of ethanol and treated with 8.5 g. of periodic acid in 60 ml. of ethanol with cooling and then kept at room temperature for thirty minutes.

The reaction mixture was poured into water and extracted with ether. The acid half-aldehydes were separated from the normal aldehydes by aqueous carbonate washing of the ether extract, and were subsequently separately oxidized to the carboxylic acid by treatment with peracetic acid.[9] There was thus recovered 2.47 g. of liquid monocarboxylic acids which were not further examined.

From the carbonate extract there was obtained 2.81 g. of mixed dicarboxylic acids after oxidation of the half aldehydes. These acids were separated by maceration with anhydrous ether. The portion insoluble in ether (0.6 g.) was washed with benzene and then crystallized from acetone to give a pure acid which was identified as suberic acid, m. p. 140–141° by mixed melting point with an authentic sample. *Anal.* Calcd. for $C_8H_{14}O_4$: neut. equiv., 87.0. Found: neut. equiv., 88.0.

The ether soluble fraction was crystallized from water and then from methyl acetate. 0.58 g. of pure acid was obtained which was identified by analysis and mixed melting point with a known sample as azelaic acid, m. p. 105–106°. *Anal.* Calcd. for $C_9H_{16}O_4$: neut. equiv., 94. Found: neut. equiv., 95.

Summary

1. The products of autoxidation of methyl oleate at 35° in the presence of ultraviolet light have been examined.

2. The position of substitution of the hydroperoxido groups has been determined by conversion to the corresponding ketostearic acids. Substitution has been shown to occur at carbon atoms C_8, C_9, C_{10} and C_{11}.

3. Evidence has been obtained that a double bond shift occurs in the formation of two of the above hydroperoxido substitutions so that in all four compounds the olefinic group is adjacent to the hydroperoxido group. In the peroxidation and double bond shift only the carbon atoms C_8, C_9, C_{10} and C_{11} are involved.

4. The products identified strongly support a chain reaction mechanism sequence involving allylic resonance of the two free radicals initially possible.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE]

Oxidation of Some Aliphatic Alcohols with Chromic Acid

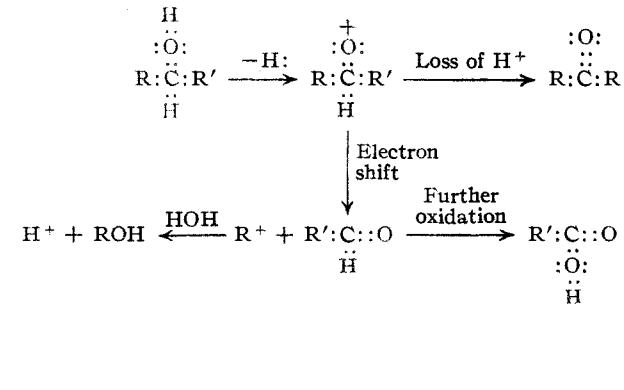
BY WILLIAM A. MOSHER AND ESLEY O. LANGERAK[1]

Mosher and Whitmore[2] recently reported the isolation of *t*-amyl alcohol from the chromic acid oxidation of methyl-*t*-amylcarbinol and isopropyl-*t*-amylcarbinol and *t*-butyl alcohol from the oxidation of methyl-*t*-butylcarbinol. A tentative mechanism involving the new concept of an intermediate containing an electronically-deficient oxygen atom was proposed. Work has been continued on this general problem by a careful search for anomalous oxidation products from other secondary aliphatic alcohols.

The secondary alcohols referred to above all have a neopentyl carbon in the alpha position to the hydroxyl-bearing carbon atom. It is probably due to the weak electron-attracting power of this type of group[3] and to the "steric strain"[4] that the splitting occurs to any appreciable extent. The first extension of the above work was to study the oxidation of secondary alcohols which had carbon atoms of lower substitution in the alpha position. The oxidation of ethyl-*s*-butylcarbinol with chromic anhydride in 80% aqueous acetic acid gave 63% of the corresponding ketone, 1% *s*-butyl alcohol, and about 1% methyl ethyl ketone probably formed by the oxidation of some of the *s*-butyl alcohol. The similar oxidation of methyl-*n*-amylcarbinol gave 83% of the corresponding ketone and a trace of *n*-amyl acetate presumably formed from the esterification of the corresponding alcohol or carbonium ion.

The question of the second part of the molecule formed by the split has been clearly answered in the case of *n*-propyl-*t*-butylcarbinol. The oxidation of this alcohol gave 41% of the corresponding ketone, 4% *n*-butyraldehyde and a corresponding amount of *t*-butyl alcohol. Traces of aldehyde have been isolated in other aliphatic alcohol oxidation but further oxidation to acid appears to be the usual course.

In the case of secondary aliphatic alcohols it would appear that some cleavage at the carbon alpha to the hydroxyl-bearing carbon is a general phenomenon. The amount of cleavage observed decreases as the electron attracting power of the group increases and the steric strain decreases. The proposed mechanism is written below in generalized form for any secondary alcohol.



(1) F. G. Cottrell Research Fellow in chemistry.
(2) Mosher and Whitmore, THIS JOURNAL, **70**, 2544 (1948).
(3) Whitmore and Bernstein, *ibid.*, **60**, 2626 (1938).
(4) H. C. Brown, *et al.*, *ibid.*, **66**, 435 (1944).

From the above mechanism it will be seen that the split of the molecule to yield carbonium ion and aldehyde occurs at the position beta to the position of electron deficiency. The electrons in this particular position are the most accessible to the oxygen atom. The position of the split, as well as the extent of splitting, is in complete harmony with the findings of Whitmore and Stahly[5] and Whitmore and Mosher.[6] This "beta-effect," discussed by Dean Whitmore[7] in 1944, has its physical basis in the fact that the beta electrons are the closest electrons to the deficient atom in which the deficient atom does not already have a part interest.

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Experimental

Preparation of Alcohols.—Methyl-*n*-amylcarbinol was obtained from Carbide and Carbon Chemical Corporation. Ethyl-*s*-butylcarbinol and *n*-propyl-*t*-butylcarbinol were prepared by the Grignard reaction from the appropriate starting materials. Materials were purified by fractionation through a Whitmore–Lux[8] total condensation, partial take-off type column packed with single turn glass helices,[9] and equivalent to 20 theoretical plates.

Oxidation.—(a) All secondary alcohols were oxidized in the following manner exemplified with ethyl-*s*-butylcarbinol: a solution of 80 g. (0.8 mole) of chromic anhydride in 50 ml. of water and 125 ml. of glacial acetic acid was added dropwise to a stirred solution of 168 g. (1.4 mole) of the carbinol in 100 ml. of glacial acetic acid over a period of 5.75 hours. The temperature was kept below 30° at all times. The oil layer formed on dilution of the reaction mixture was separated, washed with bicarbonate solution, and then with water. The aqueous layer was steam distilled and the oil layer, after washing as before, was combined with the main portion. The dried oil layers were fractionated through a column of 20 theoretical plates. From the distillation charge of 133 g. the following cuts were obtained: I (1.5 g., 0.9%), 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. with an authentic derivative of methyl ethyl ketone 116–117°; II (1.4 g., 0.8%), phenylurethan, m. p. and mixed m. p. with a derivative of *s*-butyl alcohol 64–65°; III (100.1 g., 63%), ethyl *s*-butyl ketone, 2,4-dinitrophenylhydrazone m. p. 78°. Unchanged carbinol (11.0 g., 7%) was recovered. Still residue, 8.1 g., was a dark viscous liquid.

(b) Methyl-*n*-amylcarbinol distillation charge 220 g. The corresponding ketone and *n*-amyl acetate boil very close together. The acetate was isolated from the proper fractions by removing the ketone as the bisulfite addition compound and the final traces as the semicarbazone. After drying over anhydrous sodium sulfate a trace (0.08 g., 0.03%) of *n*-amyl acetate, $n^{20}D$ 1.4039, characteristic odor, was isolated; 192 g. (83.2%) of methyl *n*-amyl ketone, 2,4-dinitrophenylhydrazone m. p. and mixed m. p. 74°, was obtained; 7.6 g. (3.4%) unoxidized carbinol was recovered. Still residue was 14.3 g.

(c) *n*-Propyl-*t*-butylcarbinol: No glacial acetic acid was used in order to facilitate isolation of any aldehydes or acids. The carbinol was added dropwise to a vigorously stirred aqueous solution of chromic anhydride. Distillation charge 180 g.; 6.8 g. (4%) of *n*-butyraldehyde, 2,4-dinitrophenylhydrazone m. p. and mixed 122–123°, and a corresponding amount of *t*-butyl alcohol, isolated as the chloride, were obtained. The main fraction (67.3 g., 40.8%), 2,4-dinitrophenylhydrazone m. p. 123–124°, consisted of the corresponding ketone; 50 g. (30.3%) of unoxidized carbinol, phenylurethan m. p. 70–71°, was recovered. Still residue amounted to 21.6 g.

Summary

1. The chromic acid oxidation of ethyl-*s*-butylcarbinol yields the expected ketone, but also small amounts of *s*-butyl alcohol and methyl ethyl ketone.

2. Methyl-*n*-amylcarbinol in acetic acid solution gives a trace of *n*-amyl acetate.

3. Oxidation of *n*-propyl-*t*-butylcarbinol gives small amounts of *t*-butyl alcohol and *n*-butyraldehyde in addition to the expected ketone.

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(5) Whitmore and Stahly, THIS JOURNAL, **55**, 4153 (1933); **67**, 2158 (1945).

(6) Whitmore and Mosher, *ibid.*, **68**, 281 (1946).

(7) Whitmore, Organic Division, American Chemical Society, New York, N. Y., September, 1944.

(8) Whitmore and Lux, THIS JOURNAL, **54**, 3448 (1932).

(9) Wilson, Parker and Laughlin, *ibid.*, **55**, 2795 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL AND COLLOIDAL CHEMISTRY, THE HEBREW UNIVERSITY]

A Reaction between Resorcinol and Glycine

BY N. LICHTENSTEIN, J. DOBKIN AND EVA HEIMANN-HOLLAENDER

Glycine dissolves with the evolution of carbon dioxide when heated in melted resorcinol at 175–185°. A colorless, crystalline substance can be isolated from the product which remains after the excess resorcinol is removed with ether. The elementary composition and chemical properties of this substance correspond to those to be expected of N-(*m*-hydroxyphenyl)-glycine anhydride (I).

The substance is insoluble in sodium bicarbonate solution, but dissolves readily in dilute sodium hydroxide. It gives positive color reactions with Millon reagent, with 2,6-dichloroquinonechlorimide,[1] and with diazotized sulfanilic acid. The picric acid reaction for diketopiperazines[2] is positive, whereas the fluorescein reaction for resorcinol and the ninhydrin color reaction give negative results. Van Slyke amino determination and titration in acetone according to Linderstrøm–Lang failed to reveal the presence of a free amino group.

Benzoylation of our substance converted it into a corresponding monobenzoyl derivative which was insoluble in dilute sodium hydroxide and gave no color reaction with Millon reagent.

The substance was hydrolyzed with hydrochlo-

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(2) E. Abderhalden and E. Komm, *Z. physiol. Chem.*, **139**, 181 (1924).