conditions. The first, **a**, proceeds in the 1,4-manner and requires conjugation of the exocyclic double bond with the aromatic nucleus, leading ultimately to the formation of II.[4] The formation of III, following the alternative route, **b**, involves electronic interactions between the exo-cyclic double bond and cyclopropane and presumably occurs in the 1.5-manner.

(4) Compare K. Alder, R. Schmitz-Josten, H. Broockmann, K. Huhn and H. Gabler, *Ann.*, **595**, 1 (1955); F. Bergmann and J. Szmuszkowicz, THIS JOURNAL, **69**, 1773, 1777, 1779 (1947); **70**, 2748 (1948).

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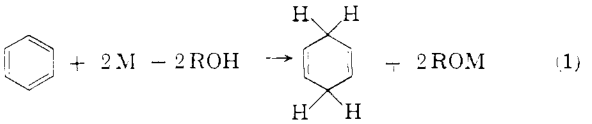
KINETICS OF THE METAL-AMMONIA-ALCOHOL REDUCTION OF BENZENE[1]

Sir:

Recently Krapcho and Bothner-By reported that the rate of "metal–ammonia–alcohol reduction of benzene and some substituted benzenes .... is governed by the law d(ArH)/dt = k(ArH)(M)(ROH)."[2] To establish this law they mixed, in liquid ammonia, benzene, alkali metal and alcohol in the stoichiometric proportions of equation 1, measured the benzene concentrations c at times



(1)

t, *assumed that the three reactant concentrations remained proportional during reduction* (*i.e.*, were c, $2c$ and $2c$, respectively), and reported that their "data provided satisfactory linear third-order plots" (*i.e.*, found plots of c^{-2} *vs.* t to be linear).

From our study of the kinetics of hydrogen evolution by the metal–alcohol reaction,[3] it appeared that this well-known irreversible reaction (equation 2) could compete with benzene reduction. Therefore, we inferred that with respect to reaction (1),

$$2ROH + 2M \longrightarrow 2ROM + H_2 \qquad (2)$$

reactant concentrations probably did not remain proportional during reduction.

To verify this inference, reactant solutions similar to those employed by Krapcho and Bothner-By were prepared under conditions which provided for the collection and measurement of evolved hydrogen. In Table I[4] the extent of reaction (1) for various metals is compared with the extent of hydrogen evolution (2) found for specified reaction times. With sodium and potassium, benzene reduction is not even the predominant reaction during that portion of the reaction studied. With lithium, although benzene reduction predominates, the extent of hydrogen evolution precludes $2c$ being the concentration of either metal or alcohol as reaction (1) proceeds.

TABLE I

Metal employed	Initial benzene molarity (c_0)[a]	Reaction time in Sec.	Percentage reaction Calcd. for (1)[b]	Percentage reaction Found for (2)[c]	Per cent. (2) of (1) + (2)
Li	0.069	15	25	3	11
Li	0.069	100	60	12	17
Na	0.094	100	2	9	82
Na	0.094	700	13	17	57
K	0.078	700	3	54	95
K	0.078	6000	17	74	81

[a] Initial metal and alcohol concentrations were each $2c_0$. [b] Per cent. benzene consumed calculated on the basis of rate constants at −34° given in Table IV, ref. 2. [c] Per cent. alcohol and metal consumed, calculated on the basis of hydrogen evolved.

In order to correlate our findings (Table I) with those of Krapcho and Bothner-By, we have examined their data carefully.[5] We conclude that these data do not provide satisfactory linear third-order plots.

We wish to emphasize that we have reached no conclusions as to the kinetic order of reaction (1). We do conclude, however, that any kinetic analysis of reaction (1) that fails to take into account reaction (2) is unwarrantable.

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(1) A portion of this study was supported by the National Science Foundation.

(2) A. P. Krapcho and A. A. Bothner-By, THIS JOURNAL, **81**, 3658 (1959).

(3) E. J. Kelly, C. W. Keenan, H. V. Secor and J. F. Eastham, Abstr. 136th Meeting, Am. Chem. Soc., Atlantic City, New Jersey, 1959, p. 17-N.

(4) For precise measurements we used the sealed system described by E. J. Kelly, Ph.D. Thesis, The University of Tennessee, 1959, p. 29. Similar results were obtained in equipment like that described in ref. 2, but modified to provide for the semi-quantitative collection of hydrogen.

(5) A. P. Krapcho, Ph.D. Thesis, Harvard University, 1957.

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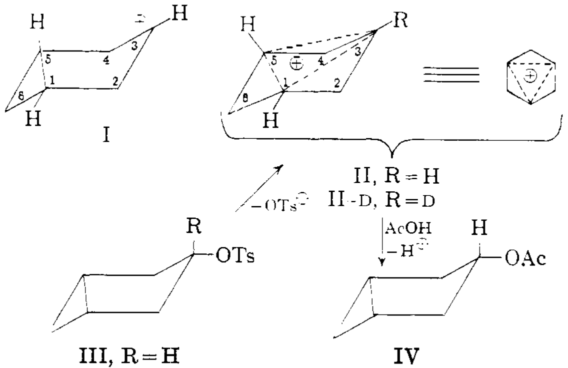
THE TRIS-HOMOCYCLOPROPENYL CATION[1]

Sir:

Examination of models of the 3-bicyclo[3.1.0]hexyl cation I suggests that little reorganization and rehybridization are required to make carbon atoms 1, 3 and 5 equivalent. On this basis it becomes conceivable that the cation I would possess the symmetrical non-classical structure II. We now report the results of experiments with the *cis*- and *trans*-3-bicyclo[3.1.0]hexyl toluenesulfonates which bear out this expectation.



I

II, R = H
II-D, R = D

III, R = H
V-D, R = D

IV

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(1) This research was supported by a grant from The Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.