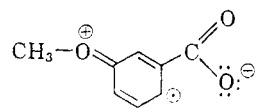
pothetical reactions from a *meta* substituent as well as from a *para* substituent. By analogy, *meta* substituents in allyl *X*-phenyl ethers may have a similar effect upon the Claisen rearrangement as *para* substituents.

Unfortunately, no similar substituent effects in mechanistically well defined situations have been reported, but systems that might be expected to show effects of this type have not yet been studied. However, the decompositions of substituted benzoyl peroxides[21,22] exhibit substituent effects similar in some respects to those found in the Claisen rearrangement. Thus, it is found that *m*-methoxybenzoyl peroxide is abnormally reactive, pyrolyzing several times faster than the unsubstituted compound. Its Hammett σ constant indicates it should be less reactive. This might be caused by stabilization of the incipient radical by structures such as



XIV

which are analogous to those postulated for the transition state of the rearrangement of allyl *m*-methoxyphenyl ether.

In summary, the kinetic and isomer distribution data on the Claisen rearrangement of allyl *m*-*X*-phenyl ethers are interpretable in terms of a transition state involving contributions from structures such as I, II, III, IV, V, and VI.

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Notes

Stereochemistry of Hydroboration

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Received February 19, 1962

The recent discovery by H. C. Brown and coworkers[2-4] of the anti-Markownikoff hydration of olefins, by hydroboration with subsequent oxidation, has already found many and significant applications in organic syntheses. Brown and Zweifel[5] have shown that the process involves stereospecific *cis* addition of diborane to the olefin followed by peroxidation to a borate ester with retention of configuration, so that the net result after hydrolysis of the latter is *cis* addition of water to the olefin. While the least substituted alcohols are always formed from aliphatic or alicyclic unsymmetrical olefins, polar effects seem to influence the direction of diborane addition in substituted styrenes.[6]

Steroid olefins represent ideal substrates to test conformational and steric effects in hydroboration. Addition of diborane to Δ^5-steroids took place predominately from the α-side,[7] suggesting that steric factors may be important in the reaction. In that case, however, the major product (a 6α-hydroxy-5α-steroid) was also the thermodynamically more stable one. We therefore decided to study the hydroboration of symmetrically substituted steroid olefins, where polarity effects are largely absent, in order to evaluate steric versus conformational effects. A recent description of similar work[8] prompts us to submit our results, which represent a more complete picture of the reaction of 2-cholestene.

From hydrolysis experiments on cholestanol acetates it is known that the 3-position is less hindered than the 2-position[9] in such compounds. If conformational factors were controlling the hydroboration of 2-cholestene, the products should be largely the equatorial 3β- and 2α-cholestanol with the former predominating. If steric factors were in control, one would expect mainly the α-cholestanols (predominantly 3α-cholestanol). Addition of diborane to 2-cholestene followed by alka-

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(2) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1135 (1957); *J. Am. Chem. Soc.*, **81**, 6423, 6428 (1959).

(3) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **81**, 247 (1959).

(4) For a recent review see H. C. Brown, *Tetrahedron*, **12**, 117 (1961).

(5) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961).

(6) H. C. Brown and G. Zweifel, *ibid.*, **82**, 4708 (1960); E. L. Allred, J. Sonnenberg, and S. Winstein, *J. Org. Chem.*, **25**, 26 (1960).

(7) W. J. Wechter, *Chem. Ind.* (London), 294 (1959); S. Wolfe, M. Nussim, Y. Mazur, and F. Sondheimer, *J. Org. Chem.*, **24**, 1034 (1959).

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(9) A. Furst and Pl. A. Plattner, *Helv. Chim. Acta*, **32**, 275 (1949).

line peroxidative work-up gave a mixture of alcohols which were separated by means of digitonin and by chromatography on alumina into all four possible alcohols. Almost 50% of the product consists of 3α-cholestanol. The 2α-alcohol was isolated in about 25% yield and the 3β-alcohol in 20% yield. Traces of 2β-cholestanol were also found. These results agree with Sondheimer's[8] findings that the α-alcohols are the predominant products but also show that a reasonable amount of β-alcohols is formed in the reaction. The predominance of the α-alcohols, particularly of the 3α-isomer, indicates that conformational effects are not significant and that steric control is the major factor in determining the stereochemistry of hydroboration in this steroid olefin. These conclusions are in accord with those reached by Brown and co-workers[5] with simpler compounds.

Experimental

Hydroboration of 2-Cholestene.—Diborane, prepared by dropwise addition of 1.2 g. of sodium borohydride in diglyme to a stirred solution of 8 g. of boron trifluoride etherate in diglyme, was bubbled into a solution of 1 g. of 2-cholestene[10] (m.p. 75–76°) in 10 ml. of dry tetrahydrofuran at 10–15°. The suspension of alkylborane was left to stand for 1 hr. Excess diborane was destroyed with ice and then 8 ml. of 3 *N* sodium hydroxide and 5 ml. of 25% hydrogen peroxide were added. After 30 min. the mixture was extracted with ether. Removal of solvent in vacuum from the dried ether solution left a mixture of cholestanols in 85 to 94% yield.

Direct Chromatography of Cholestanols.—The product (350 mg.) obtained from hydroboration of 2-cholestene was chromatograhed over Merck alumina. With petroleum ether (b.p. 45–55°) 20 mg. (6%) of 2-cholestene was eluted. The fractions eluted with benzene–petroleum ether (95:5) gave 160 mg. (46%) of 3-α-cholestanol, m.p. 178–183°, which upon recrystallization from aqueous ethanol furnished 105 mg. of pure product m.p. 180–182°, $\alpha^{23}D$ +23° (*c* = 2, chloroform); no depression when mixed with authentic 3α-cholestanol. 2α-Cholestanol (82 mg., 23%, m.p. 174–180°) was obtained from the benzene and benzene–ether (9:1) fractions. Recrystallization furnished 53 mg. of pure alcohol, m.p. 177–179°, $\alpha^{23}D$ +26° (*c* = 2, chloroform) identical with authentic sample; lit.[11] m.p. 180°. Other chromatographic fractions yielded mixtures of alcohols (70 mg.).

Digitonide Separation.—To a solution of 340 mg. of cholestanols, obtained from hydroboration of 2-cholestene, in 95% ethanol was added a hot solution of digitonin (460 mg.) in 95% ethanol. After one day the precipitated digitonide was collected by filtration (310 mg.). This corresponded to a 22% yield of β-sterols. Decomposition of the digitonide (210 mg.) with hot pyridine followed by precipitation of the released digitonin with ether and usual work-up gave 40 mg. of cholestanols. Chromatography of the latter yielded 30 mg. of, 3β-cholestanol, m.p. 139–141°, identical with authentic sample, and 1 mg. of 2β-cholestanol m.p. 149–153° (lit.[11] m.p. 155°).

The mixture (220 mg.) of 2α- and 3α-cholestanols, isolated from the filtrate after digitonide precipitation, was chromatographed to furnish 96 mg. of 3α-cholestanol (m.p. 181–182° after recrystallization) and 64 mg. of 2α-cholestanol (m.p. 179–180° after recrystallization).

Acknowledgment.—Financial assistance of this work by the National Institutes of Health, Grant CY-4474, is gratefully acknowledged.

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A Determination of the H_R Acidity Function for Sulfuric Acid–Aqueous Acetic Acid

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Received July 6, 1961

In the course of another study it was desired to determine pK_{R^+} values for a series of slightly soluble alcohols. The use of the H_R values for aqueous sulfuric acid determined by Deno and co-workers[3] would have served well for this purpose except for the fact that the alcohols were very insoluble in sulfuric acid–water mixtures. It was therefore decided to use sulfuric acid diluted with an 80% acetic acid 20% water solution. All of the alcohols were easily dissolved.

The change in diluent from water to aqueous acetic acid required a complete re-determination of H_R. For this purpose seven easily prepared aryl carbinols were chosen such that the indicator ranges overlapped each other and included 4 to 86% sulfuric acid.

The criterion for indicators used to determine acidity function[4] that

$$\log (C_{R^+}/C_{ROH}) - \log (C_{R'^+}/C_{R'OH})$$

be constant for any pair of indicators over their useful indicator range, is obeyed by the indicators used for this determination.

In Table I are listed the indicators used, their pK_{R^+} values, the wave length of maximum absorption in the visible spectrum of the associated car-

(1) Taken from the Ph.D. thesis presented by Charles A. Stout, 1961.

(2) Sinclair Oil Co. Fellow, 1959–1960 and Monsanto Fellow, 1960–1961.

(3) N. C. Deno, J. J. Jaruzelski, and A. A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955). These authors define the function

$$H_R = pK_{R^+} - \log (C_{R^+}/C_{ROH}),$$

where $pK_{R^+} = -\log (a_{ROH}\, a_{H^+}/a_{ROH}\, a_{R^+})$. C_{R^+} and C_{ROH} are, respectively, the concentrations of the carbonium ion, meaured spectrophotometrically, and the unprotonated alcohol, obtained by difference. The assumptions made by Deno *et al.* that the species which absorbs in the visible spectrum is in fact the carbonium ion, and that no protonated but undissociated acohol, ROH_2^+, exists in solution, are made by the present authors also.

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