configuration of the two oxides can be assigned by molecular rotation differences as compared with α- and β-cholesteryl oxides. The oxide obtained through the bromohydrin is evidently the β-oxide and therefore the bromohydrin from which it is formed is 5α-bromocholestane-3β,6β,7β-triol. The addition of hypobromous acid to the 5,6-double bond therefore is contrary to Markownikoff's rule, as has been observed in the addition of halogens[4] and hypochlorous acid,[5] and is controlled by steric factors.[6]

EXPERIMENTAL[7]

Oxidation of Δ^4-cholestene-3β,6β-diol. Δ^4-Cholestene-3β,6β-diol (430 mg.) in hot dioxane (75 ml.) containing 2 ml. of water was treated with *N*-bromosuccinimide (400 mg.) and the mixture was warmed on the steam bath until complete solution was effected. The solution turned yellow and then colorless. At this stage the reaction mixture was poured into water and the precipitate collected by suction. A first crystallization from benzene–petroleum ether gave 80 mg. (17% yield) of colorless needles m.p. 191–193° identified as *Δ^4-cholestene-6β-ol-3-one* by direct comparison with an authentic sample of this compound. From a second crop of the initial solution a crystalline product, m.p. 169–170°, α_D +3.2, was obtained, which was not depressed on admixture with a pure sample of *3,6-cholestandione*. Yield, 200 mg. (42%).

5α-Bromocholestane-3β,6β,7β-triol was obtained from the reaction of Δ^5-cholestene-3β,7β-diol (450 mg.) with NBS (287 mg.) in dioxane-water (6 ml., 0.8 ml.), 6 hr., 25°. It forms small prisms when crystallized from petroleum ether, m.p. 179–180°, α_D +28.6°.

Anal. Calcd. for $C_{27}H_{47}O_3Br$: C, 64.91; H, 9.48; Br, 15.99. Found: C, 64.99; H, 9.53; Br, 15.93.

The 3,7-dibenzoate was obtained by a similar reaction from Δ^5-cholestene-3β,7β-diol dibenzoate; 89% yield, m.p. 142–143°, α_D −60.6°.

Anal. Calcd. for $C_{41}H_{55}O_5Br$: C, 69.57; H, 7.83. Found: C, 69.93; H, 7.53.

When refluxed with 2% potassium hydroxide for 1 hr. the bromohydrin is converted into the β-oxide of 7β-hydroxycholesterol in 92% yield; plates from petroleum ether, m.p. 166–167°, α_D +50°. The oxide is reconverted into the bromohydrin by the action of hydrogen bromide.

Anal. Calcd. for $C_{27}H_{46}O_3$: C, 77.45; H, 11.07. Found: C, 77.12; H, 10.99.

The 3,7-dibenzoate of the β-oxide was obtained from the corresponding bromohydrin; 64% yield, m.p. 151–153°, α_D +86°.

7β-Hydroxycholesteryl α-oxide was obtained by refluxing Δ^5-cholestene-3β,7β-diol (800 mg.) for 6 hr. with a solution of perphthalic acid (800 mg.) in ether (40 ml.). After the usual work-up, chromatography afforded some starting material (60 mg.); the α-oxide, 250 mg., 30% yield, m.p. 153–155°, α_D +12°; intermediate nonhomogeneous fractions; and finally the β-oxide, 12% yield, m.p. 166–167° α_D +50° (no melting point depression on admixture with the oxide from the bromohydrin).

Anal. Calcd. for $C_{27}H_{46}O_3$: C, 77.45; H, 11.07. Found: C, 76.86; H, 11.22.

Acknowledgement. I am indebted to Professor and Mrs. L.F. Fieser for their help and suggestions in connection with this work.

DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY
CAMBRIDGE, MASS.

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[4] D. H. R. Barton, E. Miller, and H. T. Young, *J. Chem. Soc.*, 2598 (1951).

[5] S. Mori, *J. Chem. Soc. Japan*, **71**, 600 (1950); *Chem. Abstr.*, **45**, 9069 (1951).

[6] L. F. Fieser, *Experientia*, **6**, 312 (1950).

[7] Melting points are not corrected. Optical rotations were taken in chloroform solution. Analyses were carried out by Dr. S. M. Nagy and associates.

Reaction of Ethyl Acrylate with Methyl *n*-Hexyl Ketone

JOHN J. MILLER[1] AND PETER L. DE BENNEVILLE

Received March 25, 1957

It has been reported that the reaction of ethyl acrylate with methyl *n*-hexyl ketone in the presence of an excess of sodium ethoxide gives 1-hendecene-3,5-dione.[2] When this reaction was repeated, a product (I) with the reported melting point 69–70° and composition (corresponding to $C_{11}H_{18}O_2$) was obtained. Although examination of the infrared spectrum confirmed the presence of a 1,3-diketone by a very broad band[3] at about 1600 cm.$^{-1}$, there was no indication of the presence of a double bond. The compound did not absorb hydrogen in the presence of either Pt or Pd catalyst. The diketone had a neutralization equivalent of 178 and molecular weight (ebulliometric) of 182. It did not give a color in the ferric chloride test.

Two possible structures for the product were 2-pentyl-1,3-cyclohexanedione (II) and 4-pentyl-1,3-cyclohexanedione (III), which could be formed, respectively, by an initial Michael condensation of the two reactants at the methyl or the methylene carbon atom, followed by a cyclization reaction. Whereas II would give only one product on basic hydrolysis, 5-ketohendecanoic acid, III would give a mixture of 2-pentyl-5-ketohexanoic acid and 4-pentyl-5-ketohexanoic acid. Hydrolysis of I with barium hydroxide solution[4] gave after acidification a clear oil which resisted attempts at crystallization. This oil had a neutralization equivalent of 205 (calcd. for $C_{11}H_{20}O_3$, 200). The infrared spectrum was consistent with the keto acid structure, the carbonyl groups absorbing in a single band at about 1715 cm.$^{-1}$ A weak iodoform test was obtained, showing the presence of some material containing the CH_3CO— group. The resistance of the keto acid to crystallization and this iodoform test indicated that the original product was III, and that hydrolysis had given the mixed keto acids.

III has been prepared by the hydrogenation of 4-pentylresorcinol, in alkaline solution and in the presence of Raney nickel catalyst.[5] Repetition of

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[1] Present address: Rohm & Haas Co., Redstone Arsenal Research Division, Huntsville, Ala.

[2] C. Hurd & C. Kelso, *J. Am. Chem. Soc.*, **62**, 2184 (1940).

[3] R. Rasmussen, D. Tunnicliff, and R. Brattain, *J. Am. Chem. Soc.*, **71**, 1068 (1949).

[4] H. Setter and W. Dierichs, *Ber.*, **15**, 1061 (1953); *Angew. Chem.*, **67**, 769 (1955).

this synthesis gave a product, m.p. 68.5–70° (reported m.p. 67°), which when mixed with I showed no depression of melting point. The infrared spectrum of the substance was identical with that of I.

I is therefore properly formulated as 4-pentyl-1,3-cyclohexanedione.

EXPERIMENTAL

Ethyl acrylate was commercial grade used without purification. Methyl *n*-hexyl ketone was freed of capryl alcohol by refluxing for 28 hr. with 1.5% of its weight of boric acid and removing the water produced. It was then carefully distilled, b.p. 83° at 30 mm.

Product I from ethyl acrylate and methyl hexyl ketone. To a suspension of sodium ethoxide in xylene, prepared by addition of absolute ethanol (17.4 g.) to a suspension of sodium (6.90 g., 0.3 g. atom) in xylene (200 cc.) was added ethyl acrylate (40 g., 0.4 mole). The mixture was cooled in an ice bath and methyl *n*-hexyl ketone (20 g., 0.15 mole) was added dropwise. Heat was evolved and the mixture became viscous. As the mixture was stirred at 0° for 0.5 hr., the solution became less viscous. Stirring was continued overnight (17 hr.) at room temperature and 100 cc. of water was introduced. After the mixture had been stirred for another hour, the aqueous and xylene layers were separated and the aqueous layer was acidified with glacial acetic acid. The oil which separated on acidification crystallized while standing in the refrigerator. Recrystallization of the gummy yellow solid from ethyl acetate gave 8 g. (27%) I, colorless crystals, m.p. 69–70°.

Anal., Calcd. for $C_{11}H_{18}O_2$: C, 72.5; H, 10.0. Found: C, 72.6; H, 10.1.

Hydrolysis of I. A suspension of $Ba(OH)_2 \cdot 8H_2O$ (34.7 g., 0.11 mole) and I, (4 g., 0.022 mole) in 100 ml. of water was heated at reflux for 28 hr. Solid carbon dioxide was introduced until the mixture was neutral to *p*H paper. The precipitated barium carbonate was removed by filtration. The mixture was heated to reflux again and the hot solution was filtered. When the filtrate was treated with 20 ml. of 2*N* hydrochloric acid, a clear oil separated. The oil was extracted with ether and the ethereal solution was dried over magnesium sulfate. Evaporation of the ether left an oil which resisted attempts at crystallization. Some iodoform was obtained in the iodoform test on this oil. Treatment of it with 2,4-dinitrophenylhydrazine gave an oil which could not be crystallized.

4-n-amyl-1,3-cyclohexanedione (III). 4-Pentylresorcinol was prepared by the method of Dohme, Cox, and Miller.[6] The procedure of Adams and Baker[5] was followed in the reduction to III. The product was obtained in 88% yield, m.p. after recrystallization from pentane, 68.5–70°, mixture m.p. with I, 68.5–70°.

ROHM and HAAS COMPANY
PHILADELPHIA, PA.

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(5) R. Adams and B. R. Baker, *J. Am. Chem. Soc.*, **62**, 2208 (1940).

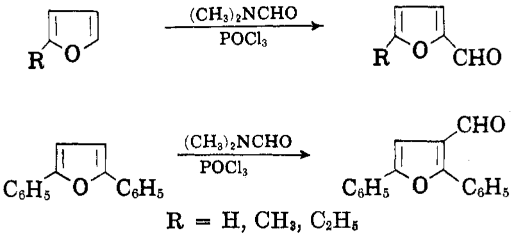
(6) A. Dohme, E. Cox, and E. Miller, *J. Am. Chem. Soc.*, **48**, 1688 (1926).

Formylation of Furans

VINCENT J. TRAYNELIS, JOHN J. MISKEL, JR.,
AND JOHN R. SOWA

Received March 25, 1957

In recent years the use of dimethylformamide and phosphorus oxychloride as a formylating agent has found many applications in the heterocyclic series. The systems studied contained sulfur[1] and nitrogen[2] heteroatoms. In this report the authors wish to extend the scope of this reaction to the oxygen systems, namely furan and its derivatives.



The formylation of furan, 2-methylfuran, and 2-ethylfuran proceeded under mild conditions and gave furfural (64%), 5-methyl-2-furaldehyde (76%) and 5-ethyl-2-furaldehyde (80%), respectively. These aldehydes were identified by physical constants, solid derivatives, and, in the case of furfural, by comparison of the infrared spectrum with that of an authentic sample (experimental section).

Conversion of the above furans to the corresponding aldehydes by the Gatterman reaction has been reported by Reichstein;[3] however, the dimethylformamide-phosphorus oxychloride method gives better yields by 15 to 30%. In view of the commercial availability of 2-methylfuran, this reaction presents an excellent procedure for the preparation of 5-methyl-2-furaldehyde.

When two substituents are introduced into the α positions of the furan nucleus, the formylation with dimethylformamide and phosphorus oxychloride becomes more difficult. In the case of 2,5-dimethylfuran resinification took place; however, 2,5-diphenylfuran gave 2,5-diphenyl-3-furaldehyde (40%) m.p. 89–90°, oxime, m.p. 170–171° (reported[4] m.p. of aldehyde 90–92°, m.p. of oxime 171–173°) and starting material (39%). This reaction presents an example of direct formylation in the β-position of the furan ring. Generally these aldehydes are prepared by conversion of some functional group in the β-position to an aldehyde.

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(1) (a) E. Campaigne and W. L. Archer, *J. Am. Chem. Soc.*, **75**, 989 (1953); (b) W. E. Parham and V. J. Traynelis, *J. Am. Chem. Soc.*, **76**, 4960 (1954); (c). W. E. Parham, T. M. Roder, and W. R. Hasek, *J. Am. Chem. Soc.* **75**, 1647 (1953); (d) N. P. Buu-Hoi, P. Demerseman, and R. Royer; *Compt. rend.*, **237**, 397 (1953); (e) W. S. Emerson and T. M. Patrick, U. S. Patent **2,581,009** (1952); *Chem. Abstr.* **46**, 9610 (1952).

(2) (a) R. M. Silverstein, E. E. Ryskiewicz, C. Wellard, and R. C. Koehler, *J. Org. Chem.*, **20**, 668 (1955); (b) E. Ju-Hwa Chu and T. C. Chu, *J. Org. Chem.*, **19**, 266 (1954); (c) G. F. Smith, *J. Chem. Soc.*, 3842 (1954); N. P. Buu-Hoï and N. G. Hoan, *J. Org. Chem.*, **16**, 1327 (1951).

(3) T. Reichstein, *Helv. Chim. Acta*, **13**, 345 (1930).

(4) P. S. Bailey and R. E. Lutz, *J. Am. Chem. Soc.* **67**, 2232 (1948).