at 80° *in vacuo*. This crude product was purified by stirring with 10 l. of methylene chloride for 2 hr at room temperature, filtration, and repetition of this treatment. Drying of the product at 80° *in vacuo* afforded 1.577 kg of triol (**1a**). The analytical sample was obtained by recrystallization from methanol: mp 256–257°; $[\alpha]D$ −8°; ν_{max} 3440, 2870, 2940, 2960, 960–970 cm^{-1}; nmr, 5.13 (22, 23-H), 4.32–4.42 (3α-OH and 6α-H and 3α-H), 1.05 (19-H), 0.642 ppm (18-H).

Anal. Calcd for $C_{27}H_{50}O_3$: C, 77.97; H, 11.28; O, 10.75. Found: C, 77.88; H, 11.31; O, 10.78.

24-Ethylcholest-22-ene-3β,5α,6β-triol 3,6-Diacetate (1b).—A mixture of 1.530 kg of the triol **1b**, 3 l. of pyridine, and 1.5 l. of acetic anhydride was heated with stirring and under anhydrous conditions for 4 hr on the steam bath, and the resulting solution was left at room temperature overnight.

The reaction mixture was poured into 50 l. of water and stirred for 1 hr to hydrolize the excess acetic anhydride. The mixture was acidified with dilute hydrochloric acid, then extracted with methylene chloride; the extracts were washed with water until neutral, dried with anhydrous sodium sulfate, and concentrated to dryness *in vacuo* to yield an amorphous residue of crude 24-ethylcholest-22-ene-3β,5α,6β-triol 3,6-diacetate (**1b**). A pure specimen was obtained after filtration of the crude product through a column of silica gel, eluting with methylene chloride. The material resisted all attempts at crystallization but was shown to be homogeneous by thin layer chromatography: $[\alpha]D$ −61°; ν_{max} 3847, 2875, 2960, 3600, 1730, 1215, 960–970 cm^{-1}; nmr 5.16 (22, 23-H), 4.83–5.5 (3α-H), 4.78 (6α-H), 3.25 (OH), 2.31, 2.08 (2AcO), 0.704, (18-H), 0.988 ppm (19-H).

Anal. Calcd for $C_{33}H_{54}O_5 \cdot H_2O$: C, 74.39; H, 10.59; O, 15.02. Found: C, 74.56; H, 10.12; O, 15.17.

3β,5α,6β-Trihydroxy-23,24-bisnorcholan-22-oic Acid 3,6-Diacetate (1c).—The total crude residue from the above concentration was dissolved in 25 l. of ethyl acetate, cooled to −80° by means of an external acetone–Dry Ice bath and a stream of oxygen containing 6% of ozone[6] was bubbled in at a rate of 6.5 l. per minute for a total of 18 hr. The reaction vessel was removed from the cooling bath and a mixture of 1.08 l. of 40% peracetic acid[7] in 1.08 l. of water was added. The mixture was allowed to reach room temperature overnight under continuous mechanical stirring.

The mixture was washed with 10% aqueous sodium iodide solution, 10% aqueous sodium thiosulfate solution, and finally with water. The ethyl acetate layer was concentrated to dryness under reduced pressure. The residue was dissolved in ether and extracted with 5% aqueous potassium carbonate solution. The aqueous layer was washed several times with ether to eliminate neutral components and then acidified with concentrated aqueous hydrochloric acid. The mixture was extracted with methylene chloride, the extracts were washed with water until neutral, then d[illegible] anhydrous sodium sulfate, and distilled to dryness under reduced pressure to yield a crystalline residue of 3β,5α,6β-trihydroxy-23,24-bisnorcholan-22-oic acid 3,6-diacetate (**1c**). The pure specimen was prepared by several crystallizations from acetone–hexane: mp 193–194°; $[\alpha]D$ −58°; ν_{max} 3460, 1740, 1715, 1250 cm^{-1}; nmr 5.35–5.1 (3α-H), 4.7 (6α-H), 2.06 and 2.00 (2AcO), 1.28 (21-H), 1.15 (19-H), 0.71 ppm (18-H).

Anal. Calcd for $C_{26}H_{40}O_7$: C, 67.21; H, 8.68; O, 24.11. Found: C, 67.58; H, 8.72; O, 23.82.

3β,5α,6β-Trihydroxy-23,24-bisnorcholan-22-oic Acid (1d).—The total crude diacetate (**1c**) from the above operation was dissolved in 8 l. of methanol under reflux, then a solution of 520 g of potassium hydroxide in 500 ml of water was added slowly and the mixture was allowed to reflux for 4 hr, then was left overnight at room temperature. The solution was then concentrated to *ca.* 2.8 l. and carefully acidified with dilute hydrochloric acid. The mixture was then diluted to *ca.* 28 l. with 5% aqueous sodium chloride solution. The crystalline precipitate of 3β,5α,6β-trihydroxy-23,24-bisnorcholan-22-oic acid (**1d**) was collected by filtration, washed with water, and dried at 80° *in vacuo* to afford 940 g of **1d** (51.2% over-all from stigmasterol). The pure specimen was obtained by recrystallization from methanol: mp 275°; $[\alpha]D$ −20° (dioxane); ν_{max} 3840, 3450, 1710 cm^{-1}; nmr (in DMSO) 3.72–3.42 (OH), 3.3 (MeOH), 1.14 (21-H), 1.01 (19-H), 0.63 ppm (18-H).

(6) A Welsbach Ozonator style T-816 was used. (The Welsbach Corporation, Ozone Products Division, Philadelphia, Pa.

(7) 40% Peracetic acid in acetic acid, Becco peracetic acid, F.M.C. Corp., Inorganic Chemical Division, Buffalo, N. Y.

Anal. Calcd for $C_{22}H_{36}O_5 \cdot CH_3OH$: C, 64.83; H, 9.98; O, 25.19. Found: C, 65.82; H, 9.20; O, 24.95.

3β,5α,6β-Trihydroxy-23,24-bisnorcholan-22-oic Acid Methyl Ester (1e). A. By Esterification with Methanol–Sulfuric Acid.—A solution of 5 g of the carboxylic acid **1d** in 50 ml of methanol containing 2% (w/w) of concentrated sulfuric acid was heated under reflux for 2 hr on the steam bath. The reaction mixture was poured into 500 ml of 1% aqueous potassium hydroxide solution. The material that precipitated was collected by filtration and crystallized from ethyl acetate to yield 2.3 g of the methyl ester **1e**, (mp 228–230°, $[\alpha]D$ −18°) identical in all respects with an authentic specimen.[2a]

B. By Treatment with Methyl Iodide and Sodium Bicarbonate in Dimethyl Acetamide.—A solution of 872 g of crude carboxylic acid (**1d**) from the last reaction in 4.5 l. of dimethyl acetamide was treated with 450 g of sodium bicarbonate and 945 g of methyl iodide under anhydrous conditions. The mixture was stirred at room temperature in the dark for 48 hr, then poured into 90 l. of 10% aqueous sodium chloride solution. The crystalline material thus obtained was collected by filtration; washed with water, and dried *in vacuo* at 80° to afford 826 g of the methyl ester **1e**: mp 227–230°; $[\alpha]D$ −17°. This material did not depress the melting point of the authentic sample.[2a] It also exhibited similar ir and nmr spectra.

Registry No.—**1a**, 16118-24-4; **1b**, 16214-82-7; **1c**, 16176-01-5; **1d**, 16118-25-5; **1e**, 5241-14-5; stigmasterol, 83-48-7.

α,α-Di-*t*-butyl-β-propiolactone and Methyldi-*t*-butylacetic Acid from Di-*t*-butylketene[1]

MELVIN S. NEWMAN AND ARIE LEEGWATER[2]

Evans Chemistry Laboratory of The Ohio State University, Columbus, Ohio 43210

Received October 9, 1969

In earlier work, the preparation of di-*t*-butylketene (I) and its unreactivity was reported.[3] Herein we describe attempts to effect the reaction of I with a number of reagents which normally react with olefinic and carbonyl groups.

The first series of reactions involved attempts to add carbenes to the olefinic function of I. Di-*t*-butylketene was recovered almost quantitatively from the following treatments: (1) a mixture of I, methylene iodide, and Zn–Cu alloy in ether under reflux for 24 hr;[4] (2) a mixture of I, ethyl trichloroacetate, and sodium methoxide in pentane at 0° for 6 hr;[5] (3) a solution of I and phenyltrichloromethylmercury in benzene at 75° for 18 hr;[6] (4) a mixture of I, phenyltrichloromethylmercury, and sodium iodide in 1,2-dimethoxyethane (glyme) at room temperature for 15 hr;[7] and (5) a solution of I, bromomalononitrile,

(1) This work was supported by Grant GP-5552 of the National Science Foundation.

(2) Details of this work can be found in the Ph.D. thesis of A. Leegwater presented to The Ohio State University in 1967.

(3) M. S. Newman, A. Arkell, and T. Fukunaga, *J. Amer. Chem. Soc.*, **82**, 2498 (1960).

(4) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959). R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

(5) W. E. Parham, E. E. Schweizer, and S. A. Mierzwa, *Org. Syn.*, **41**, 76 (1960).

(6) D. Seyferth, J. M. Burlitch, and J. K. Heeren, *J. Org. Chem.*, **27**, 1491 (1962).

(7) D. Seyferth, J. Y-P. Mui, M. E. Gordon, and J. M. Burlitch, *J. Amer. Chem. Soc.*, **87**, 681 (1965).

and triethylamine in ether[8] at −30° for 2 hr. In the first of these experiments a complex which had no ketene band at 4.8 μ was obtained in solution. However, on concentration or warming an exothermic reaction occurred and I was recovered. In one attempt to generate a sulfene[9] in the presence of I, no addition was obtained and 67% of the starting I was recovered. Similarly, 80% of I was recovered from an attempt at reaction of dimethylsulfoxonium methylide[10] with I. When benzyne was generated[11] in the presence of I the latter was recovered in 87% yield. Finally, no reaction occurred when a solution of diazomethane in methylene chloride[12] was added to I at 0° and the solution later allowed to come to room temperature. Catalysis of this reaction by cuprous chloride[13] was also ineffective.

On addition of gaseous formaldehyde to an ether solution of I containing catalytic amounts of boron trifluoride α,α-di-*t*-butyl-β-propiolactone (II) was formed in 68% yield. However, attempts to condense acetaldehyde or acetone under similar conditions afforded only di-*t*-butylacetic acid. The latter probably resulted from the reaction of water, formed in the aldol reactions of acetaldehyde and of acetone, with I.

All attempts to reduce II with sodium, zinc in formic acid, or with isoproplymagnesium iodide resulted in recovery of II. However, treatment with lithium aluminum hydride resulted in the formation of methyldi-*t*-butylacetic acid in 70% yield. This reduction of the carbon–oxygen single bond in II stands in marked contrast to the reduction of tetramethyl-β-propiolactone[14] and of α,α-diphenyl-β-propiolactone[15] to 1,3-propanediols.

Experimental Section

α,α-Di-*t*-Butyl-β-propiolactone (II).—To a magnetically stirred solution of 4.8 g of I in 20 ml of dry ether containing a few drops of BF_3–etherate in a 100-ml flask was passed the formaldehyde generated by heating 4.5 g of paraformaldehyde (dried for 2 weeks over P_2O_5) during 1 hr. After stirring for an additional 1.5 hr at room temperature the mixture was filtered to remove solids and the filtrate was added to water. The ether layer obtained by extraction was dried over $MgSO_4$ and the ether was removed by evaporation. Crystallization of the residue from hexane at −70° yielded 3.9 g (68%) of colorless II, mp 116–118°. The analytical sample (mp 118–119°) was obtained by sublimation and showed a strong absorption at 5.51 μ (1815 cm^{-1}).[16] The nmr spectrum showed a singlet (9 H) at τ 8.82 and a singlet (1 H) at τ 5.98.

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.7; H, 10.9. Found:[17] C, 71.8; H, 11.1.

Methyldi-*t*-butylacetic Acid.—A solution of 1.84 g of II and 0.6 g of $LiAlH_4$ in 30 ml of THF was refluxed for 16 hr. After the usual isolation procedure 1.48 g of crude acid was obtained. Recrystallization from methanol–water gave 1.3 g (70%) of pure acid, mp 179–180°.

Anal. Calcd for $C_{11}H_{22}O_2$: C, 70.9; H, 11.9. Found:[17] C, 71.1; H, 12.0.

The nmr spectrum in CCl_4 showed two singlets at τ 8.86 and 8.81 in the ratio of about 5.8:1 (there was some difficulty in integration owing to the proximity of the peaks[18]).

Registry No.—Methyl-di-*t*-butylacetic acid, 16021-12-8; II, 16021-13-9.

(18) We thank Professor Robert Ouellette for this determination.

(8) J. S. Swenson and D. J. Renaud [*J. Amer. Chem. Soc.*, **87**, 1394 (1965)] generated dicyanocarbene in this way.

(9) W. E. Truce and J. R. Norell, *ibid.*, **85**, 3231 (1963).

(10) E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1353 (1965).

(11) G. Wittig and L. Pohmer, *Ber.*, **89**, 1334 (1956).

(12) W. B. Hammond and N. J. Turro, *ibid.*, **88**, 3672 (1966).

(13) W. von E. Doering and W. Roth, *Tetrahedron*, **19**, 715 (1963).

(14) G. Natta, G. Mazzanti, G. Pregaglia and M. Binaghi, *J. Amer. Chem. Soc.*, **82**, 5511 (1960).

(15) H. E. Zautgg and B. W. Horrom, *Anal. Chem.*, **20**, 1026 (1948).

(16) Y. Etienne and N. Fischer, "Heterocyclic Compounds with Three- and Four-membered Rings," part II, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 779.

(17) Microanalyses by Galbraith Laboratories, Inc., Knoxville, Tenn.

Quantitative Studies in Stereochemistry. Electrochemistry. II. The Ratio of Diastereomeric Glycols Formed in the Electrolytic Bimolecular Reduction of Benzaldehyde and Propiophenone

JACK H. STOCKER AND ROY M. JENEVEIN

Department of Chemistry, Louisiana State University in New Orleans, New Orleans, Louisiana 70122

Received September 27, 1967

Previously reported[1] isotope dilution studies in the title area described the ratios of *dl*- to *meso*-acetophenone pinacol observed in acid and alkaline media. A mechanism to account for the change from a ratio of approximately 1.2 *dl*/*meso* in acid media to 2.7–3.2 in alkaline media was proposed. The present note extends these studies to include the corresponding ratios resulting from the electrolytic reduction of carbon-14-labeled benzaldehyde and propiophenone. The two pairs of diastereomeric glycols needed for the dilution studies are known and their stereochemical identities were previously established.[2]

When the study was essentially complete, it was observed that adequately quantitative data could also be determined for the benzaldehyde system by nmr techniques.[3] Several such runs are included with the isotope dilution studies tabulated in Table I. Two new acetophenone runs by this technique, complementing those previously reported, are also included for useful comparisons.

With the exception of the results for the benzaldehyde system in alkaline media, the ratios show very little change from those observed when acetophenone is electrolytically reduced. In acid media, the reaction is slightly stereoselective in favor of the *dl* form for all three carbonyl compounds. There would appear to be a very slight increase in *dl*/*meso* ratio in the order benzaldehyde-acetophenone-propiophenone. The increase, if real, is very small.

The *dl*/*meso* ratios of pinacols formed in alkaline media fall in essentially the same range for acetophenone and propiophenone, 2.7–3.2. However, those for benzaldehyde drop sharply to an average of 1.2, unchanged from acid solution. Two possible explanations of the phenomenon can be made: (a) the

(1) J. H. Stocker and R. M. Jenevein, *J. Org. Chem.*, **33**, 294 (1968).

(2) For the assignment of diastereomeric hydrobenzoins, see G. Berti and F. Battari, *ibid.*, **25**, 1286 (1960). For the propiophenone pinacols, see W. A. Mosher and N. D. Heindel, *ibid.*, **28**, 2154 (1963).

(3) The relative heights of the *meso*- and *dl*-hydrobenzoin benzylic proton peaks provided the desired ratio; an area comparison with the total aromatic protons, after normalization, permitted yield calculations. Unreacted benzaldehyde may be determined from the aldehydic proton area. For analogous studies with substituted acetophenones, see J. H. Stocker, D. H. Kern, and R. M. Jenevein, *ibid.*, **33**, 412 (1968).