scale.

Our reagent is also effective in reducing compounds which contain functional groups in the aromatic ring, but a fuller treatment of this subject will be announced later.

CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF PURDUE UNIVERSITY
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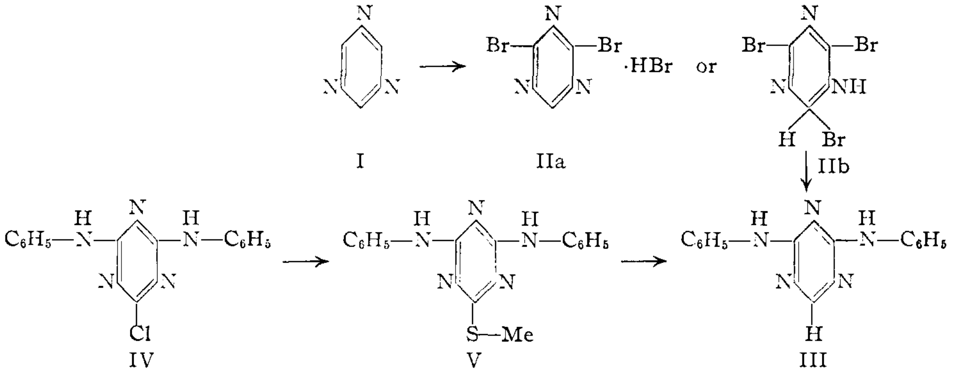
1,3,5-TRIAZINE[1,2]

Sir:

Our recently published experiments on the mixed polymerization of nitriles to unsymmetrically substituted triazines with hydrogen halides as catalyst[3] failed with the simplest nitrile known, *viz.*, hydrocyanic acid. This led us to a more detailed study of the reaction of hydrocyanic acid with hydrogen chloride the first product of which is the so-called "sesqui-hydrochloride of hydrocyanic acid," 2HCN·3HCl, recently formulated as $CHCl_2–NH–CHCl–NH_2$.[4] As demonstrated by Hinkel, *et al.*,[5] this compound easily loses two moles of HCl to a compound 2HCN·HCl, regarded as $CHCl{=}N—CH{=}NH$, which splits off its last molecule of HCl by treatment with dehydrohalogenating agents, *e.g.*, quinoline, to the so-called "dimeric hydrocyanic acid", $C_2H_2N_2$, first obtained by a different route by J. U. Nef.[6] $C_2H_2N_2$ is consequently then formulated as $C{=}N—CH{=}NH$, imino-formyl-carbyl-amine.


I IIa ·HBr or IIb III IV V

However, some of the physical as well as chemical properties of this substance raised serious doubts as to its constitution. Therefore we reinvestigated the molecular weight of the "dimeric hydrocyanic acid" which led to the surprising result that this apparently well known substance is really a trimer of hydrocyanic acid, $C_3H_3N_3$.[7] (Calcd. for $C_3H_3N_3$: mol. wt., 81. Found: mol. wt. (Rast), 89. 9, 90.1, 84.0, 88.5; mol. wt. cryoscopic (benzene) 78.0, 78.0.) As hydrolysis even under very mild conditions yields HCOOH and NH_3 quantitatively,[8] any formula with C–C or N–N groups is definitely excluded. Most obvious is a symmetrical ring structure I suggesting that the "dimeric hydrocyanic acid" is in fact the yet unknown 1,3,5-triazine, the parent compound of so many technical important substances which for a long period many chemists have tried in vain to prepare.

The ultraviolet and the infrared absorption spectra of $C_3H_3N_3$ are closely related to other simple 1,3,5-triazine derivatives of established structure, *e.g.*, 2,4,6-trimethyl-1,3,5-triazine and 2,4,6-trichloro-1,3,5-triazine. The highly symmetrical formula I representing a symmetrically shaped molecule is in agreement with the extreme volatility and the comparatively high melting point (86°) of $C_3H_3N_3$.

Bromination of $C_3H_3N_3$ yields a very sensitive bromo compound which contains three atoms of bromine per one C_3N_3 unit, but is not identical with the known cyanuric bromide. (Calcd. for $C_3H_2N_3Br_3$: Br, 74.97. Found: Br, 72.25, 73.18.) This compound reacts with aniline to 2,4-dianilido-1,3,5-triazine(III) (m.p. 316°. Calcd. for $C_{15}H_{13}N_5$: C, 68.40; H, 4.98; N, 26.60. Found: C, 68.36, 68.45; H, 4.95, 5.17; N, 26.60, 26.62) which we have also prepared from 2,4-dianilido-6-chloro-1,3,5-triazine[9] (IV) through the intermediate V (m.p. 170–171°. Calcd. for $C_{16}H_{15}N_5S$: C, 62.11; H, 4.89; N, 22.64. Found: C, 61.83, 61.80; H, 5.04, 5.05; N, 22.78, 22.89) by a method recently developed for the replacement of halogen by hydrogen in the triazine series.[10] Both compounds were found to be identical which adds a further chemical support to the assumed triazine structure of $C_3H_3N_3$ and also makes it probable that the bromo compound is either 2,4-dibromo-1,3,5-triazine hydrobromide (IIa) or 2,4,6-tribromo-1,2-dihydro-1,3,5-triazine (IIb).

There still remains the task of explaining the formation of triazine from the adducts of hydrocyanic and hydrochloric acid which occurs so easily and under certain conditions with such good yields. Work along these lines is now in progress. A reinvestigation of the known reactions of $C_3H_3N_3$

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[1] This article is based on work performed under Project 116-B of the Ohio State University Research Foundation sponsored by the Mathiesen Chemical Corporation, Baltimore, Md.

[2] Triazines VI: communication by Ch. Grundmann, L. Schwennicke and E. Beyer, *Ber.* in press.

[3] Ch. Grundmann, G. Weisse and S. Seide, *Ann.*, **577**, 77 (1952).

[4] L. E. Hinkel and G. H. R. Summers, *J. Chem. Soc.*, 2813 (1952).

[5] L. E. Hinkel, *et al.*, 1834 (1930); 2793 (1932); 674 (1935); 184 (1936); 407 (1940); 1953 (1949); 2813 (1952).

[6] J. U. Nef, *Ann.*, **287**, 377 (1895).

[7] The discoverer of this compound, J. U. Nef,[6] based the formula $C_2H_2N_2$ on a single cryoscopic determination in benzene, which gave a value of 64 (instead of 54 for $C_2H_2N_2$). Feeling unsatisfied with this result which he attributed to the poor quality of the benzene available in his laboratory, Nef promised a redetermination as soon as he could obtain pure benzene, but apparently this has never been published.

[8] L. E. Hinkel, E. E. Ayling and J. H. Beynon, *J. Chem. Soc.*, 676 (1935).

[9] J. T. Thurston, *et al.*, THIS JOURNAL, **73**, 2981 (1951).

[10] Ch. Grundmann, H. Ulrich and A. Kreutzberger, *Ber.*, **86**, 181 (1953).