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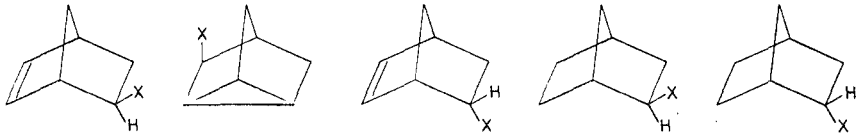
DRIVING FORCE OF THE HOMOALLYLIC REARRANGEMENT IN ACETOLYSIS OF *exo*-DEHYDRONORBORNYL *p*-BROMOBENZENESULFONATE[1]

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.

(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

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

(2) Wilzbach and Van Dyken, to be published.

activity of the gas at time, t, to that at equilibrium. The rate of the exchange reaction is proportional[3] to $a\ \mathrm{d}\log(1-F)/\mathrm{d}t$, where a represents the quantity of hydrogen gas.

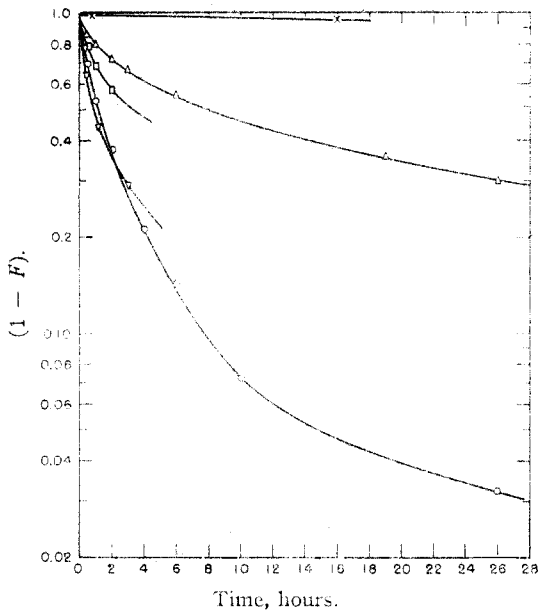

Fig. 1.—Rate of exchange of 1835 millimoles of lithium hydride with hydrogen gas in a one-liter flask; temp., mg. atoms of H_2; x, 25°, 5.5; △, 170°, 36.5; ⊡, 170°, 6.7; ▽, 170°, 2.25; ⊙, 200°, 38.2. F is the fraction of equilibrium concentration of tritium in the gas.

The non-linearity of these plots, judged by the criteria[3,4] of Zimens, indicates that the rate of exchange is controlled by a diffusion process within the solid. This conclusion is substantiated by our observation that the rate of formation of HD in a mixture of H_2 and D_2 in contact with lithium hydride at 40° is tenfold faster than the rate of exchange with the solid. The increase in exchange rate with hydrogen pressure at constant temperature rules out diffusion of hydride ions as the rate-controlling process but would be consistent with a mechanism involving diffusion of hydrogen molecules, possibly as H_3^- ions.

Equilibration experiments at 200°C. gave a value 3.7 for the equilibrium constant, $K = (HT)(LiH)/(H_2)(LiT)$, in agreement with a value 3.66 calculated from the published partition functions[5] for the various isotopic species.

The availability of lithium hydride-t has made possible the preparation[6] of lithium aluminum hydride-t, from which a wide variety of tritium labeled organic compounds can be prepared in high yields.[7] As an example, ethanol-1-t has been obtained in a radiochemical yield of 80% by reduction of ethyl acetate.

An attempt to prepare lithium aluminum hydride-t by the direct exchange of commercial lithium aluminum hydride with a hydrogen-tritium mixture at 100° was unsuccessful.

Acknowledgments.—We are indebted to Dr. B. Weinstock for the mass-spectrometric deuterium analyses, and to Prof. W. G. Brown for many helpful suggestions.

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(3) Norris, *J. Phys. Colloid. Chem.*, **54**, 777 (1950).
(4) Zimens, *Arkiv. Kemi, Mineral., Geol.*, **A20**, No. 18 (1945).
(5) Urey, *J. Chem. Soc.*, 562 (1947).
(6) Finholt, Bond and Schlesinger, THIS JOURNAL, **69**, 1199 (1947).
(7) W. G. Brown in R. Adams, "Organic Reactions," Vol. VI, in press.

THE STRUCTURE OF HEPARIN[1]

Sir:

Benzidine-purified heparin fractionated from water as its neutral barium salt yields in its lesser-soluble fraction a product which, as the sodium salt, is homogeneous by electrophoresis (mol. wt. by diffusion *ca.* 20,000) and by the Craig countercurrent technic; anticoagulant potency *ca.* 700 Roche ACU/mg. Its crystalline barium acid salt shows essentially the analysis previously reported[2] with the N:S = 2:5 (per tetrasaccharide unit) established. Periodate titer shows the presence of 1.0 α-glycol group per tetrasaccharide unit. Desulfated, acetylated heparin[3] (somewhat degraded), characterized as the amorphous sodium acid salt of $[\alpha]^{24}D$ +16.5° ($CHCl_3$), gives with barium methoxide *N*-acetyl desulfated heparin whose amorphous barium salt, $[\alpha]^{25}D$ +76° (water), consumed 1.0 mole of periodate per disaccharide unit (extrapolated, 3 to 6°, initial *p*H 4.5) without formation of formaldehyde or formic acid and with destruction of the hexuronic acid portion only. Partial acid hydrolysis (*c* 2, 0.5 *N* sulfuric acid, eighteen hours reflux) gave an amorphous reducing disaccharide, $[\alpha]^{22}D$ +79° (water), isolated through its amorphous cupric salt. This, designated heparosinsulfuric acid, contained one sulfate ester group, hexosamine and hexuronic acid with C-1 of the latter free (yellow precipitate with barytes[4]). Periodate assay performed under conditions minimizing formate ester hydrolysis[5] (initial pH 6.8) showed oxidant consumption of 3.0 moles (per mole) with the formation of 1.0 mole of formic acid and no formaldehyde and with the destruction of both the hexosamine and hexuronic acid portions (negative color tests). Amorphous *N*-acetylheparosinsulfuric acid was prepared with silver acetate and acetic anhydride in methanol; periodate assay (moles per mole);

(1) Supported by fellowship funds granted by The Ohio State University Research Foundation to the University for aid in fundamental research.
(2) M. L. Wolfrom, D. I. Weisblat, J. V. Karabinos, W. H. McNeely and J. McLean, THIS JOURNAL, **65**, 2077 (1943).
(3) M. L. Wolfrom and R. Montgomery, *ibid.*, **72**, 2861 (1950).
(4) P. A. Levene and C. C. Christman, *J. Biol. Chem.*, **122**, 204 (1937).
(5) K. Meyer and P. Rathgeb, *Helv. Chim. Acta*, **32**, 1102 (1949).