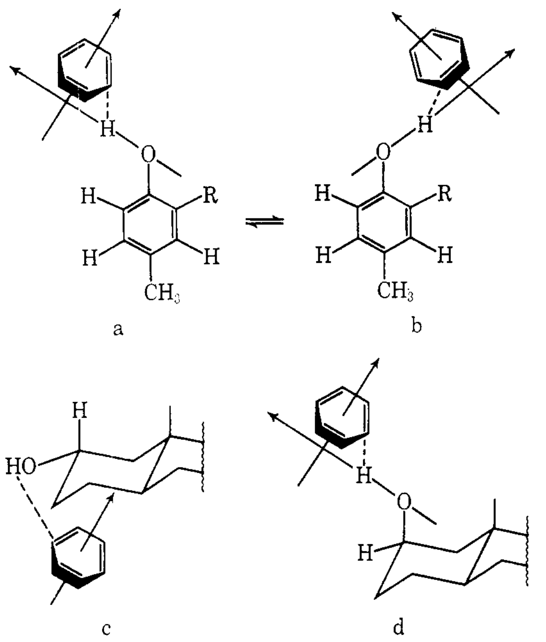

Figure 3.—Proposed model for stereochemical nature of benzene–alcohol association.

component. Thus, for compound **1** in benzene, the over-all net effect should be one of increased shielding for all solute protons. This is indeed observed to be the case, since $H_2(H_6)$, $H_3(H_5)$, and *p*-CH_3 illustrate increased shieldings of 0.08, 0.06, and 0.16 ppm, respectively.

Increase in the steric size of the *ortho* substituent in phenols will seriously disturb the population equilibrium between a and b such that, as R increases in size, the population of species b becomes smaller. Thus, progressive increases in the steric bulk of R from H, as in **1**, to -CH_3, as in **2**, to -$C(CH_3)_3$, as in **3**, should result in corresponding increases and decreases in the shielding of solute protons *syn* and *anti*, respectively, to the site of association. That this is observed to be the case is evidenced by the recorded Δ values for protons in **1**, **2**, and **3**. It is seen that H_2 becomes increasingly shielded [0.08 (**1**), 0.14 (**2**), and 0.38 (**3**)], while R [0.08 (**1**), 0.04 (**2**), and −0.11 (**3**)] and H_5 [0.06 (**1**), 0.01 (**2**) and −0.17 (**3**)] become increasingly deshielded. Parallel observations are observed for protons in **4**, **5**, and **6**, (see Figure 2) and add further support for the proposed model.

Hydroxy Steroids.—Small, but nevertheless significant, Δ values are recorded for the H-18 and H-19 protons in a number of monohydroxy steroids. Results, summarized in Table I, indicate that these protons experience increased shielding in benzene ($\Delta \cong 0.1$) except in those cases where hydroxyl and methyl groups are situated 1,3 diaxial (**9**, **13**, **15**, and **17**) to each other. In such cases, shifts to lower field are noted ($\Delta \cong -0.1$ ppm). The stereochemical nature of the benzene–solute complexes which rationalize these observations is shown in Figure 3c and 3d for solutes 5α-androstan-2α-ol, respectively, and demonstrate that in the former case benzene associates from the α face while in the latter case association takes place from the β face of the steroid molecule. The above findings indicate that, in addition to other solvent shift techniques,[9] benzene Δ values may be useful in establishing both the location and the stereochemical nature of protons situated in the vicinity of hydroxyl functions.

Although the model proposed above (Figure 1c) for benzene–hydroxyl function association is qualitatively in good agreement with observed solvent shift data, it is naive to presume that this model represents the total physical picture for such interactions. Indeed, it is possible that secondary association of benzene to solute phenol molecules, in a manner similar to that demonstrated for benzene association to toluene and *t*-butyl benzene,[2] could give rise to complexes of greater than 1:1 stoichiometry. Our interpretation of observed Δ values (Figure 2), however, if correct, suggests that the contribution to the total screening coefficient from such secondary associations is small.

Experimental Section

Nmr spectra were recorded at 100 MHz at normal probe operating temperature (30 ± 1°) using TMS as internal lock and reference. Sample concentrations were maintained at less than 5% w/v. Peak positions were recorded by observing difference 1 on the frequency counter (*i.e.*, the difference between the manual and sweep oscillator frequencies) and phenolic proton resonance positions calculated from first-order analysis of their spectra.

Phenols **1–6** were commercially available compounds and were used without further purification. Hydroxy steroids (**7–19**), recorded in Table I, were synthetically prepared. Experimental details regarding their synthesis will be published elsewhere. These compounds display the requisite spectral properties and give correct elemental analyses.

Registry No.—**1**, 106-44-5; **2**, 105-67-9; **3**, 2409-55-4; **4**, 95-48-7; **5**, 576-26-1; **6**, 2311-05-9; **7**, 2287-84-5; **8**, 20707-85-1; **9**, 1225-47-4; **10**, 7657-50-3; **11**, 1224-92-6; **12**, 20707-77-1; **13**, 20707-78-2; **14**, 1090-01-3; **15**, 734-66-7; **16**, 1032-14-0; **17**, 1032-15-1; **18**, 19037-37-7; **19**, 1225-43-0.

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Carbonium Ions. XXII. The Formation of Transient, Primary Carbonium Ions by Oxidation of Carboxylic Acids

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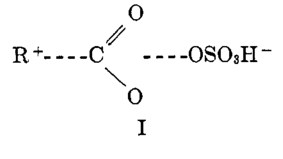
Received March 6, 1969

Solutions of $K_2S_2O_8$ in sulfuric acid or oleum oxidize carboxylic acids at 25°. The structures of the products are in accord with a mechanism involving formation of a mixed anhydride of the carboxylic acid and peroxymonosulfuric acid (Caro's acid) followed by exothermic decomposition of the mixed anhydride as shown.



$$R^{+}{-}{-}{-}{-}C(=O)(O){-}{-}{-}{-}OSO_3H^{-}$$

I

The reaction possesses two points of interest. The intermediate R^+ forms $ROSO_3H$ in respectable yields. Since these alkyl hydrogen sulfates can be hydrolyzed in dilute acids to the alcohols, the reaction is a method for converting fatty acids into the alcohol with one less carbon. For example, butyric acid produces 1-propanol (eq 1).

$$\mathrm{CH_3CH_2CH_2COOH \longrightarrow CH_3CH_2CH_2OSO_3H \longrightarrow CH_3CH_2CH_2OH} \tag{1}$$

The second point of interest is that the products are analogous to those formed in electrolytic oxidation of carboxylic acids, loss of N_2 from RN_2^+, loss of CO from ROC^+ in deoxidation, and loss of CO_2 from $ROCO^+$. This is most evident where R is branched and extensive rearrangements occur. The decomposition shown in I can thus be added to the above list[1] of methods for generating highly reactive, extensively rearranging carbonium ions. Such ions have been variously termed hot, encumbered, or free.[2]

The reactions are conducted by dissolving $K_2S_2O_8$ into 96% H_2SO_4 (or 25% oleum) in the ratio 1:3. The carboxylic acid is then cautiously added. The reaction is exothermic, so cooling is required and the CO_2 evolution can be vigorous. Reverse addition, *i.e.*, addition of $K_2S_2O_8$ to a stirred solution of the RCOOH in the acid, gives about the same results in the examples described below.

Acetic acid is notably more reluctant to react than its higher homologs. A fivefold excess of oxidant in 96% H_2SO_4 gave ultimately only 2% methyl hydrogen sulfate. However, in 25% oleum, a fivefold excess of oxidant gave 60% methyl hydrogen sulfate and more oxidant led ultimately to complete conversion. In the reaction in 96% H_2SO_4, an nmr band at δ 2.35 appeared and disappeared. This was interpreted as formation of a peracetic acid derivative, which decomposed back to acetic acid. The methyl hydrogen sulfate and acetic acid (protonated) were identified by adding methanol and acetic acid directly to the reaction mixture and establishing exact coincidence of nmr bands. This method of identification was used throughout.

Propionic acid was converted to 36% ethyl hydrogen sulfate with 51% unchanged propionic acid using 1 equiv of $K_2S_2O_8$ in 96% H_2SO_4. The yield based on reacted propionic acid is thus 72%. Accompanying the ethyl hydrogen sulfate was 4% acetic acid and 10% ethylene glycol, as its hydrogen sulfate. The glycol is believed to arise by some of the intermediate ethyl cation losing a proton to form ethylene, which epoxidizes. It was independently demonstrated that ethylene produces ethylene glycol under the reaction conditions and that ethyl hydrogen sulfate does not.

In 25% oleum, there was a far greater tendency to produce ethylene. Using equimolar $K_2S_2O_8$, the major product is ethionic acid ($HO_3SOCH_2CH_2SO_3H$, nmr triplets at δ 3.80 and 4.60, $J = 5.2$ cps), the known product of ethylene and oleum,[3] with lesser amounts of ethyl hydrogen sulfate and a trace of ethylene glycol hydrogen sulfate. Again the reaction uses the oxidant more efficiently in the oleum, but the greater preponderance of alkene derivatives is a disadvantage in designing RCOOH to ROH conversions.

Butyric acid with an equimolar quantity of $K_2S_2O_8$ in 96% H_2SO_4 gave 34% 1-propyl hydrogen sulfate, 29% unreacted butyric acid, 18% acetic acid, 9% 2-propyl hydrogen sulfate, 7% acetone, and 4% methyl hydrogen sulfate.

A number of larger fatty acids have been examined and all react, but conditions for optimum yields have not been determined.

A typical branched acid is 3-methylbutyric acid. Using a threefold excess of oxidant in 96% H_2SO_4, the products were 32% 2,3-butanediol hydrogen sulfate,[4] 26% ethyl hydrogen sulfate, 29% acetic acid, and 13% methyl hydrogen sulfate. The large preponderance of 2,3-butanediol and ethanol is remarkable, because these are formed from 2-butanol and $K_2S_2O_8$ in sulfuric acid, but are not formed from either isobutyl or *t*-butyl alcohols.[5]

It is concluded that the intermediate isobutyl cation largely rearranges by methyl shift to form the 2-butyl cation. This partly loses a proton to form 2-butene, which undergoes a normal epoxidation and opening to form 2,3-butanediol. The remainder oxidizes to 2-butanone, which undergoes a Baeyer–Villiger cleavage to ethanol and acetic acid. These interpretations were supported by demonstrating that *cis*- or *trans*-2-butene gave 2,3-butanediol (>90%) and that 2-butanone gave ethanol (>90%) and acetic acid when oxidized by solutions of $K_2S_2O_8$ in 96% H_2SO_4.

The preponderance of methyl shift (to form 2-butyl cation) relative to hydride shift (to form *t*-butyl cation) has been observed before as in the anodic oxidation of 3-methylbutyric acid,[6,7] deoxidation of isobutyl alcohol,[6] and aprotic deaminations of isobutylamine,[8] but never in as high a ratio as the 20:1 estimated from the above results.

The reactions described do not occur to any appreciable extent in 80% and more dilute sulfuric acids, and are only indirectly related to peroxymonosulfate[9] and persulfate[10] oxidations in aqueous media.[8]

Registry No.—Butyric acid, 107-92-6; acetic acid, 64-19-7; propionic acid, 79-09-4; 3-methylbutyric acid, 79-31-2.

Acknowledgment.—Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this work.

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(4) In all cases, primary and secondary alcohol groups are presumably present as the hydrogen sulfates, since it has been shown that such conversions are general in 96% sulfuric acid (N. Deno and M. S. Newman, *ibid.*, **72**, 3852 (1950).

(5) A later paper will describe the products from these alcohols.

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