oleic acid, the side reactions being less important. Reaction of elaidic acid under the optimum conditions was essentially similar to that of oleic acid.

Reaction between Perchloric Acid and Undecylenic Acid.—Undecylenic acid (49.3 g, 268 mmol) and perchloric acid (70.2%, 37.9 g, 261 mmol) were heated at 100° for 3 hr and worked up using procedures similar to those for oleic acid. The acid fraction of the reaction product was polymeric, as indicated by its complete retention on glpc columns. The total residue contained 2.8% of α,β-conjugated carbonyl-containing compounds (λ_{max} at 230 mμ), 2-alkyl-substituted 2-cyclopentenone and 2-cyclohexenone. Fractional distillation of the neutral residue through a spinning-band column gave the colorless γ-undecalactone (bp 146° at 4.5 mm) in 48% yield.

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.43; H, 10.76.

Registry No.—I, 112-80-1; II, 502-26-1; XI, 16317-08-1; γ-erucalactone, 16317-09-2; 4-hydroxyoctadecanoic acid, 2858-39-1; γ-undecalactone, 104-67-6; perchloric acid, 7616-81-1.

The Electrochemical Oxidation of Epimeric β-Hydroxycycloalkylacetic Acids[1]

LEON RAND AND C. SOMESWARA RAO

Department of Chemistry, University of Detroit, Detroit, Michigan 48221

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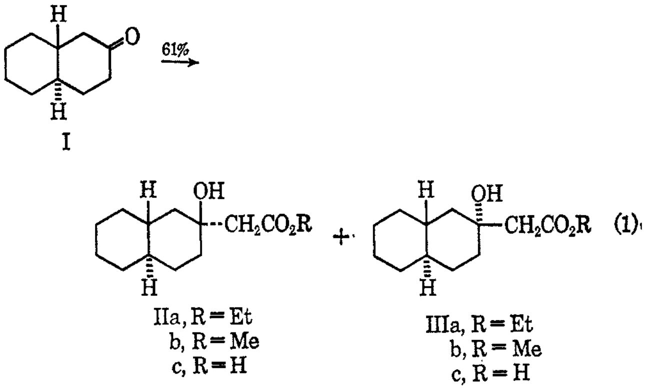
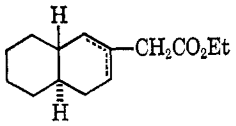
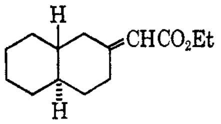
Chemical and spectral evidence for the configurations of the epimeric Reformatsky products from *trans*-2-decalone and cholestanone is presented. Electrochemical oxidation–decarboxylation of each of the epimeric β-hydroxycarboxylic acids derived from *trans*-2-decalone gave products *via* both radical and carbonium ion intermediates. No significant product differences attributable to the different configurations of the acids were found. Methyl substitution α to the carboxyl led to no specific bond migration in the rearrangement of the carbonium ion leading to homologated ketones.

In order to ascertain the possible effect of configurational differences on product distribution in the Kolbe electrosynthesis reaction, a study of the electrooxidation of epimeric β-hydroxycycloalkylacetic acids was undertaken. This reaction, which gives rise to ring homologated ketones *via* carbonium ion intermediates, was briefly described by Corey and his coworkers[2] in 1960. It seemed reasonable that steric differences might bear upon the electrode absorptivity requirements for the electrode processes leading to intermediates and possibly to the products as well. This report deals with the preparation and characterization of isomeric Reformatsky products from *trans*-2-decalone and cholestanone and the electrolysis of the pair of epimeric acids derived from the former.





IV



V

Results and Discussion

The Reformatsky reaction of *trans*-2-decalone with ethyl bromoacetate and zinc in tetrahydrofuran gave a 61% yield of the two epimeric hydroxy esters, IIa and IIIa, in a 1:1 ratio after column chromatography (eq 1). The isomer that was eluted first (IIa) was assigned the axial (β) hydroxyl configuration. Chemical evidence for the hydroxyl configurations was obtained by dehydration of the hydroxy esters with pyridine–phosphoryl chloride.[3] The α isomer (IIIa), with an equatorial hydroxyl, gave as the major product an exocyclic olefin (V), while the β isomer gave an endocyclic olefin (IV).

The nmr spectra of the two epimers in dimethyl sulfoxide showed a chemical-shift difference of 0.23 ppm for the hydroxyl protons, the equatorial OH in IIIa resonating at a lower field in agreement with the observations of Chapman and King[4] (Table I).

TABLE I

NMR SPECTRA (δ) OF EPIMERS IIa AND IIIa (IN PARENTHESES)[a]

DMSO-d_6	$CDCl_3$	Benzene	Pyridine
1.09 (1.10)	1.27 (1.30)	0.34 (0.34)	0.57 (0.46) (ester CH_3, three protons, T, J = 7 cps)
2.25 (2.37)	2.40 (2.59)	1.68 (1.89)	1.90 (2.06) ($-CH_2CO-$, two protons, S)
4.13 (4.36)	3.62 (3.16)	2.73	4.36 (4.65) (OH, one proton)
3.99 (3.99)	4.16 (4.22)	3.34 (3.37)	3.48 (3.50) ($-OCH_2-$, two protons, Q, J = 7 cps)

[a] T = triplet; S = singlet; Q = quartet.

The nmr spectra of these epimeric esters exhibited two interesting features. One was the singlet resonance of the geminal methylene protons of the acetic ester side chain instead of an AB quartet, even though the adjacent ring carbon is asymmetric. The other feature was that the axial methylene in IIIa resonated at a lower field than the equatorial one although one might expect the reverse because of C–C bond anisotropies. Surprisingly, these methylene resonances were reversed in the nmr spectra of the corresponding car-

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[1] (a) Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967. (b) Supported by the Michigan Cancer Foundation.

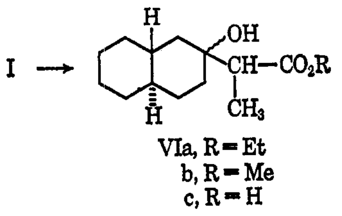
[2] E. J. Corey, N. L. Bauld, R. T. LaLonde, and J. Casanova, Jr., *J. Amer. Chem. Soc.*, **82**, 2645 (1960).

[3] D. H. R. Barton, A. da S. Campos-Neves, and R. C. Cookson, *J. Chem. Soc.*, 3500 (1956); J. L. Beton, T. G. Halsak, E. R. H. Jones, and P. C. Phillips, *ibid.*, 753 (1957).

[4] O. L. Chapman and R. W. King, *J. Amer. Chem. Soc.*, **86**, 125 (1964).

boxylic acids in which the axial methylene resonated at a higher field. Comparison of the nmr spectra of the esters in $CDCl_3$ and in benzene did not reveal any differences, the axial and equatorial methylenes both having nearly equal upfield shifts of *ca.* 0.7 ppm which indicates similar geometries for the collision complexes. Pyridine also caused equal upfield shifts of *ca.* 0.5 ppm. The ester methyl and methylene protons also showed large upfield shifts in both of these solvents.

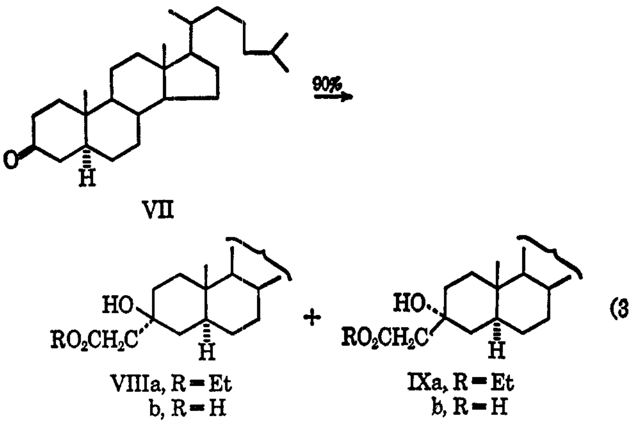
To determine the effect on the electrolytic behavior of an alkyl group α to the carboxyl, the Reformatsky product of *trans*-2-decalone and ethyl α-bromopropionate was prepared. Hydrolysis of the ester followed by fractional recrystallization of the resulting acid mixture yielded one of the isomers (VIc) whose configuration was not determined (eq 2).



VIa, R = Et
b, R = Me
c, R = H

(2)

The Reformatsky reaction of cholestanone with ethyl bromoacetate, which was studied earlier by Campos-Neves,[5] was repeated. The *cis*- and *trans*-hydroxy esters VIIIa and IXa, in a 3:2 ratio, were obtained in 90% yield after column chromatography (eq 3). The *trans* isomer which was eluted first was the higher melting and the more sparingly soluble of the two. As was found with the hydroxy esters derived from *trans*-2-decalone, the axial and equatorial methylenes of the acetic ester side chain had an appreciable chemical-shift difference, the former resonating at a lower field as a singlet. Because of the insolubility of the esters in DMSO, the nmr spectra were taken in pyridine[6] in which solvent the hydroxyl resonances had a chemical-shift difference of 0.48 ppm; the equatorial hydroxyl (VIIIa) resonating at a lower field (see Table II).



VII

VIIIa, R = Et
b, R = H

IXa, R = Et
b, R = H

(3)

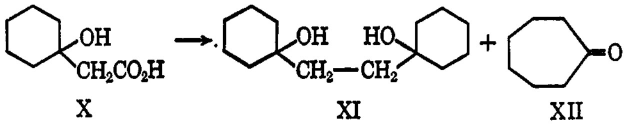
TABLE II
CHEMICAL SHIFTS AND MULTIPLICITY[a] OF SOME ALCOHOLS IN PYRIDINE

Compound	Chemical shift (δ)	Multiplicity	Coupling constant, J, cps
Methanol	4.7	Q	5.5
2-Hexanol	4.73	D	5
Allyl alcohol	5.7	T	5
Benzyl alcohol	5.92	T	5.5
1,3,5-Triisopropylbenzyl alcohol	5.25	T	4.5
Cholesterol	4.77	D (partially) resolved)	4.5

[a] Q = quartet; T = triplet; D = doublet.

Electrolysis Studies

Electrolysis of 1-Hydroxycyclohexylacetic Acid.[2,7]—To gain an insight into the reaction, an attempt was made to optimize the yield of cycloheptanone but yields greater than *ca.* 50% could not be realized. Electrolysis at lower temperatures were carried out at a carbon anode[8] which appeared to avoid the surface coating problems encountered with a platinum anode. While no dimer was obtained with the solvents acetonitrile, dimethylformamide, or 10% water in pyridine using a carbon anode, substantial dimer XI formation was observed with N-methylformamide as the solvent (eq 4).



X XI XII

(4)

Dimer formation could not be suppressed even at −40° in methanol. At 0° the yield of dimer had trebled while the yield of cycloheptanone was not changed appreciably (Table III).

Electrolysis of (2β-Hydroxy-2-*trans*-decalyl)acetic Acid (IIc) and the Epimeric Acid (IIIc).—Electrolysis of the β-hydroxy acid (IIc) in DMF using a carbon anode gave 76% CO_2, 56% a mixture of the two possible homodecalones XIII and XIV (75% in N-methylformamide as solvent), 2% dimer XVa, 15% an hydroxy ester probably of the structure XVIa, and 2.9% a nitrogen-containing substance assigned the structure XVII. The 2,4-dinitrophenylhydrazone of the homodecalone mixture had a wide melting point range, but neither this derivative nor the ketonic mixture could be resolved by chromatographic techniques. Structure assignment to the nitrogen-containing substance (XVII) was based on the ir and nmr spectra supported by the mass spectrum. The nmr spectrum in DMSO showed the tertiary nature of the hydroxyl by its singlet resonance at δ 4.65, a doublet for the N-methyl group coupled with the NH proton, a higher field singlet for the side-chain methylene attached to the amide carbonyl, and a broad lowfield signal for the NH proton. The mass spectrum exhibited a

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(5) A. da S. Campos-Neves, *Bol. Escola. Farm. Univ. Coimbra*, **19-20**, 207 (1959-1960); *Chem. Abstr.*, **56**, 4821 (1962).

(6) R. T. Oulette [*J. Amer. Chem. Soc.*, **86**, 4378 (1964)] has observed the chemical-shift difference of hydroxyls in *cis*- and *trans*-4-*t*-butylcyclohexanols in pyridine, but no mention was made of any observation of spin-spin coupling of the hydroxyl proton and the proton on the carbon bearing the hydroxyl.

Primary, secondary, and tertiary alcohols can be differentiated by observing the multiplicity of the hydroxyl resonance in the nmr spectra in dry pyridine (10% solution). Some values for hydroxyl peaks are shown in Table II. Where comparisons had been made with DMSO as solvent it was seen that the hydroxyl resonances occur farther downfield in pyridine than in DMSO, possibly indicating the formation of stronger H bonds with pyridine.

(7) Triethylamine was used in all the electrolyses to effect partial neutralization.

(8) J. Koehl, Jr., *J. Amer. Chem. Soc.*, **86**, 4686 (1964).

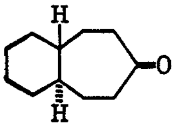
TABLE III

ELECTROLYSIS OF 1-HYDROXYCYCLOHEXYLACETIC ACID

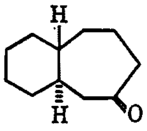
Amount, g (mol)	Solvent (ml)	NEt_3, ml (mol)	Anode	Applied voltage, V	Temp, °C	Current, mA	CO_2, %	% yield Dimer XI	% yield Ketone XII
3.16 (0.02)	DMF (35)	0.6 (0.004)	Pt	100	60–70	400	91	18–20	9
3.16 (0.02)	DMF (40)	0.6 (0.004)	Pt	150	100–110	1000	90	40	5
3.16 (0.02)	CH_3CN (18)	0.9 (0.006)	C	54–130	10	400	55	0	50
4.0 (0.025)	CH_3CN (15)	1.8 (0.012)	C	40–140	10–15	500	54	0	47
4.0 (0.025)	DMF (15)	0.9 (0.006)	C	50–120	10–15	450	55	0	50
3.0 (0.019)	10% H_2O in pyridine	1 (0.0066)	C	70–140	15–20	300	...	0	55
3.0 (0.019)	N-Methylformamide	1 (0.0066)	C	30–90	10–15	450	82	14	50
10 (0.063)	CH_3OH (30)	5.4 (0.036)	C	45–120	−40	450	...	8.3	27
10 (0.063)	CH_3OH (30)	2.7 (0.018)	C	24–60	0	470	70	23.3	30

molecular ion at *m/e* 225 and intense peaks at M − 18, M − 153, M − 195, etc. The M − 153 peak may be the result of a simple β cleavage of the N-methylacetamido group not accompanied by H rearrangement. The intense peak at *m/e* 30 (M − 195) is attributed to the species $(NH_2{=}CH_2)^+$ characteristic of many secondary amide spectra.[9]

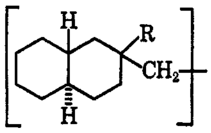
Electrolysis of the α-hydroxy acid (IIIc) under conditions similar to those employed for the epimeric acid (IIc) gave 72% CO_2, 50% the mixture of homodecalones (XIII and XIV), 2% dimer XVb, and 12% an hydroxy ester probably of the structure XVIb.



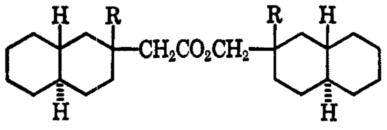
XIII



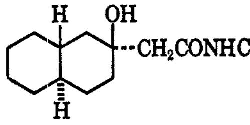
XIV



XVa, R = β-OH
b, R = α-OH



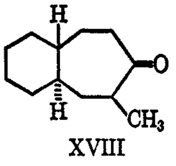
XVIa, R = β-OH
b, R = α-OH



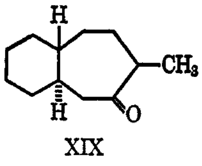
XVII

The 2,4-dinitrophenylhydrazone of this homodecalone mixture had a large melting point range similar to that of the homodecalone mixture obtained from the β-hydroxy acid (IIc), and from which information the similar composition was judged. Except for the somewhat lower yields of the ketonic product from the α epimer there did not appear to be any significant differences in the electrolytic behavior of these epimeric acids based on the equal distribution of dimeric, ketonic, and ester products.

Electrolysis of α-(2-Hydroxy-2-*trans*-decalyl)propionic Acid (VIc).—In order to determine the effect of α-alkyl substitution on the product distribution the α-methylhydroxy acid (VIc) was electrolyzed under conditions similar to those described above. No dimeric or ester products could be isolated but the two possible α-methylhomodecalones were obtained in 58% yield in a 1:1 ratio based on the integrated nmr spectrum in which the two methyls showed distinct doublets.



XVIII



XIX

Attempted Electrolysis of 3-Carboxymethylcholestan-3-ol.—The hydroxy acids VIIIb and IXb were quite sparingly soluble in the preferred solvents such as DMF, acetonitrile, and pyridine. Hexamethylphosphoramide was the best solvent found for these acids but at the low temperatures employed (10–15°) during electrolysis the solution viscosity was high and current density low. In methanol-hexamethylphosphoramide mixtures as solvent, electrolysis could be carried out but only quite low yields of dimeric product could be isolated and the reaction was not investigated further.

Experimental Section

The nmr spectra were recorded downfield relative to TMS at 0 ppm as an external standard using a Varian A-60A spectrometer. Multiplicity of the signals is denoted by S = singlet, D = doublet, T = triplet, and Q = quartet. The ir spectra were obtained with a Beckman IR-5 spectrophotometer. Mass spectra were obtained using a CEC Model 110-B mass spectrometer. Melting points are uncorrected. The petroleum ether used had bp 30–45°.

Reformatsky Reaction of *trans*-2-Decalone.—To a gently refluxing, stirred solution of 55 g (0.36 mol) of *trans*-2-decalone and 67 g (0.4 mol) of freshly distilled ethyl bromoacetate in 500 ml of dry tetrahydrofuran was added 36 g (0.55 mol) of activated zinc[10] in three lots, the first addition being followed by a crystal of iodine. The reaction mixture was refluxed for 2 hr, cooled to 5°, acidified with 2 l. of 5% H_2SO_4 at 5° and worked up by ether extraction. Removal of solvent gave 84 g of yellow viscous liquid which was chromatographed in two lots on two 1-kg portions of alumina, elution being carried out initially with 5% ethyl acetate in benzene and finally with ethyl acetate. A total of 22.1 g of hydroxy ester IIa, mp 32–35°, 25.6 g of hydroxy ester IIIa, mp 40–43°, and 5.8 g of a mixture of these two were obtained. Total yield was 53.5 g (61%). The nmr spectra of the epimers IIa and IIIa are given in Table I. Each ester was saponified with a fourfold excess of 20% NaOH solution at 70–80° for 6 hr, cooled to 5°, and acidified with 5% H_2SO_4. The acid was filtered, washed, dried in a vacuum desiccator, and recrystallized from anhydrous ether.

(2β-Hydroxy-2-*trans*-decalyl)acetic acid (IIc) exhibited the following characteristics: mp 118–119°; $\nu_{max}^{CHCl_3}$ 3546–3175 (broad, OH and carboxylic OH) and 1709 cm^{-1} (carboxylic C=O); nmr ($CDCl_3$), δ 2.65 (–CH_2CO–, two protons, S) and 7.54 (OH and CO_2H, two protons, disappeared upon addition of D_2O).

Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.93; H, 9.63. Found: C, 68.25; H, 9.30.

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[9] J. A. Gilpin, *Anal. Chem.*, **31**, 935 (1959); H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, 1964, Chapter 4.

[10] L. F. Fieser and W. S. Johnson, *J. Amer. Chem. Soc.*, **62**, 575 (1940).

(2α-Hydroxy-2-*trans*-decalyl)acetic acid (IIIc) exhibited the following characteristics: mp 143–144°; $\nu_{\max}^{CHCl_3}$ 3546–3175 (broad, OH and carboxylic OH) and 1709 cm^{-1} (carboxylic C=O); nmr ($CDCl_3$), δ 2.49 (–CH_2CO–, two protons, S) and 7.16 (OH and CO_2H, two protons, disappeared upon addition of D_2O).

Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.93; H, 9.63. Found: C, 68.17; H, 9.49.

The methyl esters were prepared by reaction with diazomethane and recrystallized from petroleum ether.

Methyl (2β-hydroxy-2-*trans*-decalyl)acetate (IIb) exhibited the following characteristics: mp 47.5–48.5°; nmr (DMSO-d_6), δ 2.36 (–CH_2CO–, two protons, S), 3.59 (OCH_3, three protons, S), and 4.17 (OH, one proton, S).

Anal. Calcd for $C_{13}H_{22}O_3$: C, 69.03; H, 9.73. Found: C, 69.29; H, 9.84.

Methyl (2α-hydroxy-2-*trans*-decalyl)acetate (IIIb) exhibited the following characteristics: mp 75.5–76.0°; nmr (DMSO-d_6), δ 2.46 (–CH_2CO–, two protons, S), 3.59 (OCH_3, three protons, S), and 4.4 (OH, one proton, S).

Anal. Calcd for $C_{13}H_{22}O_3$: C, 69.03; H, 9.73. Found: C, 69.43; H, 9.34.

Pyridine–Phosphoryl Chloride Dehydrations.—A solution of 0.52 g of ethyl (2α-hydroxy-2-*trans*-decalyl)acetate (IIIa) in 20 ml of dry pyridine was treated in the cold with 5 ml of freshly distilled phosphoryl chloride and allowed to stand overnight at room temperature. The solution was added to ice-cold water and worked up by ether extraction to give 0.54 g of a liquid with no OH absorption in the ir spectrum. Distillation at 120° (0.1 mm) in a short-path distillation tube gave a colorless liquid which was predominantly the exocyclic olefin (V) contaminated with *ca.* 20% of the endocyclic isomer (IV): $\nu_{\max}^{film}$ 1712 (ester C=O) and 1645 cm^{-1} (strong C=CH); nmr ($CDCl_3$), δ 1.3 (ester methyl, T, *J* = 7 cps), 4.19 (–OCH_2–, Q, *J* = 7 cps), and 5.65 (=CH, S).

Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.67; H, 9.97. Found: C, 75.62; H, 10.10.

A solution of 0.5 g of ethyl (2β-hydroxy-2-*trans*-decalyl)acetate (IIa) in 20 ml of pyridine was similarly dehydrated with 5 ml of phosphoryl chloride. The crude product was distilled at 120° (0.1 mm) to give predominantly the endocyclic olefin (IV) contaminated with *ca.* 20% of the exocyclic isomer: $\nu_{\max}^{film}$ 1730 (ester C=O) and 6.08 (medium, C=CH); nmr ($CDCl_3$), δ 1.29 (ester methyl, T, *J* = 7 cps), 2.98 (CH_2 flanked by a double bond and an ester C=O, S), 4.19 (–OCH_2–, Q, *J* = 7 cps), and 5.59 (C=CH, broad).

α-(2-Hydroxy-2-*trans*-decalyl)propionic acid (VIc).—The Reformatsky reaction was carried out essentially as described above with 22 g of *trans*-2-decalone, 27 g of ethyl α-bromopropionate in 200 ml of tetrahydrofuran, and 10 g of activated zinc. The reaction product (36 g) was chromatographed on 1 kg of basic alumina. The eluate (27 g) from 5% MeOH–EtOAc and 20% MeOH–EtOAc was saponified with 150 ml of 10% NaOH solution at 70–80° with stirring for 6 hr, cooled, and acidified with 2% H_2SO_4 at 5–10°. Work-up by ether extraction gave 19.8 g of a brown viscous liquid. Crystallization from petroleum ether–dry ether gave 8 g of a white crystalline material, mp 155–158°. Recrystallization from petroleum ether gave VIc as white needles: mp 157–158°; $\nu_{\max}^{CHCl_3}$ 3448 (OH and CO_2H, broad) and 1709 cm^{-1} (carboxylic C=O), addition of 2 drops of triethylamine shifted the carbonyl band to 1597 cm^{-1}; nmr ($CDCl_3$ + 1 drop of pyridine), δ 1.22 (CH_3, three protons, D, *J* = 7 cps) and 2.46 (CH_3**CH**–, one proton, Q, *J* = 7 cps).

Anal. Calcd for $C_{13}H_{22}O_3$: C, 69.03; H, 9.73. Found: C, 69.38; H, 9.88.

The methyl ester prepared by reaction with diazomethane was crystallized from petroleum ether to give methyl α-(2-hydroxy-2-*trans*-decalyl)propionate (VIb) as white needles, mp 64.5–65.5°.

Anal. Calcd for $C_{14}H_{24}O_3$: C, 70.88; H, 10.24. Found: C, 70.38; H, 9.99.

Reformatsky Reaction with Cholestanone.—The Reformatsky reaction of 33 g of cholestanone [dried at 132° (2 mm) for 4 hr] was carried out as described above for *trans*-2-decalone, using 18 g of ethyl bromoacetate and 12 g of activated zinc to give 40 g of the crude reaction product. Chromatography of 35 g on 900 g basic alumina gave 13.2 g of the *trans*-hydroxy ester (IXa), mp 95–98° (from 3 l. of 10% EtOAc in benzene), 0.27 g of a mixture, and 18.3 g of the *cis* isomer (VIIIa), mp 70–73° (from 2.5 l. of EtOAc). Both the epimers were recrystallized from absolute methanol.

3-Carboethoxymethylcholestan-3α-ol (IXa) exhibited the following characteristics: white flakes; mp 96.5–97.5° (lit.[5] mp 98.5–99°); $\nu_{\max}^{CCl_4}$ 3546 (OH) and 1724 cm^{-1} (ester C=O); nmr ($CDCl_3$), δ 1.38 (ester methyl, T, *J* = 7 cps), 2.42 (–CH_2CO–, two protons, S), 4.18 (–OCH_2–, two protons, Q, *J* = 7 cps), and 2.97 (OH, broad); nmr (pyridine), δ 4.52 (OH one proton, S) and 1.98 (–CH_2CO–, two protons, S).

Anal. Calcd for $C_{31}H_{54}O_3$: C, 78.47; H, 11.39. Found: C, 78.70; H, 11.39.

3-Carboethoxymethylcholestan-3β-ol (VIIIa) exhibited the following characteristics: mp 72.5–73.5°; $\nu_{\max}^{CCl_4}$ 3546 (OH) and 1727 cm^{-1} (ester C=O); nmr ($CDCl_3$), δ 1.25 (ester methyl, T, *J* = 7 cps), 2.58 (–CH_2CO–, two protons, S), 4.18 (–OCH_2–, two protons, Q, *J* = 7 cps; nmr (pyridine), δ 5.0 (OH, one proton, S) and 2.12 (–CH_2CO–, two protons, S).

Anal. Calcd for $C_{31}H_{54}O_3$: C, 78.47; H, 11.39. Found: C, 78.67; H, 11.85.

Saponification with 10% alcoholic KOH gave the *trans* acid (IXb), mp 198–200° (lit.[5] mp 198.5–200°), and the *cis* acid (VIIIb), mp 219–220° (lit.[5] mp 219–220°).

Electrochemical Oxidation Experiments.—Ascarite bulbs were used to trap CO_2 liberated during the electrolysis. The electrolytic cell has been described previously.[11] A coolant at −15° was run through the outer jacket of the cell. The carbon anode when used, was a rod 3 mm in diameter and protruding 2 cm from a glass sleeve. The platinum electrodes employed circular Pt foil 1 cm in diameter. The electrodes were separated by a distance of 5 mm. The yields of dimeric, ketonic, and ester products in the electrolyses were calculated based on the starting hydroxy acid.

Electrolysis of 1-Hydroxycyclohexylacetic Acid (X).—A solution of the hydroxy acid was partially neutralized with triethylamine and then electrolyzed between Pt electrodes or a carbon anode and a Pt cathode. The various conditions are shown in Table III. When the neutral product from the electrolysis was warmed with petroleum ether the dimer separated out as a white powder. The residue from the mother liquors was treated with excess 2,4-dinitrophenylhydrazine reagent to afford the cycloheptanone derivative. Recrystallization from petroleum ether–ethyl acetate gave yellow needles, mp 150–151°, mixture melting point with an authentic sample undepressed. The dimer was recrystallized from a large volume of ether to give 1,2-bis(1-hydroxy-1-cyclohexyl)ethane (XI) as colorless, fine needles, mp 132–133° (lit.[12a] mp 129°, 130–131°[12b]). The mass spectrum showed M^+ at *m/e* 226.

Anal. Calcd for $C_{14}H_{26}O_2$: C, 74.33; H, 11.57. Found: C, 74.61; H, 11.55.

Electrolysis of (2β-Hydroxy-2-*trans*-decalyl)acetic Acid (IIc).—A solution of 2.96 g of the hydroxy acid in 11 ml of DMF (dried over Linde 5A Molecular Sieves) containing 1 ml of triethylamine was electroyzed using a carbon anode at an initial applied voltage of 54 V and at 15°. To maintain the current at *ca.* 300 mA the applied voltage was increased slowly to 140 V during 5 hr; electrolysis was continued for 19 hr. The dark electrolysate was poured into ice-cold water and extracted thoroughly with ether, and the ether extract was successively washed with ice-cold 3 *N* HCl, 5% NaOH solution, and brine, dried ($MgSO_4$), and distilled to give 2.3 g of a brown liquid. On dilution with petroleum ether, 50 mg of a crystalline solid separated out. Repeated recrystallization from absolute methanol gave 1,2-bis(2β-hydroxy-2-*trans*-decalyl)ethane (XVa) as white flakes: mp 207–207.5°; $\nu_{\max}^{KBr}$ 3333 cm^{-1} (OH); M^+ in the mass spectrum at *m/e* 334.

Anal. Calcd for $C_{22}H_{38}O_2$: C, 79.04; H, 11.38. Found: C, 79.44; H, 11.48.

The mother liquors were concentrated and chromatographed on 70 g of neutral alumina. Elution with 400 ml of benzene gave 1.32 g of a mixture of ***trans*-bicyclo[5.4.0]undecan-3-one** (XIII) and ***trans*-bicyclo[5.4.0]undecan-4-one** (XIV) of uncertain proportion. The 2,4-dinitrophenylhydrazone of this mixture was recrystallized from 95% ethanol: mp 114–135°; M^+ in the mass spectrum was at *m/e* 346

Anal. Calcd for $C_{17}H_{22}N_4O_4$: C, 58.95; H, 6.36; N, 16.19. Found: C, 59.36; H, 6.44; N, 16.15.

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(11) L. Rand and A. F. Mohar, *J. Org. Chem.*, **30**, 3156, 3885 (1965).

(12) (a) C. D. Nenitzescu and I. Necsoiu, *J. Amer. Chem. Soc.*, **72**, 3483 (1950); (b) A. S. Bailey, D. G. M. Diaper, and M. V. H. Schwemin, *Can. J. Chem.*, **39**, 1147 (1961).

The eluate (0.35 g) from 500 ml of ethyl acetate, a brown viscous gum, was warmed in petroleum ether from which 15 mg of a white powder and 90 mg of a hard crystalline substance separated. Recrystallization of the larger fraction from petroleum ether–ether gave white needles of 2-(N-methylacetamido)-*trans*-decalin-2β-ol (XVII): mp 109.5–110°; ν_{max}^{KBr} 3497, 3289 and 3125 (OH and NH) and 1639 cm^{-1} (amide C=O); nmr ($CDCl_3$), δ 2.26 ($-CH_2CO-$, two protons, S), 2.8 (CH_3, three protons, D, J = 5 cps) and 4.34 (OH, one proton, disappeared upon addition of D_2O); nmr (DMSO-d_6), δ 2.16 ($-CH_2CO-$, two protons, S), 2.59 (CH_3, three protons, D, J = 5 cps), 4.65 (OH, one proton, S), and 7.76 (NH, one proton, broad); M^+ in the mass spectrum at *m/e* 225, intense peaks at M − 18, M − 17, M − 70, M − 71, M − 89, M − 153, M − 166, and M − 195.

Anal. Calcd for $C_{13}H_{23}NO_2$: C, 69.25; H, 10.31; N, 6.21. Found: C, 69.56; H, 10.32; N, 6.27.

The smaller fraction accompanying the above compound was shown to be the dimer (XVa) by mixture melting point and ir spectra.

Elution with 400 ml of 50% ethyl acetate in benzene gave 0.47 g of a viscous liquid, considered to be the hydroxy ester (XVIa): ν_{max}^{film} 3448 (OH) and 1724 cm^{-1} (ester C=O). This material decomposed on attempted distillation under high vacuum.

Similar electrolysis of 3 g of the hydroxy acid (IIc) in 10 ml of N-methylformamide containing 1.1 ml of triethylamine for 32 hr at 10° gave, after chromatography, a 75% yield of a mixture of homodecalones XIII and XIV. The 2,4-dinitrophenylhydrazone, after recrystallization, melted at 110–132°.

Electrolysis of (2α-Hydroxy-*trans*-2-decalyl)acetic Acid (IIIc).—A total of 15 g of the hydroxy acid was electrolyzed in five 3-g lots, each in DMF containing triethylamine, and under conditions similar to those for the epimeric acid (IIc). The neutral fraction which was obtained was chromatographed on 250 g of neutral alumina. Elution with 1 l. of 1:1 benzene–ether gave 5.8 g of a mixture of the homodecalones XIII and XIV. The 2,4-dinitrophenylhydrazone melted, after recrystallization from 95% ethanol, at 113–128°. Its mass spectrum exhibited M^+ at *m/e* 346.

Anal. Calcd for $C_{17}H_{22}N_4O_4$: C, 58.95; H, 6.36; N, 16.19. Found: C, 59.21; H, 6.33; N, 16.07.

Elution with ether gave 1.8 g of an hydroxy ester fraction XVIb which could not be purified: ν_{max}^{film} 3448 (OH) and 1724 cm^{-1} (ester C=O).

Elution with 10% methanol in ethyl acetate gave 3.2 g of a viscous liquid. This was dissolved in warm petroleum ether and allowed to stand overnight to afford two crystalline forms (140 and 90 mg). Both showed similar ir spectra and were considered to be polymorphic forms of the dimer. Recrystallization of the larger fraction from absolute methanol gave transparent peaks of 1,2-bis(2α-hydroxy-2-*trans*-decalyl)ethane (XVb): mp 215–216.5°; ν_{max}^{KBr} 3448 cm^{-1} (OH); M^+ in the mass spectrum at *m/e* 334. The smaller fraction on recrystallization from absolute methanol gave feathery needles of the dimer (XVb): mp 152.5–153.5°; ν_{max}^{KBr} 3333 cm^{-1} (OH); M^+ in the mass spectrum at *m/e* 334.

Electrolysis of α-(2-Hydroxy-2-*trans*-decalyl)propionic Acid (VIc).—A solution of 3.19 g of the hydroxy acid in 15 ml of DMF containing 0.85 ml of triethylamine was electrolyzed at a C anode and the dark brown electrolysate was worked up as above. When 3.04 g of the neutral product was diluted with petroleum ether and allowed to stand overnight, a small amount of a dark solid separated out. The residue from the mother liquors was chromatographed on 100 g of basic alumina. Elution with 1:1 benzene–ether gave 1.5 g of a mixture of *trans*-4-methylbicyclo[5.4.0]undecan-3-one (XVIII) and *trans*-3-methylbicyclo[5.4.0]undecan-4-one (XIX). Distillation in a short-path distillation tube at 120° (0.1 mm) gave a colorless liquid with a strong band in the ir at 1695 cm^{-1}. The nmr spectrum ($CDCl_3$) showed two methyl doublets (J = 7 cps) at 1.08 and 1.11 with nearly equal integrated intensities.

Anal. Calcd for $C_{12}H_{20}O$: 80.00; H, 11.11. Found: C, 80.16; H, 11.57.

The 2,4-dinitrophenylhydrazone was chromatographed on basic alumina and crystallized from petroleum ether, mp 72.5–76°.

Anal. Calcd for $C_{18}H_{24}N_4O_4$: C, 59.98; H, 6.71; N, 15.56. Found: C, 60.32; H, 6.85; N, 15.22.

Registry No.—IIa, 16666-51-6; IIb, 16666-52-7; IIc, 16666-53-8; IIIa, 16666-54-9; IIIb, 16666-55-0; IIIc, 16666-56-1; V, 16666-57-2; VIb, 16666-58-3; VIc, 16666-59-4; VIIIa, 16666-60-7; IXa, 16666-61-8; 2,4-dinitrophenylhydrazone of XIII, 16666-66-3; 2,4-dinitrophenylhydrazone of XIV, 16666-67-4; XVa, 16666-62-9; XVb, 16666-63-0; XVII, 16666-64-1; XVIII, 16666-65-2; 2,4-dinitrophenylhydrazone of XVIII, 16666-36-7; XIX, 16666-37-8; 2,4-dinitrophenylhydrazone of XIX, 16666-38-9.

The Preparation of *cis*-β-Acetylacrylic Acid[1]

STANLEY SELTZER AND KENNETH D. STEVENS

Chemistry Department, Brookhaven National Laboratories, Upton, New York 11973

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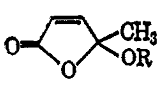
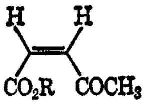
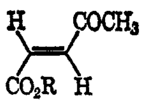
Kinetic studies have been carried out to determine the best conditions for the hydrolysis of the pseudo-ethyl ester of *cis*-β-acetylacrylic acid leading to the *cis* acid without the concurrent formation of the *trans* acid. *cis*-β-Acetylacrylic acid has been isolated in crystalline form. Nmr, uv, and ir spectra indicate that the *cis* acid is cyclic but that the anion exists in open form.

In connection with studies of *cis–trans*-catalyzed isomerizations[2] it became necessary to synthesize *cis*-β-acetylacrylic acid. An examination of the literature indicated that there still was some doubt in the structural assignment for the β-acetylacrylic acid isomer (mp 125–126°) that Wolff[3] had prepared more than 75 years ago by the dehydrobromination of bromolevulinic acid. Shaw[4] prepared the acid by Wolff's method but, because of its ultraviolet maximum at 220 mμ, he suggested the pseudo-acid structure, Ia, for Wolff's compound rather than IIa or IIIa. By treatment with diazomethane, Shaw isolated a methyl ester which he assigned as Ib on the basis of the similarity of its ultraviolet absorption to that for Ia. The ester Ib appears to be different from the ester derived from partial catalytic reduction of methyl acetylpropiolate obtained


Ia, R = H
b, R = CH_3
c, R = C_2H_5


IIa, R = H
b; R = CH_3


IIIa, R = H
b, R = CH_3

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(2) K. D. Stevens, and S. Seltzer, to be published.

(3) L. Wolff, *Ann.*, **264**, 229 (1891).

(4) E. Shaw, *J. Amer. Chem. Soc.*, **68**, 2510 (1946).