benzenesulfonic acid, represented by the short line numbered 5. The rate for coarser resins drops off slightly faster than for the finer size. Curves 1 and 2, like curves 1 and 2 of Fig. 1, show a maximum reaction rate for equal weights of resins. As far as the reaction rates of the initial methyl galactoside formation and the conversion of β- to α-isomers are concerned, therefore, the resin-catalyzed reaction becomes more and more like the dissolved acid-catalyzed reaction as crosslinking is decreased and is almost identical for a 1% crosslinked resin.

In order to determine whether there was any fundamental difference in furanoside and pyranoside distribution in the α- and β-isomer fractions produced by dissolved benzenesulfonic acid on the one hand and the ion exchange resins on the other, the percentage furanoside, calculated according to the method previously[6] described, was plotted against percentage α-isomers for each of the chromatographic fractions. The circles in Fig. 3 represent the points obtained for benzenesulfonic acid reactions and the dots points obtained for the resin reactions. The maximum errors expected due to drying and weighing the sirups are indicated, an allowance of 0.1 g. in either direction being made. Curve 2, representing percentage furanoside in the β-isomer fractions, indicates an insignificant difference between furanoside distribution in the resin and the benzenesulfonic acid catalyzed reactions. Curve 1, however, representing % furanoside in the α-isomer fractions, indicates a tendency for the resins to produce a slightly higher % furanoside than the dissolved acid. No relationship was observed between % furanoside produced and the degree of crosslinking or subdivision of the resins. The fact that values of % furanoside greater than 100 have been obtained in some of the resin reactions can be explained on the basis of not quite complete separation of the α- and β-isomer fractions by the chromatographic column. Preliminary evidence for this has been obtained by subjecting the column effluent to anthrone analysis for total carbohydrate. Rough calculations of the effect of this incomplete separation have indicated that it will cause in all probability less than 5% error in the % of α- or β-isomers or % furanoside in the β-isomer fractions but may cause the calculated % furanoside in the α-isomer fractions to be quite high. Since this matter affects both this and the previous paper of this series, it will be considered further in a future communication. Paper chromatograms, which are capable of separating D-galactose and all four of the methyl galactosides except the two α-isomers, give no indication of the presence of a fifth substance of low optical activity which could account for the high α-furanoside values.

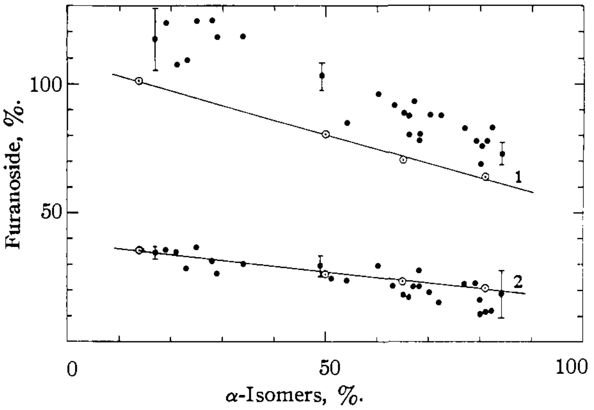

Fig. 3.—Methyl galactofuranoside distribution in α- and β-isomer fractions produced by ion exchange resins (●) and dissolved acid (⊙): 1, α-isomer fractions; 2, β-isomer fractions.

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RIPON, WISCONSIN

NOTES

Vinyl Ether–Alcohol Interchange[1]

BY ROBERT L. ADELMAN

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Vinyl ethers are known to react rapidly with compounds containing primary hydroxyl groups near 0° in the presence of strong acids as catalysts to form acetals.[2,3] We have observed that under considerably milder conditions of temperature and acidity than those mentioned above, and in the presence of mercuric sulfate as catalyst, the rate of acetal formation may be greatly reduced, and vinyl ethers and certain aliphatic compounds containing primary hydroxyl groups undergo an interchange reaction to form the vinyl ether of the hydroxy compound and the corresponding alcohol.

$$\xrightarrow{\mathrm{HgSO_4}} \quad \begin{array}{l}\mathrm{R{-}O{-}H + R'{-}O{-}CH{=}CH_2} \\ \mathrm{R{-}O{-}CH{=}CH_2 + R'{-}O{-}H}\end{array}$$

Successful interchanges were accomplished using vinyl butyl ether with ethanol (expt. I), and vinyl ethyl ether with tetrahydrofurfuryl alcohol (expts. II, III). Successful interchanges in scouting runs were indicated for vinyl ethyl ether with ethylene glycol, and vinyl ethyl ether with methyl glycolate. In the case of vinyl ethyl ether with tetrahydrofurfuryl alcohol, interchange conditions sufficiently mild were found (−78°/2 hours) that no acetal formation was observed.

Mercuric sulfate appears to be a specific catalyst for the reaction as the extent of interchange is negligible in the presence of mercuric acetate or sulfuric acid (expts. IV, V). A vinyl ether appears to be a necessary reactant as no interchange of diallyl ether with ethanol occurred. Also, it appears that vinyl ethers do not undergo interchange with other ethers, as no reaction was observed in a vinyl ethyl ether–diallyl ether–mercuric sulfate mixture.

Discussion

Hill has suggested that an equilibrium exists between vinyl ethers, alcohols and acetals in the presence of acid catalysts.[2]

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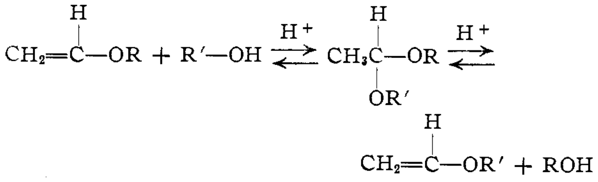
(1) From work presented at the New York City Meeting of the American Chemical Society, September, 1954. See also U. S. Patent 2 579,412.

(2) H. S. Hill, THIS JOURNAL, **50**, 2727 (1928).

(3) W. J. Croxall, F. J. Glavis and H. T. Neher, *ibid.*, **70**, 2805 (1948).



$$\mathrm{CH_2{=}\overset{H}{C}{-}OR + R'{-}OH \overset{H^+}{\rightleftharpoons} CH_3\underset{OR'}{\overset{H}{C}}{-}OR \overset{H^+}{\rightleftharpoons} CH_2{=}\overset{H}{C}{-}OR' + ROH}$$

However, Hill's mechanism appears to be inapplicable to mercuric sulfate-catalyzed interchanges of vinyl ethers with alcohols, for (1) the vinyl ether–alcohol interchange reaction occurs more readily than acetal formation from vinyl ethers and alcohols, and under much milder conditions than acetal cleavage to vinyl ethers and alcohols[4]; (2) mercuric sulfate appears to be a specific catalyst under these conditions, whereas Hill's experiments were acid-catalyzed; (3) I observed no reaction of the acetal of methyl glycolate with vinyl ethyl ether at −20° for 1.5 hours in the presence of mercuric sulfate. If Hill's mechanism were applicable, a mixture of acetals, the acetal of methyl glycolate and the mixed acetal of methyl glycolate and ethanol, should have been isolated.

On the other hand, experimental data thus far obtained may be explained adequately by a reaction course previously offered for other interchange reactions of vinyloxy compounds.[5,6] This reaction course assumes the dissociation of the vinyl ether into an acetylene–mercury complex and an alcohol. On reassociation, a mixture of vinyl ethers would be formed.

Experimental

I. Preparation of Vinyl Ethyl Ether from Vinyl Butyl Ether and Ethanol.—Two moles (200 g.) of vinyl butyl ether (b.p. 92° (750 mm.), $n^{21}\mathrm{D}$ 1.3995), 0.5 mole (23 g.) of ethanol (absolute, $n^{21}\mathrm{D}$ 1.3602), 0.4 g. of mercuric acetate and 3 drops of concentrated sulfuric acid were added in the above order with good stirring to a flask held at −20°. After standing for 2.5 hours, 10 g. of sodium carbonate was stirred into the reaction solution and the mixture was then distilled. The fractions obtained were as follows: (a) 15 g. (0.21 mole, 42%), b.p. 35–36°, with the infrared spectrum, odor and polymerization character of vinyl ethyl ether; (b) 3 g., b.p. 37–87°; (c) 82 g. (0.82 mole, 41%), b.p. 87–94°, recovered vinyl butyl ether; (d) 5 g., b.p. 138–145°; (e) 119 g., initial b.p. 145°; the distillation was discontinued after 13 g., b.p. 145°, $n^{21.5}\mathrm{D}$ 1.3969; fraction e contains a mixture of acetals.

II. Preparation of Vinyl Tetrahydrofurfuryl Ether from Vinyl Ethyl Ether and Tetrahydrofurfuryl Alcohol at −78°. Solution A.—Two grams of mercuric acetate and 0.001 g. of hydroquinone were dissolved in 3 moles (216 g.) of vinyl ethyl ether (b.p. 35°).

Solution B.—Seven-tenths of a gram of concentrated sulfuric acid was dissolved in 1 mole (103 g.) of tetrahydrofurfuryl alcohol (b.p. 79° (17 mm.), $n^{25}\mathrm{D}$ 1.4499).

Solution A and B were cooled to −70° and then mixed with agitation. No exotherm was observed. The external temperature was kept at −78° for 2 hours. Six grams of anhydrous sodium acetate was then added with vigorous shaking and the mixture was heated at reduced pressures in a 3-foot fractionating column filled with protruded stainless steel packing. The fractions obtained were as follows: (a) 200 g., b.p. <30° (45 mm.) (recovered vinyl ethyl ether); (b) 96 g., b.p. 63–76° (17–12 mm.); (c) 26 g. hold-up plus residue.

Fraction b was washed three times with fourfold volumes of water; the washed organic layer weighed 29 g. It was dried with a mixture of anhydrous sodium sulfate and sodium carbonate for 5 days at 0°. Fifteen grams of the product was distilled in a spinning band column of approximately 30 theoretical plates efficiency. (b_1) 1.6 g., b.p. 68–77° (40–42 mm.); (b_2) 11.1 g., b.p. 77–77.8° (42 mm.), $n^{25}\mathrm{D}$ 1.4468; C, 65.82; H, 9.25. The infrared spectrum was identical with the spectrum of samples of the vinyl ether prepared by other methods. No absorption band characteristic of hydroxyl groups was present at 3.0 μ, and new absorption bands characteristic of vinyloxy groups were present at 6.1 μ (v.s.), 7.6 μ (v.s.), 10.45 μ (v.s.), 14.3 μ (w). (Properties of the vinyl ether of tetrahydrofurfuryl alcohol are: b.p. 80–81 (45 mm.), $n^{20}\mathrm{D}$ 1.4480; C, 65.63; H, 9.38);[6] (b_3) 1.5 g. hold-up and residue, straw-colored liquid.

Thus, approximately 0.17 mole (17% conversion) of the vinyl ether was formed and less than 2% acetal could be isolated. Over 75% of the tetrahydrofurfuryl alcohol was recovered from the aqueous extracts by salting out with potassium carbonate and distillation.

III. Preparation of Vinyl Tetrahydrofurfuryl Ether from Vinyl Ethyl Ether and Tetrahydrofurfuryl Alcohol at 20°.—One mole (103 g.) of tetrahydrofurfuryl alcohol, 4 moles (288 g.) of vinyl ethyl ether, 0.86 g. of mercuric acetate, 0.3 g. of sulfuric acid and 0.001 g. of hydroquinone were mixed and reacted as in I for 3.5 hours at −20°. There was obtained the vinyl ether of tetrahydrofurfuryl alcohol in 9% conversion and tetrahydrofurfuryl alcohol was recovered to an extent of 66%. The remaining material was a mixture of acetals.

IV. Reaction of Vinyl Ethyl Ether and Tetrahydrofurfuryl Alcohol at −78° with Sulfuric Acid as Catalyst.—This reaction was carried out as in II but with no mercuric acetate addition. After 2 hours at −78°, less than 2% vinyl ether of tetrahydrofurfuryl alcohol was isolated, approximately 30% of the tetrahydrofurfuryl alcohol was recovered, and the remaining product was composed of a mixture of acetals.

V. Attempted Reaction of Vinyl Ethyl Ether and Tetrahydrofurfuryl Alcohol at −78° with Mercuric Acetate as Catalyst.—This reaction was carried out as in II but with no sulfuric acid addition. After 2 hours at −78°, the vinyl ethyl ether and tetrahydrofurfuryl alcohol were recovered almost quantitatively (99%).

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[4] Acetal cleavage at 270–400° occurs over palladium-on-asbestos (K. Bauer, U. S. Patent 1,931,858), over thoria (M. Cabanac, *Compt. rend.*, **190**, 881 (1930)), and over silver-on-asbestos (D. D. Coffman, G. H. Kalb and A. B. Ness, *J. Org. Chem.*, **13**, 223 (1948)). Pyrolysis of unsymmetrical acetals over strong acid catalysts at 140–150° is described by N. F. Shostakovskii, B. I. Mikhant'ev and N. N. Ovchinnikova (*Izvest. Akad. Nauk, S.S.S.R. Otdel Khim Nauk*, 1099 (1952); see *C. A.*, **48**, 1242^e (1954)).

[5] R. L. Adelman, *J. Org. Chem.*, **14**, 1057 (1949).

[6] R. L. Adelman, THIS JOURNAL, **75**, 2678 (1953).

Some Reactions with N-Bromosuccinimide

BY MOHAMED ZAKI BARAKAT, MOHAMED FATHY ABD EL-WAHAB AND MOHAMED MAHMOUD EL-SADR

RECEIVED MAY 17, 1954

N-Bromosuccinimide (NBS) has been used as a brominating agent[1] for a wide variety of organic compounds and as an oxidizing agent for the conversion of primary and secondary aliphatic alcohols to the corresponding aldehydes and ketones; in many cases its action is highly selective.[2,3] N-Chlorosuccinimide[4] has been shown to react with the aromatic secondary alcohol, benzhydrol, to give the corresponding ketone. α-Aminoacids[5] (alanine) and aliphatic dicarboxylic acids[6] (oxalic acid) are degraded in aqueous solution at room temperature by NBS.

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[1] C. Djerassi, *Chem. Revs.*, **43**, 271 (1948).

[2] L. F. Fieser and S. Rajagopalan, THIS JOURNAL, **71**, 3935 (1949); **71**, 3938 (1949).

[3] M. Z. Barakat and G. M. Mousa, *J. Pharm. Pharmacol.*, **4**, 115 (1952).

[4] Hebbelynck and R. H. Martin, *Experientia*, **5**, 69 (1949).

[5] A. Schönberg, R. Moubasher and M. Z. Barakat, *J. Chem. Soc.*, 2504 (1951).

[6] M. Z. Barakat, *J. Pharm. and Pharmacol.*, **4**, 582 (1952).