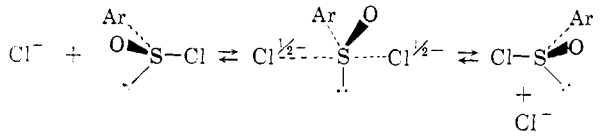
If the asymmetric sulfur undergoes a displacement reaction by inversion and a re-esterification in the same manner, no epimerization should occur. However, if reaction through II is rate determining, a subsequent rapid interchange of chloride ions by the sulfinyl chloride with racemization at the sulfur could account for the epimerization.



If this picture of the reaction is correct, equation 1 must be replaced by equation 9,

$$\ln(\alpha_1 - \alpha_2) = \left[k_1'\left(1 - \frac{k'_{-1}}{k'_{-1} + k'_{-2}}\right) + k_2'\left(1 - \frac{k'_{-2}}{k'_{-1} + k'_{-2}}\right)\right] t + C \quad (9)$$

Here the specific rate constants for the forward and reverse reactions of the simple epimerization equation are diminished by that fraction of the racemized sulfinyl chloride that reverts to the epimeric ester from which it was formed.

Although the accelerating effect of the *p*-methoxyl on the rate is relatively small, it suggests an increase in positive charge on the sulfur in the transition state.

Experimental[19]

l-Menthyl l-Benzenesulfinate.—Benzenesulfinyl chloride[20] from 34.7 g. (0.244 mole) of benzenesulfinic acid in an equal volume of dry ether was caused to react with 38.0 g. (0.243 mole) of *l*-menthol in 20 ml. of dry pyridine. Removal of the ether *in vacuo* after washing with water, dilute hydrochloric acid, twice again with water, and drying over sodium sulfate gave an almost colorless oil. The higher-melting epimer was separated from the mixture by careful cooling, with solid carbon dioxide, of a solution in three volumes of methanol. The colorless crystals, 20 g. (0.071 mole, 29%), of *l*-menthyl *l*-benzenesulfinate were collected, washed with cold, aqueous methanol, and recrystallized from methanol. Another recrystallization from methanol and three from pentane gave a product of m.p. 49–51°, $[\alpha]^{25}D$ −205.5° (*c* 2.0 in acetone), $[\alpha]^{25}D$ −210.4° (*c* 1.1 in nitrobenzene).

Anal. Calcd. for $C_{16}H_{24}O_2S$: C, 68.51; H, 8.62; S, 11.43. Found: C, 68.63; H, 8.80; S, 11.25.

(19) Analyses were performed by Clark Microanalytical Laboratory, Urbana, Ill.

(20) J. v. Braun and W. Kaiser, *Ber.*, **56B**, 549 (1923).

The oil which remained from the original crystallization had not solidified in a refrigerator after three months, but one week after adding hydrogen chloride gas more solid ester was recovered: 17.4 g. after one recrystallization.

l-Menthyl l-p-toluenesulfinate was prepared as reported previously,[2] except that after separation of the initially-formed solid ester, a few crystals of tetraethylammonium chloride and some hydrogen chloride gas were added. A second crop was removed after one day, and retreatment with quaternary chloride and hydrogen chloride gave yet another crop. The total yield of *l*-ester was 90.7%.

l-Menthyl l-p-Methoxybenzenesulfinate.—*p*-Methoxybenzenesulfinic acid[21] (27 g., 0.157 mole) was added gradually to 21.5 g. (0.18 mole) of thionyl chloride, the excess thionyl chloride was removed *in vacuo*, and the residue cooled and diluted with 50 ml. of dry ether. With cooling, 20 g. (0.128 mole) of *l*-menthol in 11 g. (0.14 mole) of pyridine and 10 ml. of dry ether was added. More ether was added and the solution washed with dilute hydrochloric acid. The ester, which was not very soluble in ether, was recovered by filtration, hydrogen chloride was passed into the solution and it was refrigerated for three days. Ester, which had crystallized after this time, was separated and the ether was evaporated from the filtrate to give additional product; yield 27.7 g. (0.089 mole, 69%). After six recrystallizations from aqueous acetone, the ester had a m.p. 116–117.5° and a constant rotation of $[\alpha]^{25}D$ −190.3° (*c* 1.2, acetone), $[\alpha]^{25}D$ −193.5° (*c* 1.0, nitrobenzene).

Anal. Calcd. for $C_{17}H_{26}O_3S$: C, 65.77; N, 8.44; S, 10.33. Found: C, 65.93; H, 8.32; S, 10.11.

Tetraethylammonium chloride stock solutions in nitrobenzene were prepared as previously.[2] Care was necessary to assure that in the preparation of the chloride from the hydroxide no excess of hydrochloric acid was used, as it was impossible to remove hydrogen chloride from the salt by recrystallization.

Hydrogen chloride stock solutions, in nitrobenzene, were prepared by passing dry hydrogen chloride into dry nitrobenzene. Exact concentrations were determined immediately preceding use, since hydrogen chloride is lost quite rapidly even from dilute solutions in nitrobenzene.

The kinetic determinations were made at 25.00 ± 0.05°, as reported previously. The spent solutions from a series of kinetic runs with *l*-menthyl *l*-*p*-toluenesulfinate, in one instance, were combined and the nitrobenzene was removed at 10^{-3} mm., at 50°. Initially 1.0 g. of ester, 0.008 g. of tetraethylammonium chloride and 0.018 g. of hydrogen chloride were present. A residue, 0.9 g., largely crystalline, remained, which after recrystallization weighed 0.67 g. and had a m.p. 102–103°. A mixed m.p. with pure *l*-menthyl *l*-*p*-toluenesulfinate was undepressed.

After distillation of the nitrobenzene, a few mg. of white crystals deposited in the side-arm of the distilling flask. The odor, m.p. 69°, and mixed m.p. showed these to be *p*-toluenesulfonyl chloride.

l-Menthol, dissolved in nitrobenzene with added hydrogen chloride and tetraethylammonium chloride, was unchanged in rotation after 16 hours at 25°.

TROY, N. Y.

(21) L. Gattermann, *ibid.*, **32**, 1136 (1899).

COMMUNICATIONS TO THE EDITOR

CONVENIENT NEW PROCEDURES FOR THE HYDROBORATION OF OLEFINS

Sir:

The hydroboration reaction provides a convenient new route from olefinic derivatives to organoboranes,[1] and to the many derivatives to which organoboranes can be converted.[1,2]

We have described procedures which utilized sodium borohydride, diglyme (diethylene glycol dimethyl ether) as solvent, and boron trifluoride etherate to liberate diborane from the salt. We have learned that the unavailability of one or more

(1) H. C. Brown and B. C. Subba Rao, THIS JOURNAL, **78**, 5694 (1956); *J. Org. Chem.*, **22**, 1135 (1957).

(2) H. C. Brown and G. Zweifel, THIS JOURNAL, **81**, 247, 1512 (1959); H. C. Brown and K. Murray, *ibid.*, **81**, 4108 (1959); J. B. Honeycutt, Jr., and J. M. Riddle, *ibid.*, **81**, 2593 (1959); M. F. Hawthorne and J. A. Dupont, *ibid.*, **80**, 5830 (1958).

of the intermediates abroad has created difficulties in applying the reaction.[3] We have established the applicability of numerous other systems, and are led to publish these in the hope that they may provide a wider selection of reagents and solvents.

Lithium borohydride is readily soluble in both ethyl ether and tetrahydrofuran. Olefin and lithium borohydride in either solvent may be treated with (1) hydrogen chloride, (2) boron trifluoride or trichloride etherates, or (3) aluminum chloride to achieve hydroboration.

A solution of 18.8 g. (200 mmoles) of norbornene and 1.98 g. (90 mmoles) of lithium borohydride in 100 ml. ether at 0° was treated over a period of 1 hour with 17 g. (0.120 mole) of boron trifluoride etherate. After a second hour at 0°, water was added to destroy residual hydride, alkali added, and the product carefully oxidized with 21 ml. of 30% hydrogen peroxide. There was obtained 15.9 g. of norborneol, m.p. 123–124°, 70% yield.

Sodium borohydride is essentially insoluble in ethyl ether or tetrahydrofuran. However, treatment of a suspension of sodium borohydride in tetrahydrofuran with hydrogen chloride results in the formation of a solution of diborane in the solvent. Addition of the olefin to this solution results in ready hydroboration.

To a well-stirred suspension of 3.0 g. (80 mmoles) of sodium borohydride and 100 ml. tetrahydrofuran at 0° was added over a period of 2 hours 45 ml. of 1.5 *M* hydrogen chloride (67 mmoles) in tetrahydrofuran. To the resulting solution of diborane was added 22.4 g. (200 mmoles) of 1-octene. The product was oxidized and isolated as usual: 21 g. of 1-octanol, 80%, b.p. 98–100° at 23 mm., $n^{20}D$ 1.4295.

In diglyme solution, sodium borohydride and an olefin may be treated with hydrogen chloride, benzyl chloride, boron halide,[1] or aluminum chloride[1] to achieve hydroboration. In this solvent, sodium hydride and boron trifluoride etherate can also be utilized.[4]

Potassium borohydride is insoluble in these sol vents. However, in two hours at room temperature an equimolar stirred suspension of potassium borohydride and lithium chloride in tetrahydrofuran undergoes metathesis to form a solution of lithium borohydride[5] (80% yield). The solution may be utilized as described above.

Finally, lithium aluminum hydride can be utilized in ethyl ether with boron trifluoride etherate[3] or with boron trichloride etherate.[6] Alternatively, it is possible to utilize an equimolar mixture of borate ester and aluminum chloride as a substitute for boron trichloride.

To a solution of 100 mmoles of 1-octene, 30 mmoles of lithium aluminum hydride and 40 mmoles of methyl borate in 50 ml. of ether at 0° was added a solution of 40 mmoles of aluminum chloride in 30 ml. of ether. After 1 hour, Vapor Phase Chromatography examination showed 90% conversion of olefin to organoborane.

Amine-boranes also can serve as hydride in the presence of Lewis acids, but the procedures are less convenient than those already described.

RICHARD B. WETHERILL LABORATORY
PURDUE UNIVERSITY HERBERT C. BROWN
LAFAYETTE, INDIANA GEORGE ZWEIFEL

RECEIVED JUNE 29, 1959

(3) Dr. Franz Sondheimer of the Weizmann Institute of Science, Rehovoth, Israel has communicated that he has utilized the action of boron trifluoride on a mixture of olefin and lithium aluminum hydride to overcome this difficulty. This useful modification of the hydroboration reaction by Dr. Sondheimer and his co-workers will be published shortly.

(4) Unpublished research of Dr. B. C. Subba Rao.

(5) R. Paul and N. Joseph, *Bull. soc. chim.*, 550 (1952).

(6) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, THIS JOURNAL, **69**, 1199 (1947).

STEROIDS. CXXIX.[1] A NEW GENERAL ROUTE TO FLUORINATED STEROIDS

Sir:

A recent publication[2] describing the conversion of a $\Delta^{9(11)}$-steroid into its 9α-bromo-11β-fluoro analog by the use of N-bromoacetamide and anhydrous hydrogen fluoride prompts us to record the synthesis of a number of mono fluoro-bromo steroids by the addition of Br-F to a *wide variety of unsaturated steroids*. The method involves addition of 1.1 molar equivalents of N-bromoacetamide to a solution of the steroid in methylene dichloride–tetrahydrofuran containing a large excess of anhydrous hydrogen fluoride (25–100 mols) at −80°. After 1 hour at −80° the reaction mixtures were kept at 0° for 2 to 16 hours. This novel fluorination procedure represents by far the best route to the biologically important 6α-fluoro steroid hormones.[3] Δ^5-Pregnene-3β,17α-diol-20-one 17-acetate (I) afforded 5α-bromo-6β-fluoropregnane-3β,17α-diol-20-one 17-acetate (II)[4] m.p. 290–292° (all mps. uncorr.), $[\alpha]_D$ +5° (all rotns. in $CHCl_3$). Oxidation of II in acetone solution with 8*N* chromic acid in aqueous sulfuric acid gave the corresponding C-3-ketone (III)[4] m.p. 171–173°, $[\alpha]_D$ +17°, converted into 6β-fluoro-17α-acetoxyprogesterone (IV)[4] m.p. 207–208°, $[\alpha]_D$ −18° λ_{max}^{EtOH} 232–234 mμ ε 13,000, by sodium acetate in methanol. Either III or IV with hydrogen chloride in acetic acid[3a,b] gave 6α-fluoro-17α-acetoxyprogesterone (V).[1,3b,c] Similarly Δ^5-pregnene-3β-ol-20-one and Δ^5-pregnene-3β,17α,21-triol-20-one 17,21-diacetate gave the 6β- and thence the 6α-fluoro analogs of progesterone[3a,c] and compound "S" diacetate.[5] Previous approaches[1,3,5] to 6α-fluoro-Δ^4-3-ketones have always been *via* 5α,6α-epoxides obtained by peracid treatment. Such an approach is often precluded with poly-unsaturated steroids; thus, $\Delta^{5,9(11)16}$-pregnatriene-3β-ol 20-one[6] led to a complex mixture from which the 5α,6α-monoepoxide could be isolated only in poor yield. *A much higher degree of selectivity* was obtained

(1) Part CXXVIII, A Bowers, L. C. Ibáñez and H. J. Ringold, THIS JOURNAL, in press.

(2) C. H. Robinson, L. Finckenor, E. P. Oliveto and D. Gould, *ibid.*, **81**, 2191 (1959).

(3) (a) A. Bowers and H. J. Ringold, *Tetrahedron*, **3**, 14 (1958); (b) A. Bowers and H. J. Ringold, THIS JOURNAL, **80**, 4423 (1958); (c) J. A. Hogg, *et al.*, *Chemistry and Industry*, 1002 (1958); (d) A. Bowers, E. Denot, M. B. Sánchez and H. J. Ringold, *Tetrahedron*, in press.

(4) All new compounds gave satisfactory results upon elemental analysis.

(5) A. Bowers, L. C. Ibáñez and H. J. Ringold, *Tetrahedron*, in press.

(6) A. Bowers, M. B. Sánchez, E. Denot, F. Neumann and C. Djerassi, manuscript in preparation.