hydrazone, m.p. 226–229°, λ_{max} 390 mμ (ϵ 20,000)). Dihydrogenation of IV yielded a saturated alcohol, V (m.p. 89.6–90.2°, $[\alpha]^{25}D - 3.6°$), which was converted into a crystalline tosylate (m.p. 89.0–90.5°, $[\alpha]^{25}D + 3.6°$). The tosylate upon reaction with activity III alumina yielded olefin VI (m.p. 90.6–91.8°, $[\alpha]^{25}D + 88.2°$) which possessed an exocyclic methylene group (ν_{max} 880 cm.$^{-1}$). Ozonolysis of VI gave rise to formaldehyde and the known A-norcoprostane-3-one[8] (m.p. 75.8–76.8°, $[\alpha]^{25}D + 126°$; semicarbazone, m.p. 265–268°). The tosylate upon reaction with activity I alumina yielded the known olefin, 3-methyl-$\Delta^{3(5)}$-A-norcholestene, VIII[9] (m.p. 63–64°, $[\alpha]^{25}D + 59.6°$; identical with authentic sample). These data establish the structure of IV and show that no asymmetric centers present in the original diene have been affected in the irradiation reaction.

When the structure of IV is coupled with the fact that II can be transformed to a conjugated cyclopropane-ene possessing two vinyl hydrogens, only the 6-ethoxy-3,5-*cyclo*steroid structure II is possible. Since either the 6α- or 6β-oxy derivatives of 3α,5α-*cyclo*cholestane are known to yield cholesterol under the conditions in which II yielded IV,[10] the difference must lie in the stereochemistry of the cyclopropane ring, and II must possess the 3β,5β-*cyclo* structure shown in X. The mechanistic implications of the diaxial elimination leading from II to IV will be discussed in the completed manuscript.

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(8) A. Windaus, *Ber.*, **52**, 170 (1919); B. B. Smith and H. R. Nace, THIS JOURNAL, **76**, 6119 (1952).

(9) H. Schmid and K. Kägi, *Helv. Chim. Acta*, **33**, 1582 (1950).

(10) S. Winstein and E. M. Kosower, THIS JOURNAL, **81**, 4399 (1959).

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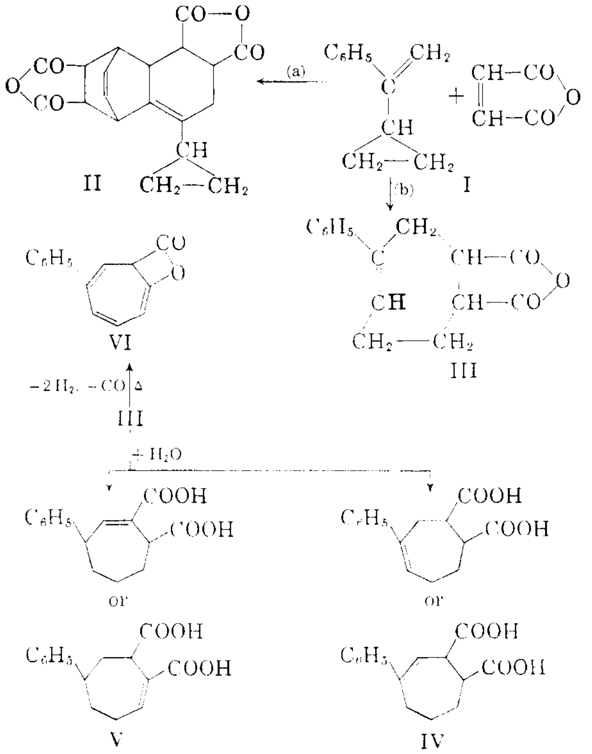
RECEIVED OCTOBER 22, 1959

A NOVEL CONJUGATIVE 1,5-ADDITION REACTION INVOLVING THE VINYLCYCLOPROPANE SYSTEM

Sir:

Although there is considerable evidence that cyclopropane can enter into conjugation similarly to a double-bond,[1] no evidence exists of a successful cyclic addition reaction involving either a vinylcyclopropane[2] or a dicyclopropyl[3] system, analogous to the Diels–Alder reaction. This communication presents evidence that vinylcyclopropane is an active conjugated system when properly activated, for example, by a phenyl substituent.

A mixture of equimolar quantities of α-cyclopropylstyrene (I) λ^{EtOH}_{max} 242 mμ (ϵ 9700) and maleic anhydride in dry benzene was refluxed for 48 hours. After removal of solvent and starting materials the residue was extracted with methanol leaving behind an insoluble white bis-adduct (II) (12% yield), m.p. 255–257°, showing no bands for phenyl in the infrared (*Anal.* Found for $C_{19}H_{16}O_6$: C, 67.18; H, 4.78). The residue from the methanolic extract was distilled at reduced pressure giving 4-phenylcyclohept-4-ene-1,2-dicarboxylic anhydride (III) (40% yield) as light-yellow oil (b.p. 170–180° (2 mm.), λ_{max} 240 mμ, ϵ 8500, λ^{liquid}_{max} 5.60μ, 5.80μ; *anal.* found for $C_{15}H_{14}O_3$: ϵ, 73.8; H, 6.1; mol. wt., 228 (benzene); sapn. equiv., 115). In platinum-catalyzed hydrogenation III absorbed one mole of hydrogen, providing an oily dihydro derivative having no maximum at 240 mμ. Oxidation of III by means of CrO_3–H_2SO_4 provided benzoic acid. Hydrolysis of III and chromatography over Florisil provided two isomeric diacids: (1) (IV) m.p. 103–105°, λ^{EtOH}_{max} 211 mμ (ϵ 11800), 243 mμ (ϵ 11400); λ^{KBr}_{max} 5.82μ, (*anal.* found for $C_{15}H_{16}O_4 \cdot H_2O$: C, 64.5; H, 6.2), and (2) (V) m.p. 190–192°, λ^{EtOH}_{max} 233–236 mμ (ϵ 8000), λ^{KBr}_{max} 5.82μ, 5.88μ (*anal.* found for $C_{15}H_{16}O_4$: C, 69.29; H, 6.15). Compounds IV and V show no bands for C-methyl in the infrared. The distillation of III was accompanied with white crystals of a new β-lactone (VI) (8% yield) (m.p. 161–162°, λ^{EtOH}_{max} 230 mμ (ϵ 6300), 277 mμ (ϵ 6600), λ^{KBr}_{max} 5.5μ; *anal.* found for $C_{14}H_{10}O_2$: C, 80,2; H, 5.1; mol. wt., 202 (ethylene dibromide)). The thermal oxidative-decarbonylation reaction of III and the physical and chemical properties of VI will be discussed in the full paper.



We observed that I does not isomerize on being heated in benzene for 48 hours with 10% mole of maleic anhydride. The palladium-catalyzed addition of one mole of hydrogen to I provided 2-phenylpent-2-ene (VII) (λ^{EtOH}_{max} 244 mμ, $E^{1\%}_{1\,cm}$ 44.5) in quantitative yield. The osmium tetroxide-catalyzed periodate oxidation of VII afforded acetophenone as the only identifiable ketone.

The data clearly indicate that I adds maleic anhydride by two different routes under the same

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(1) For more fully documented accounts of certain aspects of the problem see E. N. Trachtenberg and G. Odian, THIS JOURNAL, **80**, 4018 (1958).

(2) R. van Volkenburgh, K. W. Greenlee, J. M. Derfer and C. E. Boord, *ibid.*, **71**, 172, 3595 (1949).

(3) L. I. Smith and E. R. Rogier, *ibid.*, **73**, 3840 (1951).

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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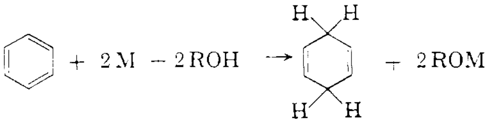
RECEIVED AUGUST 31, 1959

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.

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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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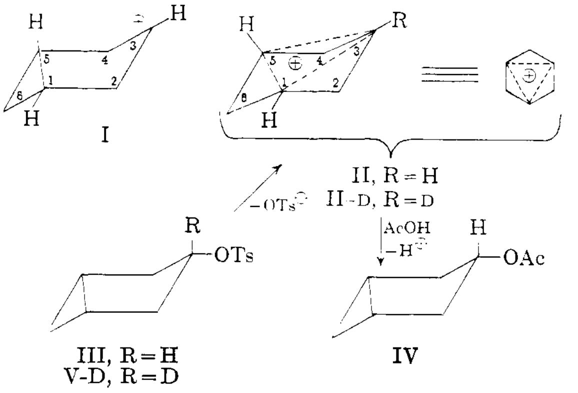
RECEIVED SEPTEMBER 25, 1959

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.



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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.