perature in an atmosphere of carbon dioxide, but no violet color of diphenyldiazomethane was observed.

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A New Steroid Coupling Product from Cholesterol

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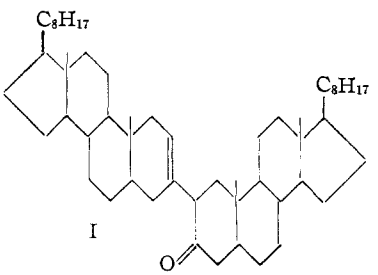
The catalytic hydrogenation of cholestanone over platinum in di-*n*-butyl ether containing a small amount of concentrated aqueous hydrobromic acid affords epicholestanol as the major product together with a small amount of cholestanol.[2,3] We have found, however, that if the hydrogenation is carried out in anhydrous medium using an acetic acid solution of hydrogen bromide instead of a concentrated aqueous solution a new substance, $C_{54}H_{90}O$, is formed in *ca.* 40% yield. Furthermore, the same substance can be obtained in the absence of hydrogen and platinum simply by heating cholestanone in dibutyl ether–acetic acid–hydrogen bromide solution. The new compound is an unsaturated, non-conjugated ketone as is indicated by the infrared spectrum (carbonyl absorption at 1710 cm.$^{-1}$), formation of a yellow 2,4-dinitrophenylhydrazone, yellow coloration with tetranitromethane and lack of high-intensity absorption in the ultraviolet. Only one structure (I) seems to accommodate these facts and to be consistent with the conditions of the transformation. The attachment of the cholestene moiety to C_2 follows from the preferred direction



I

of enolization of cholestanone and the position of the double bond follows from the greater stability of Δ^2- over Δ^3-cholestene. The more stable α-orientation of the cholestene substituent seems probable because the compound is not isomerized even by long treatment with strong acid.

Although the coupling product reacts rapidly with bromine in carbon tetrachloride to form an unstable, bromine-containing material (presumably a dibromide), all attempts to reduce either the double bond or the carbonyl group catalytically were unsuccessful.

Experimental

Aldol Coupling of Cholestanone.—A solution of 5 g. of cholestanone in 125 ml. of di-*n*-butyl ether containing 15 ml. of 3.3% hydrogen bromide in acetic acid was heated to 60° for four hours. The catalyst was removed by filtration and the filtrate was washed with 10% aqueous sodium hydroxide, then with water, and evaporated under reduced pressure. Recrystallization of the residual solid from methylene chloride–acetone afforded 2.28 g. of crude product, m.p. *ca.* 175°. Further recrystallization furnished 2.0 g. of pure material as a colorless, granular solid, m.p. 209–211°, $[\alpha]_D$ +40.9° (*c* 2.3, chloroform).

Anal. Calcd. for $C_{54}H_{90}O$: C, 85.63; H, 12.24; mol. wt., 757.26. Found: C, 85.51; H, 12.27; mol. wt., 706 (ebullioscopic, benzene).

The same product was obtained when the reaction mixture was shaken with hydrogen and pre-reduced platinum catalyst; identified by m.p., mixture m.p. and infrared spectra.

The 2,4-dinitrophenylhydrazone was prepared in the usual way and recrystallized from methylene chloride–acetone, m.p. 150° dec. The same dinitrophenylhydrazone was made from samples of I formed by condensation in the presence or absence of hydrogen–platinum.

Anal. Calcd. for $C_{60}H_{94}O_4N_4$: C, 76.87; H, 10.32; N, 5.97. *Found:* C, 77.14; H, 10.46; N, 6.05.

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2,5-Di-*t*-butyl-4-methoxyphenol and 2,6-Di-*t*-butyl-4-methoxyphenol

BY CLINTON D. COOK, RICHARD G. INSKEEP, ARTHUR S. ROSENBERG AND EARL C. CURTIS, JR.

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During a study[1] of the thermal decomposition of bis-(1,3,5-tri-*t*-butyl-2,5-cyclohexadiene-4-one) peroxide[2] a product believed to be 2,6-di-*t*-butylbenzoquinone was isolated. Bickel and Kooyman[3] have reported this compound from the reaction of 2,4,6-tri-*t*-butylphenol with oxygen initiated by 2,2′-azoisobutylnitrile. However, they cite no structural evidence. To prove the identity of our product, it was reduced to the corresponding hydroquinone and alkylated with methyl sulfate to give 2,6-di-*t*-butyl-4-methoxyphenol. This product has been reported by Sears and Kitchen[4] as a result of the alkylation of 4-methoxyphenol with isobutylene by the method of Stillson, Sawyer and Hunt.[5] In our hands the products prepared by these two methods were not identical.[6] Further investigation showed that the major product formed on isobutylene alkylation—under conditions closely approximating those cited by Stillson, *et al.*, for the preparation of 2,4,6-tri-*t*-butylphenol—is 2,5-di-*t*-butyl-4-methoxyphenol. Our evidence is as follows: The infrared spectrum of the product formed from the di-*t*-butylhydroquinone shows a marked absorption for the hydroxyl group at 3659 cm.$^{-1}$ but only slight indications of hydrogen bonding in the region from 3300 to 3500 cm.$^{-1}$ (see Fig. 1, A). This product was insoluble in Claisen solution. These facts are consistent with a 2,6-orientation of the *t*-butyl groups. (For comparison with a com-

(1) From the B.S. thesis of R. L. Young.

(2) G. Vavon and B. Jakubowicz, *Bull. soc. chim. France*, [4] **53**, 583 (1933).

(3) L. Ruzicka, H. Brungger, E. Eichenberger and J. Meyers, *Helv. Chim. Acta*, **17**, 1407 (1934).

(1) C. D. Cook and R. C. Woodworth, unpublished work.

(2) C. D. Cook and R. C. Woodworth, THIS JOURNAL, **75**, 6242 (1953).

(3) A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 3211 (1953).

(4) W. C. Sears and L. J. Kitchen, THIS JOURNAL, **71**, 4110 (1949).

(5) G. H. Stillson, D. W. Sawyer and C. K. Hunt, *ibid.*, **67**, 303 (1945).

(6) In a personal communication, Dr. Kitchen reports that this reaction is unusually sensitive to conditions and that, under his conditions, the 2,6-isomer predominates. He plans to report this work in a forthcoming publication.