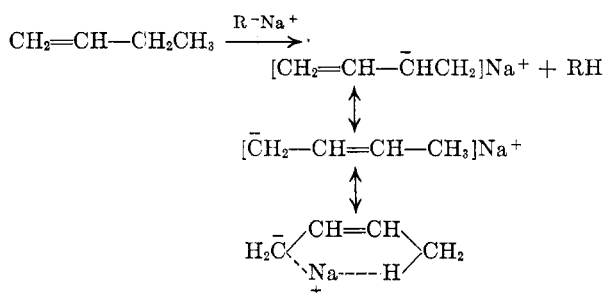


tion at much lower temperatures. It appears from the results which are presented in Fig. 1 that initially both *cis*- and *trans*-2-butene are produced at nearly constant rates, the ratio of the *cis/trans* isomers being about 15 times greater than that of the thermodynamic equilibrium mixture.⁶ This fast double bond migration is accompanied by a much slower *cis-trans* isomerization. After 50 hr. of contact the composition of the 2-butene corresponded to the calculated equilibrium mixture.

A similar but less pronounced selectivity was noticed when lithium-alumina was used as a catalyst.

This stereoselective isomerization of 1-butene has not been reported previously. The preferred formation of the less stable *cis*-2-butene in the carbanion-catalyzed reactions can be explained by postulating the participation in the transition state of a cyclic structure:



An independent study in this laboratory demonstrated that aluminas showing only weak or no acidic properties can stereoselectively isomerize at 350° 1-butene to form preferentially the less stable *cis*-2-butene. Stereoselective reactions were also observed in the catalytic dehydration of 1- and 2-butanol and 2- and 3-pentanol.

The analysis of the butenes was performed by vapor phase chromatography using a 16-ft. column of tricresyl phosphate on firebrick as the stationary phase and helium as the carrier gas. The absence of isobutylene was established by using a 12-ft. column of silver nitrate-glycol on firebrick.

In the kinetic experiments, 0.5 ml. samples were withdrawn from the reaction vessel with a syringe and charged directly into the chromatograph.

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(6) J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer, and F. D. Rossini, *J. Research Natl. Bur. Stand.*, **36**, 559 (1946).

Scyllitol Diborate

Sir:

The borate esters of the inositol isomers have been reported to exist as tridentate complexes.¹ Scyllitol, the all *trans* isomer of inositol, in its all equatorial conformation cannot form a tridentate complex and hence forms no borate derivative under mild conditions.¹ Theoretically, however, the all-axial conformation of scyllitol could form a double tridentate complex with borate (Fig. 1). In support of

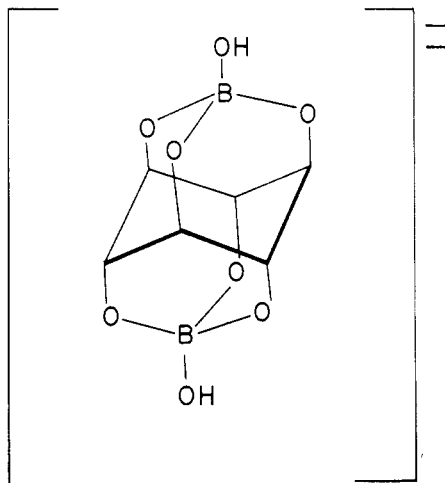


FIGURE 1

this hypothesis, scyllitol diborate has now been isolated.

The reduction of scyllo-myo-inosose with sodium borohydride has been reported to yield a mixture of 32% scyllitol and 45% myo-inositol.² During the course of this reduction, we observed that a white solid began to precipitate from the reaction mixture after a few hours. Precipitation ceased after 24–36 hours and this precipitate was collected, washed twice with small quantities of water and dried *in vacuo*. Starting with 1 gram of inosose, a yield of 0.9 gram of precipitate was obtained.

The material (I) isolated in this manner was distinguished from scyllitol, myo-inositol, and scyllo-myo inosose by paper chromatography using phenol saturated with water or acetone-water (85/15) as solvents and visualizing the spots with silver nitrate.³ Upon paper ionophoresis in 0.125*M* sodium borate, compound I was observed to migrate twice as fast as myo-inositol which has been postulated to form a monoborate of the tridentate type under these conditions. Scyllitol, in this borate ionophoresis shows no migration.¹

I is nonreducing in the Fehling or Park-Johnson

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(2) D. Raymond, *Helv. Chim. Acta*, **40**, 492 (1957).

(3) E. F. L. J. Anet, and T. M. Reynolds, *Nature*, **174**, 930 (1954).

Test.⁴ Treatment of I with acetic anhydride and sulfuric acid² yields scyllitol hexaacetate, m.p. 286°,⁵ in 60–70% yield (based on the cyclitol content of I). *Anal.* Calcd. for C₁₈H₂₄O₁₂: C 49.95, H 5.60. Found C 49.93, H 5.67. Myo-inositol hexaacetate was not detected as a product. After acidification of I with sulfuric acid, the resultant solution was subjected to repeated evaporation to dryness *in vacuo* at 50° with methanol. The final residue was taken up in water, deionized with Amberlite MB-3, and the eluate again taken to dryness *in vacuo*. The deionized residue, obtained in 90% yield from I (based on cyclitol content of I), was shown to give only one spot with the same *R_f* as scyllitol in paper chromatography with phenol-water or acetone water.

From microanalysis⁶ data, and with the assumption that it is monomolecular, compound I appears to be a monohydrate of scyllitol diborate. Calcd. for C₆H₈O₈B₂Na₂·9H₂O; C 16.45, H 5.99, B 4.94, water content 37.02. Found C 16.52, H 6.07, B 4.87. Weight loss on drying at 100° for 18 hr., 37.27.

If scyllitol is heated at 100° with 0.125*M* borate, a compound migrating at the same rate as I in borate ionophoresis is obtained. Presumably this is also scyllitol diborate. The stereochemistry of the borate complex is still unproved and is being further investigated.

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(4) J. T. Park and M. J. Johnson, *J. Biol. Chem.*, **181**, 149 (1949).

(5) Melting point determined on a Fisher-Johns melting point block.

(6) I am indebted to Dr. W. C. Alford of the National Institute of Arthritis and Metabolic Diseases, National Institutes of Health for the microanalyses.

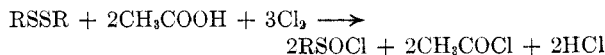
An Improved Method for Preparing Sulfinyl Chlorides

Sir:

The new method for the preparation of sulfinyl chlorides recently reported¹ represented a great improvement over previously available methods. The procedure has certain disadvantages, however, in that one has difficulty in determining when the stoichiometric quantity of chlorine has been added, a relatively large volume of inert solvent must be used to impart fluidity to the two-phase system, and the reaction must be carried out at

low temperatures to avoid the premature decomposition of the organosulfur trichloride.

We have recently found that if one mole of alkyl disulfide is mixed with exactly two moles of glacial acetic acid in the absence of solvent and chlorinated at 0° the reaction proceeds smoothly in a one-phase system and produces the desired sulfinyl chloride in high yield. On the first addition of chlorine the disulfide is transformed to the reddish orange sulfenyl chloride, RSCl. Additional chlorine apparently changes the sulfenyl chloride to the organosulfur trichloride, RSCl₃, which rapidly reacts with acetic acid to form acetyl chloride and the desired sulfinyl chloride. Since acetyl chloride is colorless and the sulfinyl chlorides are only faintly yellow, the disappearance of the reddish orange sulfenyl chloride color constitutes a good endpoint to indicate completion of the reaction. The products may be separated by fractionation of the reaction mixture without further treatment.



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Base-Catalyzed Rearrangement of α -Haloacetanilide into α -Anilinoacid Derivatives

Sir:

It has already been demonstrated that the action of sodamide in liquid ammonia upon β -chloropropionanilide and acrylanilide produces *N*-phenyl- β -lactam in fair yields.¹ In this communication we wish to report our results obtained in a study of the reaction of sodamide in liquid ammonia, and of a suspension of sodium hydride in dry benzene, upon α -chloro- α -phenylacetanilide (I). We have found that (I) gives by the action of sodamide in liquid ammonia a mixture of three compounds of which two have been identified as α -anilinophenylacetamide (III) and 2,5-diketo-1,3,4,6-tetrahydropiperazine (IV). Reaction of (I) with sodium hydride yielded IV as a major product.

To a solution of 5.1 g. (0.13 mole) of freshly prepared sodamide in 250 ml. of liquid ammonia was added 30 g. (0.12 mole) of solid (I)² with stirring during 1 hr. Within about 5 min. an orange-red solution was obtained which became brown-red at the end of the addition. The ammonia

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(1) I. B. Douglass and D. R. Poole, *J. Org. Chem.*, **22**, 536 (1957).