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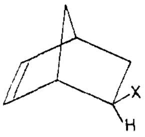
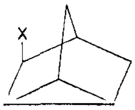
DRIVING FORCE OF THE HOMOALLYLIC REARRANGEMENT IN ACETOLYSIS OF *exo*-DEHYDRONORBORNYL *p*-BROMOBENZENESULFONATE[1]

Sir:

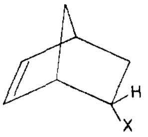
Roberts, Bennett and Armstrong[2] have very recently reported the relative solvolysis rates of *exo*-dehydronorbonyl (I), nortricyclyl (II), and *endo*-dehydronorbornyl (III) halides (X = Cl or Br) in 80% ethanol as *ca.* 5:1:1. Solvolysis of I and III gives mainly the homoallylic rearrangement product with the structure II; I is not much more reactive than III, and I and III are slower, if anything, than the saturated analogs IV and V. These workers conclude that the double bonds in I and III exert no very substantial driving force of the type postulated for cholesteryl compounds,[3] presumably because the geometry is less favorable for participation of the olefinic linkage in the ionization process. On the other hand, on the prediction that conditions in I were very favorable for substantial participation of the olefinic linkage in the ionization process, we had been studying the acetolysis of the corresponding *p*-bromobenzenesulfonates, I, m.p. 78.4–79.8° (still heavily contaminated with isomeric material; prepared from alcohol derived by stereoisomerization of *endo*-dehydronorborneol), II, m.p. 80.2–81.8° (pure material prepared from hydrolysis product from III), and III, m.p. 87.4–89.0° (pure material prepared from *endo* alcohol), all three of which yield acetate in *ca.* 80% yield, largely with the structure II from infrared and hydrogenation data.



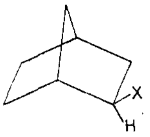
I



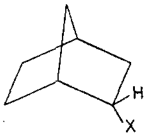
II



III



IV



V

The first order rates of acetolysis obtained give the sequence I:II:III of 7000:2000:1 at 25°. This indicates a very substantial driving force in isomer I which has the proper configuration for delocalization of the neighboring electron cloud in the rate-determining ionization, whereas in III this must occur essentially subsequent to ionization. Also, it indicates considerable reactivity of the structure II.

V and cholestanyl benzenesulfonates (with no neighboring group participation in the rate-determining ionization) have rates nearly identical with cyclohexyl.[4] III has a rate reduced somewhat (by *ca.* one power of ten) by the polar effect due to an unsaturated group (e.g., K_A for phenylacetic or vinylacetic acid). These facts make it clear that in acetolysis of *p*-bromobenzenesulfonates the driving force in I (I:III = 7000:1) is at least as large and probably somewhat larger than in cholesteryl. Also, as would be expected, it is larger than in IV, the latter being measured by the factor[4a] of 360 for IV:V.

The essential difference between our results on sulfonates and those of Roberts and co-workers[2] on halides lies in the high reactivities they report for III and V.

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[1] Research supported by the Office of Naval Research.

[2] Roberts, Bennett and Armstrong, THIS JOURNAL, **72**, 3329 (1950).

[3] Winstein and Adams, *ibid.*, **70**, 838 (1948).

[4] (a) Winstein and Trifan, *ibid.*, **71**, 2953 (1949); (b) A. H. Schlesinger, unpublished work.

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THE EXCHANGE REACTION BETWEEN HYDROGEN AND LITHIUM HYDRIDE. THE PREPARATION OF LITHIUM HYDRIDE-*t* AND LITHIUM ALUMINUM HYDRIDE-*t*

Sir:

The exchange of hydrogen between hydrogen gas and lithium hydride (solid), traced with both deuterium and tritium, occurs under unexpectedly mild conditions. At high temperatures lithium hydride exhibits a measurable degree of dissociation[1] and should therefore exhibit exchange through a mechanism of dissociation and recombination. However, the following observations indicate that exchange involves a surface reaction and a slower diffusion process occurring at rates such that exchange can be observed at room temperature and is substantially complete at 200° within twenty-four hours.

Rate measurements were made on a sample of lithium hydride-*t* which had been prepared by heating 200-mesh lithium hydride (Maywood Chemical Co.) with hydrogen gas containing tritium in a Pyrex flask at 350°. The hydride was then brought into contact with inactive hydrogen gas and the uptake of tritium in the gas phase was followed by means of ion-current measurements[2] on samples of the gas. Between runs the hydride was heated with hydrogen gas for sixteen hours at 230° to ensure uniform distribution of tritium throughout the solid phase. The measurements extend over the range from 25 to 200° and are shown in the accompanying figure as a plot of log (1 − F) with time, where F is the ratio of specific

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[1] Hurd and Moore, THIS JOURNAL, **57**, 332 (1935).

[2] Wilzbach and Van Dyken, to be published.