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).

[5] Formerly Shalom Israelashvili.

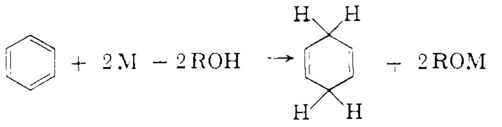
DEPARTMENT OF PHARMACEUTICAL CHEMISTRY
THE HEBREW UNIVERSITY SCHOOL OF PHARMACY
JERUSALEM, ISRAEL
SHALOM SAREL[5]
ELI BREUER

RECEIVED AUGUST 31, 1959

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]	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.

---

[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.

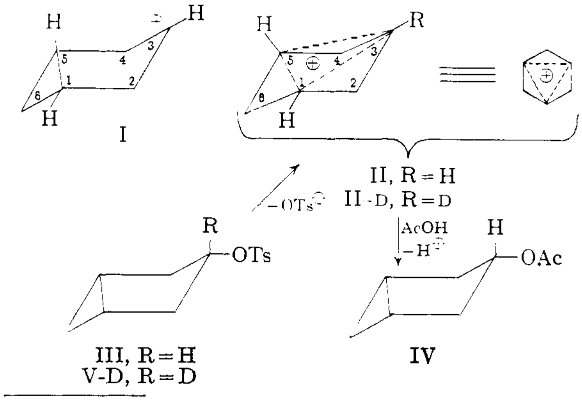
DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF TENNESSEE
KNOXVILLE, TENNESSEE
JEROME F. EASTHAM
C. W. KEENAN
HENRY V. SECOR

RECEIVED SEPTEMBER 25, 1959

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

---

[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.

The 3-bicyclo[3.1.0]hexanol[2] with presumably the *cis*-configuration, b.p. 71.0–71.5° (22 mm.), n^{25}D 1.4770, is derived most easily from the action of methylene iodide and zinc-copper couple[3] on Δ^3-cyclopentenol,[4] the yield from this highly stereospecific reaction being 75%. Oxidation of the alcohol or Dieckmann condensation from cyclopropane *cis*-1,2-diacetic acid[5] yields 3-bicyclo[3.1.0]-hexanone, b.p. 54–55° (25 mm.), n^{25}D 1.4590, 2,4-dinitrophenylhydrazone, m.p. 149–150°. Reduction of the bicyclohexanone with lithium aluminum hydride leads to an 89:11 mixture, while aluminum isopropylate gives a 40:60 mixture of the *cis*- and *trans*-alcohols, respectively. Acetolysis of 0.08 *M* *cis*-toluenesulfonate III, m.p. 51.6–51.8°, in the presence of 0.10 *M* sodium acetate at 50° leads exclusively to *cis*-acetate IV with no accompanying olefin. The *trans*-toluenesulfonate, m.p. 70.5–71.5°, gives rise to the same *cis*-acetate with considerable accompanying olefin (*ca.* 33%).

In acetolysis the *cis*-toluenesulfonate III is substantially more reactive than the *trans*-epimer. With the *cis*-toluenesulfonate III the addition of lithium perchlorate in the acetolysis at 50° gives rise to a special salt effect,[6] the magnitude being measured by a ($k^0_{\text{ext}}/k^0_{\text{t}}$) value of 3.2. A special salt effect does not occur in acetolysis of analogous toluenesulfonates, such as Δ^3-cyclopentenyl, cyclopentyl and cyclohexyl.

The factor of *ca.* 35 between the rates of acetolysis of the *cis*- and *trans*-toluenesulfonates suggests that ionization of the *cis*-toluenesulfonate III is somewhat anchimerically accelerated. The occurrence of the special salt effect in acetolysis of the *cis*-toluenesulfonate is diagnostic[6b] for the occurrence of an ion pair with a special structure for the cation, which evidently reacts stereospecifically with solvent.

That the cation from toluenesulfonate III does indeed have the non-classical structure II is suggested by the behavior of 3-deuterated bicyclohexyl toluenesulfonate V-D, m.p. 51.5–52.0°, prepared from deuterated alcohol from lithium aluminum deuteride reduction of the bicyclohexanone. The infrared spectrum of the alcohol from acetolysis of V-D shows that the product alcohol now has deuterium on the cyclopropane ring, the corresponding C-D stretching vibration occurring at 2266 cm.$^{-1}$. Analogously, the intensity of the C-D stretching absorption at 2155 cm.$^{-1}$, the major absorption band for the deuterium on the carbinol carbon atom, is much decreased, the absorption in the product alcohol being 33 ± 1% as large as that in the parent deuterated alcohol. Although the analysis is less accurate, proton magnetic resonance spectra are consistent with the 2:1 ratio of cyclopropane ring deuterium to carbinol carbon deuterium in the product. It is quite clear that the deuterium scrambling during acetolysis of the labelled toluenesulfonate V-D corresponds exactly to expectations based on the non-classical cation II.

Because of an analogy with the cyclopropenyl cation, II may be named the "tris-homocyclopropenyl" cation.

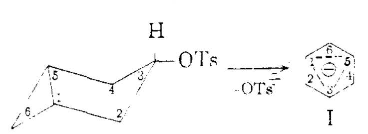
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
LOS ANGELES 24, CALIFORNIA
S. WINSTEIN
JOSEPH SONNENBERG
LOUIS DEVRIES

RECEIVED NOVEMBER 16, 1959

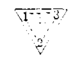
HOMO-AROMATIC STRUCTURES

Sir:

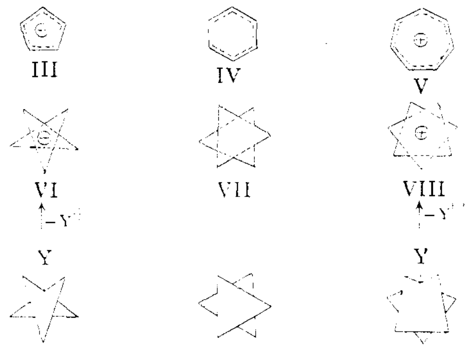
There is evidence[1] that the 3-bicyclo[3.1.0]hexyl cation has the nonclassical structure I. Except that orbital overlap is not π and the 1,3 overlap and exchange integrals are smaller in magnitude in cation I than the 1,2 integrals in the cyclopropenyl cation II, the situation in the non-classical cation I is wave-mechanically[2] quite analogous to that in the cyclopropenyl cation II. For this reason the term "tris-homocyclopropenyl" is suggested[1] for cation I.



I


II

Cation I is the non-classical tris-homo counterpart of the cyclopropenyl cation II, one of the species which fits Hückel's $(4n + 2)\pi$-electron rule for conjugated monocyclic systems.[2] Conceptually, the homo relationship of non-classical ion I to the cyclopropenyl cation II may be generalized to include homo counterparts of other examples of the $(4n + 2)$ rule, such as cyclopentadienide ion III, benzene IV, and tropylium ion V. They are pentahomocyclopentadienide ion VI, $C_{10}H_{15}^{\ominus}$, hexahomobenzene VII, $C_{12}H_{18}$, and heptahomotropylium ion VIII, $C_{14}H_{21}^{\oplus}$. Species VI could be visualized to arise from a material such as IX, structure X would represent one of the "Kekule" structures for hexahomobenzene, and the heptahomotropylium ion VIII could be formulated as the product of ionization of a material with structure XI.



III IV V
VI VII VIII
IX X XI

---

[2] Satisfactory carbon and hydrogen analyses were obtained for all the new compounds here mentioned.

[3] H. E. Simmons and R. D. Smith, THIS JOURNAL, **81**, 4256 (1959).

[4] S. Winstein, E. L. Allred and J. Sonnenberg, *ibid.*, **81**, 5833 (1959).

[5] K. Hofmann, *et al.*, *ibid.*, **81**, 992 (1959).

[6] (a) S. Winstein, *et al.*, THIS JOURNAL, **76**, 2597 (1954); *Chemistry and Industry*, 664 (1954); (b) S. Winstein, *Experientia Supplementum*, II, 137 (1955).

[1] S. Winstein, J. Sonnenberg and L. deVries, THIS JOURNAL, **81**, 6523 (1959).

[2] (a) E. Hückel, *Z. Physik*, **70**, 204 (1931); (b) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, THIS JOURNAL, **74**, 4579 (1952).