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°, α^{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°, α^{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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[10] L. F. Fieser and X. A. Dominguez, *J. Am. Chem. Soc.*, **75**, 1704 (1953).

[11] L. F. Feiser and M. Fieser, "Steroids," p. 253, Reinhold, New York, 1959.

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

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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-

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[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.

[4] L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill, New York, 1940, pp. 265–266, and L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, **54**, 2721 (1932).

bonium ion, and the extinction coefficient at this wave length.

TABLE I

INDICATOR PROPERTIES

Indicator	$-pK_{R^+}$	λ_{max}, mμ	ϵ_{max}, $\times 10^{-4}$
p-Anisyldiphenylcarbinol[a]	3.23	476	5.83
Di-p-tolylphenylcarbinol	4.39	456	5.50
p-Tolyldiphenylcarbinol	5.41	450	4.51
Triphenylcarbinol	6.65	433	3.72
p-Anisyl-p-tolylcarbinol	8.32	482	8.31
9-Phenyl-9-fluorenol	10.27	492	3.75
p-Tolylphenylcarbinol	12.29	456	7.14
Diphenylcarbinol	13.56	442	5.47

[a] Because of the difficulty in obtaining this alcohol in a pure, crystalline state, p-anisyldiphenylcarbinyl chloride was used instead. Deno *et al.* have shown the chloride ion so introduced has no effect on the acidity function.[1]

In Table II there is listed H_R as a function of per cent sulfuric acid.

TABLE II

VALUES OF H_R IN H_2SO_4 DILUTED WITH 80 WT. % AQUEOUS ACETIC ACID[a]

% H_2SO_4	$-H_R$	% H_2SO_4	$-H_R$
4	1.80	46	9.31
6	2.28	48	9.65
8	2.69	50	10.02
10	3.07	52	10.38
12	3.44	54	10.71
14	3.77	56	11.00
16	4.16	58	11.31
18	4.50	60	11.62
20	4.84	62	11.96
22	5.22	64	12.30
24	5.61	66	12.63
26	6.01	68	12.88
28	6.39	70	13.15
30	6.80	72	13.51
32	7.20	74	13.78
34	7.58	76	14.09
36	7.97	78	14.50
38	8.29	80	14.95
40	8.58	82	15.42
42	8.84	84	15.71
44	9.09	86	15.94

[a] 20.0 g. of water and 80.0 g. of acetic acid.

Experimental

Spectrophotometric measurements. A Beckman Model DU spectrophotometer equipped with a photomultiplier and thermospacers supplied with water at 24°, was used throughout. The solutions of sulfuric acid, acetic acid, and water were made up by weight in glass-stoppered flasks from 99.9% sulfuric acid, made by adding du Pont Reagent Grade 30% fuming sulfuric acid to du Pont Reagent Grade concentrated sulfuric acid to give the desired concentration. The diluent was 80% aqueous acetic acid, made up by weight from du Pont Reagent Grade acetic acid and distilled water (20.0 g. of water and 80.0 g. of acetic acid). Each sulfuric acid solution, at 25°, was then used to dilute 2.00 ml. of an acetic acid solution of the appropriate indicator to volume in a 50-ml. volumetric flask. The indicator solutions were made up with 80% aqueous acetic acid for use in measurements at sulfuric acid concentrations greater than 67%, where use of glacial acetic acid would make a significant change in the water–acetic acid ratio in the final solution. Because some of the indicator solutions showed a slow decrease in optical density with time, the optical density of each solution was measured within 5 min. of its being made up, whenever this precaution was required.

Synthesis of the aryl carbinols. Four carbinols—p-anisyldiphenylcarbinol, di-p-tolyldiphenylcarbinol, p-tolyldiphenylcarbinol, and p-tolyl-p-anisylcarbinol—were made *via* the Grignard reaction using readily available starting materials. In each case the carbonyl compound was dissolved in about 10 ml. of dry benzene. To this solution was added quite rapidly a 10 to 30% excess of an ether solution of the Grignard reagent. A deep red color developed in each case, and usually vanished within 30 sec. Water was added to the reaction mixture about 2 min. after the addition of the Grignard reagent. This was followed by enough concentrated hydrochloric acid to make the solution acid to litmus. The organic phase was separated and the aqueous phase was washed three times with ether. The combined ethereal solutions were dried over magnesium sulfate and evaporated to to a viscous oil under a stream of air. Details regarding the individual carbinols prepared are given below.

p-Anisyldiphenylcarbinyl chloride. From 200 mg. of p-anisylphenyl ketone and 2 ml. of 0.7*M* phenylmagnesium bromide in ether was obtained a light yellow oil which resisted all attempts at crystallization. It was dissolved in 5 ml. of benzene and treated with dry hydrogen chloride at room temperature for 5 min. The resulting light yellow solution was frozen in a Dry Ice–acetone bath which caused it to turn dark red. The flask containing the frozen solution was allowed to warm slowly to room temperature under 5 mm. pressure. When all of the benzene had been removed the solid yellow residue was recrystallized twice from petroleum ether (b.p. 65–69°), giving light granules which melted at 119.0–122.0° (lit.[5] m.p. 122–123°).

Di-p-tolylphenylcarbinol. From 1.6 g. of p-tolyl phenyl ketone and 25 ml. of 0.4*M* p-tolylmagnesium bromide in ether was obtained a light yellow oil which slowly crystallized to a solid mass upon cooling in ice. This material was recrystallized twice from low-boiling petroleum ether (b.p. 35–55°), giving colorless granules, melting at 75.5–76.4° (lit.[6] m.p. 76.5–77.5°).

p-Tolyldiphenylcarbinol. From 1.1 g. of p-tolyl phenyl ketone and 10 ml. of 0.7*M* phenylmagnesium bromide in ether was obtained a slightly yellow-green oil which crystallized at room temperature. Two recrystallizations from low-boiling petroleum ether gave colorless granules, melting at 70.8–72.8° (lit.[7] m.p. 73–74°).

p-Tolyl-p-anisylcarbinol. From 1 ml. of p-anisaldehyde and 25 ml. of 0.4*M* p-tolylmagnesium bromide in ether was obtained a light tan oil which yielded small, white needles from benzene–petroleum ether. These melted at 59.5–60.5°. (lit.[8] m.p. 61–62°).

p-Tolylphenylcarbinol. This compound was prepared by reducing 1.96 g. of p-tolyl phenyl ketone with 1.89 g. of sodium borohydride in ethanol solution. The reaction solution was acidified with dilute hydrochloric acid and the majority of the ethanol removed by directing a stream of air over the liquid surface. Ether was then used to extract the residue. The ether extracts were dried over magnesium sulphate and evaporated to obtain a light yellow oil. This was taken up in a few milliliters of petroleum ether. Upon cooling, a white gel formed which persisted at room temperature. After standing open for 2 days, the solvent partially evaporated and long, white needles formed. This material was dis-

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(5) A. Baeyer and V. Villiger, *Ber.*, **36**, 2789 (1903).

(6) A. Kliegl, *Ber.*, **38**, 86 (1905).

(7) A. Bistrzycki and J. Gyr, *Ber.*, **37**, 663 (1904).

(8) M. P. Balfe, E. A. W. Downes, A. A. Evans, J. Kenyon, R. Popett, C. G. Searle, and A. L. Tarnoky, *J. Chem. Soc.*, 797 (1946).

solved in petroleum ether and cooled in ice. The gel which slowly formed was seeded with the crystalline product and allowed to stand at room temperature for 4 hr. During this time long, silky, white needles grew down from the surfaces of the gel and eventually there resulted a clear, fluid mother liquor and a beautifully crystalline product, melting at 52.8–54.8° (lit.[9] m.p. 52–53°).

Triphenylcarbinol. A commercial sample melting at 159.8–161.0° (lit.[10] m.p. 159°) was used.

Diphenylcarbinol. Eastman Kodak diphenylcarbinol was employed.

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[9] E. Fischer and O. Fischer, *Ann.*, **194**, 265 (1878).

[10] E. Fischer and O. Fischer, *Ann.*, **194**, 271 (1878).

The Kinetics of the Persulfate Oxidation of 2-Propanol in the Presence of Other Organic Compounds

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Wiberg[1] has reported that allyl acetate decreases the first-order rate constant for the oxidation of 2-propanol (0.02 *M*) by potassium persulfate (0.02 *M*) from the value 0.84 hr.$^{-1}$ at 60° and pH 5 to the value observed in the absence of 2-propanol (0.014 hr.$^{-1}$). This fact was interpreted by Wiberg[1] as an "inhibition" by allyl acetate of a radical chain process, and the oxidation mechanism was represented by the following sequence of five irreversible free radical reactions, from which was derived the final rate law, $v = \sqrt{2k_1k_2k_4/k_5}\,[S_2O_8^{=}]$:

$$S_2O_8^{=} \xrightarrow{k_1} 2SO_4^{-\cdot}$$

$$SO_4^{-\cdot} + H_2O \xrightarrow{k_2} HO. + HSO_4^{-}$$

$$HO^{-\cdot} + R_2CHOH \xrightarrow{k_3} H_2O + R_2\dot{C}OH$$

$$R_2\dot{C}OH + S_2O_8^{=\cdot} \xrightarrow{k_4} R_2C{=}O + HSO_4^{-} + SO_4^{-\cdot}$$

$$R_2\dot{C}OH \quad SO_4^{-\cdot} \xrightarrow{k_5} R_2C{=}O + HSO_4^{-}$$

Results

Experiments[2] recently carried out in these laboratories suggest that Wiberg's mechanism is incorrect for the following reasons. First of all, it is not true that allyl acetate reduces the first-order rate constant to that observed in the buffer solution alone. We have found that 0.04 *M* allyl acetate reduces the rate only to approximately the value (0.063 hr.$^{-1}$) observed when it itself reacts with 0.02 *M* persulfate at pH 7 and 60°. This is 4.5 times the rate of disappearance of persulfate in the buffer alone. The results of Kolthoff, Meehan, and Carr[3] also show that the reaction with allyl acetate is significantly faster (by about 40% at the half-time) than that with the buffer alone.

What is more significant, however, is the fact that 2-butanol (which hardly can be considered a "radical trap") produces the same type of result. We find that 0.02 *M* 2-butanol gives k = 0.22 hr.$^{-1}$ when alone in the buffer solution, and 0.02 *M* 2-propanol alone gives 0.85 hr.$^{-1}$, but the two together in the same solution give 0.30 hr.$^{-1}$ (Fig. 1).[4]

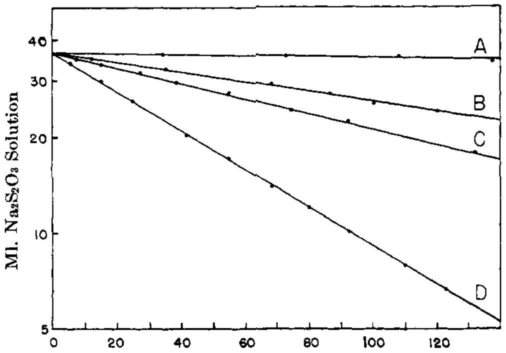

Fig. 1.—Rate of persulfate (0.02 *M*) oxidations in buffer solution at 60°: A, buffer alone; B, 2-butanol (0.02 *M*); C, 2-butanol (0.02 *M*) + 2-propanol (0.02 *M*); D, 2-propanol (0.02 *M*).

These data are summarized in Table I.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE DISAPPEARANCE OF 0.02 *M* $K_2S_2O_8$ IN BUFFERED AQUEOUS SOLUTIONS OF VARIOUS ORGANIC COMPOUNDS AT 60°

Substrate	k (hr.$^{-1}$)
Buffer solution alone	0.018
2-Propanol (0.02 *M*)	.84
Allyl acetate (0.04 *M*)	.060
Allyl acetate (0.04 *M*) + 2-propanol (0.02 *M*)	.063
2-Butanol (0.02 *M*)	.22
2-Butanol (0.02 *M*) + 2-propanol (0.02 *M*)	.30

We have also obtained similar results when equimolar concentrations of various other type organic compounds are present in the buffer solution together with isopropyl alcohol. Data for thiodiglycol sulfoxide at 70° are shown in Table II. We find, in general, that the more slowly the added compound is oxidized by persulfate, the more effective it is in diminishing the over-all rate of disap-

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[1] K. B. Wiberg, *J. Am. Chem. Soc.*, **81**, 252 (1959).

[2] The experimental procedure was identical with that previously described (ref. 10). It should be noted that we encountered no difficulty in obtaining reproducible data, though such difficulty was reported by J. O. Edwards, *et al.* (ref. 6).

[3] I. M. Kolthoff, E. J. Meehan, and E. M. Carr, *J. Am. Chem. Soc.*, **75**, 1439 (1953).

[4] It is seen from the first-order plots in Fig. 1 that the lines are perfectly straight with no evidence of the sigmoid character reported in ref. 6.