This same conclusion is reached in the recent publication mentioned earlier.[6] However, the authors did not work at pressures sufficiently high to eliminate the isomerization of the initially formed dimethylcyclopropane. Of the five experimental results presented, four yielded data in which the ratios of *cis*- to *trans*-1,2 dimethylcyclopropane are almost exactly those expected for simple isomerization of the excited molecule (bearing in mind the low efficiency of nitrogen in stabilizing the excited molecule). That nitrogen (and argon) are not as efficient as butene in stabilizing either excited 1,2-dimethylcyclopropane or 1,1-dimethylcyclopropane (from methylene + isobutene) has been indicated previously.[9,11] Unpublished experiments carried out at the time the work in references 9 and 11 was performed indicated that nitrogen was approximately 25% as efficient as butene in stabilizing the hot molecules. Precise figures were difficult to obtain owing to the twofold effect of the inert gas (*i.e.*, in also removing translational energy from the methylene) and this may be an *over*-estimate of its efficiency. That nitrogen (and argon) should be less efficient than butene in stabilizing excited dimethylcyclopropane is of course to be expected theoretically and from experimental work on unimolecular reactions. In the most closely similar system for which experimental data are available, the unimolecular isomerization of methylcyclopropane, nitrogen was found to have 20% of the efficiency of butenes in the activation–deactivation process.[12] Only in one experiment (see line 3 of table in ref. 6) does the ratio differ considerably from that expected from simple isomerization. Here, however, it seems certain that as well as the *trans*-1,2-dimethylcyclopropane formed by isomerization of the hot molecules and the *trans* compound from triplet methylene, a product from the complicated photolysis of pure diazomethane must have to some extent interfered with the analysis, since in this experiment a very large excess of diazomethane has been used.

[11] H. M. Frey, *Proc. Roy. Soc.*, **A250**, 409 (1959).

[12] J. P. Chesick, THIS JOURNAL, **82**, 3277 (1960).

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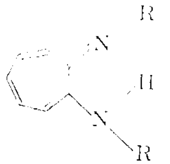
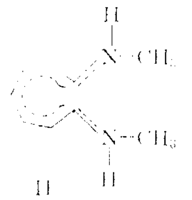
## N,N-DISUBSTITUTED-1-AMINO-7-IMINO-1,3,5-CYCLOHEPTATRIENES, A NON-CLASSICAL AROMATIC SYSTEM

*Sir:*

A general synthesis of the 1-amino-7-imino-1,3,5-cycloheptatrienes (I) together with an indication of their aromatic character was reported recently.[1]



I



II

Although these compounds are related chemically and structurally to tropolone, evidence now has been obtained that the reasons for aromaticity in these two systems are fundamentally different.

Infrared spectral studies of I (R = $CH_3$) and of its N–D derivative have shown that the hydrogen is intramolecularly bonded, even in the solid state.[2] The absorption at 3.10 $\mu$ (NH) is shifted slightly to 3.08 $\mu$ in carbon tetrachloride solutions of varying concentrations. In addition, n.m.r. studies of I (R = $CH_3$) and its N–D derivative show only a single methyl resonance, even at −80°. These results establish the equivalency of the nitrogen atoms, and suggest either a symmetrical hydrogen-bonded structure or an extremely fast intramolecular hydrogen (or deuterium) exchange. In addition, the fine structure attributable to the ring protons in I (R = $CH_3$) is essentially unchanged in the cation II (although shifted downfield approximately 1.2 p.p.m. because of deshielding) and in the nickel chelate at −70°.[3] These results indicate appreciable electron delocalization in I (R = $CH_3$).

Dipole moment studies of I (R = $CH_3$) and its 4-bromo derivative have led to the surprising conclusion that although the seven-membered ring in both tropolone and azulene is electropositive in the ground state, it is electronegative in the aminoimine. The dipole moments, determined in benzene, are: tropolone, 3.71[4]; 5-bromotropolone, 2.07[5]; azulene, 1.0[6]; I (R = $CH_3$), 1.24; 4-bromo I (R = $CH_3$), 2.52. The assumption that the dipole is directed into the ring of the aminoimine, together with the reported[7] group moment of 1.55 *D* for bromine, leads to a calculated value of 2.79 *D*[8] for the 4-bromo derivative, in good agreement with the observed moment. On the other hand, if the dipole is assumed to be directed away from the ring as is the case in tropolone, the observed moment should be about 0.3 *D*.

Verification for the relative electronegative character of the ring compared with that of tropolone was found in n.m.r. studies. The tropolone resonance occurs at lower fields (center at 2.4 $\tau$) compared with that of I (R = $CH_3$) (3.45–4.05 $\tau$), indicating less shielding, and hence more positive character for tropolone.

Clearly, the aromaticity observed in the aminoimines cannot be attributed to contributions from

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[1] W. R. Brasen, H. E. Holmquist and R. E. Benson, THIS JOURNAL, **82**, 995 (1960).

[2] Tropolone is extensively intermolecularly hydrogen bonded in the solid state. In solution the hydrogen bonding becomes intramolecular, however. See K. Kuratani, M. Tsuboi and T. Shimanouchi, *Bull. Chem. Soc. Japan*, **25**, 250 (1952).

[3] W. D. Phillips and R. E. Benson, *J. Chem. Phys.*, **33**, 607 (1960). At temperatures above −70° chemical shifts are observed that have been attributed to a ground singlet and a thermally accessible triplet state.

[4] Y. Kurita, T. Nozoe and M. Kubo, *Bull. Chem. Soc. Japan*, **24**, 10 (1951).

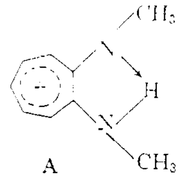
[5] Y. Kurita, T. Nozoe and M. Kubo, *ibid.*, **26**, 242 (1953). The 5-position of tropolone is equivalent to the 4-position of the aminoimine.

[6] G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).

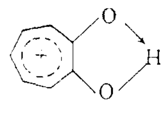
[7] W. Hückel, "Theoretical Principles of Organic Chemistry," Vol. II, Translated by F. H. Rathnann, Elsevier Publishing Co., N. Y., 1958, p. 127.

[8] Molecular orbital calculations (LCAO-MO method with conventional assumptions) by Dr. H. E. Simmons have given a moment of 0.3 *D* directed into the ring.

a form such as A, as has been done in the case of tropolone (B). In view of the predicted[9] and later demonstrated[10,11] resonance stabilization associated

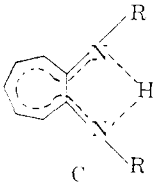


A

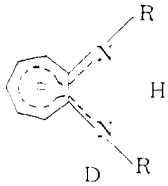


B

with a conjugated 10-$\pi$ electron system in a carbocyclic system, it is attractive to assume that a 10-$\pi$ electron system around the periphery of the molecule is achieved in these compounds through hybridization of the $\pi$-electrons of the four formal double bonds with the pair of non-bonding electrons on nitrogen of the NHR substituent. Thus, the aminoimines are most nearly represented by C with possible contribution from D.



C



D

In confirmation of their more electronegative character, the aminoimines are more susceptible than tropolone to attack by electrophilic reagents.

**Acknowledgments**.—The author expresses his thanks to Drs. W. R. Brasen, H. E. Holmquist, and W. D. Phillips for helpful discussions.

[9] E. Hückel, *Z. Elektrochem.*, **43**, 752 (1937).

[10] R. J. Windgassen, Jr., W. H. Saunders, Jr., and V. Boekelheide, This Journal, **81**, 1459 (1959).

[11] T. J. Katz, *ibid.*, **82**, 3784 (1960).

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## GENERAL ACID CATALYSIS OF THE HYDROLYSIS OF SODIUM BOROHYDRIDE[1,2]

*Sir:*

Alkali borohydrides, widely used as reducing agents,[3] are stable in basic aqueous solution but liberate hydrogen as the *p*H is lowered. The rate of

$$BH_4^- + H_3O^+ + 2H_2O = H_3BO_3 + 4H_2$$

hydrolysis is known from the work of Jensen,[3,4] Kilpatrick,[5] Pecsok[8] and J. B. Brown[9,10] to involve acid catalysis. The rate expression in dilute buffer solution is first order in hydronium ion over the *p*H range of 7.7 to 10.1, but at very high *p*H (12 to 14) the rate is less sensitive to hydronium ion concentration. The apparent order[4,9,10] decreases to about 0.4. Furthermore, the rate has been reported to depend upon the ionic strength and upon the anion component of the buffer solution. Freund[11] concluded that the rate-determining step for reduction of ferricyanide ion is the same as that for hydrolysis.

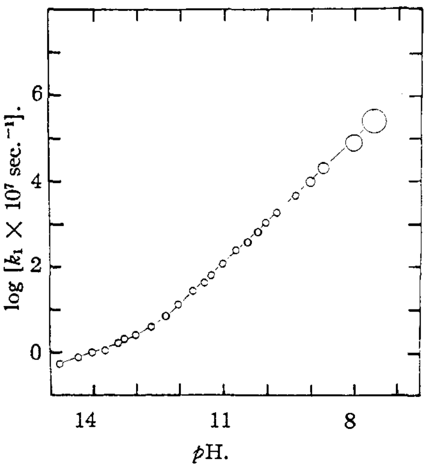

Fig. 1.—Hydrolysis of sodium borohydride in aqueous solution at 25.00°; plot of log $k_1 \times 10^7$ sec.$^{-1}$ *vs.* *p*H, where $-d[BH_4^-]/dt = k_1[BH_4^-]$.

We consequently have searched for and found general acid catalysis. The studies of the hydrolysis as a function of *p*H were repeated and agree with the earlier work as shown in Fig. 1. In the present investigation the rate of hydrolysis of sodium borohydride was measured from *p*H 7.6 to 14.8 at 25° under nitrogen. The borohydride concentration was measured volumetrically by the iodate method.[12] The buffers of Fig. 1 had 0.10 *M* ionic strength from *p*H 7.6 to 12.4 but higher above *p*H 12.4 from the high concentration of NaOH. The *p*H range was covered by these buffers: $KH_2PO_4$–NaOH (7.6–8.1); $H_3BO_3$–NaOH (7.8–10.0); $NaBO_2$–HCl (9.0–10.0); $NaBO_2$–$Na_2CO_3$ (9.2–11.0); $NaBO_2$–NaOH (9.2–12.4), $NaHPO_4$–NaOH (11–12), and NaOH (>12). We attribute the change in slope above *p*H to *general acid catalysis*.[13] Thus the rate expression is

$$\frac{-d(BH_4^-)}{dt} = (BH_4^-)\sum^{i} \Sigma\, k_i(HA_i)$$

where $HA_i$ is a general acid. The value of $K_{H_3O^+}$

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[1] Supported in part by a postdoctoral fellowship to R. E. D. from the National Science Foundation, M.I.T., 1958–1959, and research grants from the National Science Foundation at M.I.T. and the Research Corporation at Purdue.

[2] *Cf.* R. E. Davis, C. L. Kibby and C. G. Swain, This Journal, **82**, 5950 (1960).

[3] "Sodium Borohydride and Potassium Borohydride, a Manual of Techniques," Metal Hydrides, Inc., Beverly, Mass., 1958.

[4] E. H. Jensen, "A Study on Sodium Borohydride with Special Reference to its Analytical Application in Organic Chemistry," Nyt Fordisk Forlag, Arnold Busch, Copenhagen, 1954.

[5] M. Kilpatrick and C. D. McKinney, Jr., This Journal, **72**, 5474 (1950). The rate measured seems to be the rate of evolution of hydrogen from a supersaturated solution and *not* the rate of decomposition of borohydride, since their rate constant is lower than Pecsok's by a factor of $3 \times 10^5$. The Setchenow equation[5,6,7] can be expanded into a power series to explain the apparent first-order dependence of rate of evolution on hydronium ion concentration over a small range of concentration.

[6] M. Setchenow, *Ann. chim. et phys.*, [6] **25**, 226 (1892).

[7] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed., Reinhold Publishing Corp., New York, N. Y., 1958, pp. 531.

[8] R. L. Pecsok, This Journal, **75**, 2862 (1953).

[9] J. B. Brown and M. Svensson, *ibid.*, **79**, 4241, 6581 (1957).

[10] J. B. Brown and M. Svensson, *J. Sci. Labs. Denison Univ.*, **44**, 117 (1958).

[11] T. Freund, *J. Inorg. and Nuclear Chem.*, **9**, 246 (1959).

[12] D. A. Lyttle, E. H. Jensen and W. A. Struck, *Anal. Chem.*, **24**, 1843 (1952).

[13] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 191–223.