was added 5 ml. of 96% sulfuric acid and 46 ml. of a 1.3 *N* solution of hydrazoic acid in chloroform. The solution was kept at 0–10° for 15 minutes with stirring and then poured onto ice. The layers were separated and the aqueous layer extracted repeatedly with chloroform. The chloroform solution was washed with dilute alkali and evaporated. The product was recrystallized from benzene and a second crop obtained by the addition of pentane. The first crop (1.43 g.) melted over the range 110–135° and the second crop (1.33 g.) melted sharply at 101–102°.

Repeated recrystallizations of the material melting at 101–102° failed to raise the melting point. The aceto-2-thiopheneamide present in the first crop above was removed by dissolving 0.58 g. of it in a solution of 1.41 g. of mercuric acetate and 1.13 g. of sodium acetate in 30 ml. of water. The solution was heated several hours at 100°. A solution of sodium chloride was then added and the heavy flocculent precipitate formed was filtered off and dried. The solution was extracted several times with chloroform. The chloroform solution was dried and the solvent evaporated. The product was recrystallized from benzene and petroleum hexane; m.p. 108–109°; mixed m.p. with an authentic sample of 2-thenomethylamide of m.p. 113–114°, 110–112°.

At 25–80°.—This reaction was run starting with 2.14 g. (0.0170 mole) of methyl 2-thienyl ketone, 5 ml. of concentrated sulfuric acid and 0.0191 mole of hydrazoic acid in 75 ml. of benzene. The mixture was heated on the steam-bath for 10 minutes, allowed to stand overnight and the layers were separated but nothing was found in the benzene layer. The acid layer was poured into ice water, the aqueous solution then being extracted with chloroform. The aqueous solution was neutralized hot with barium carbonate, filtered and evaporated to dryness. The residue was a small amount of black glassy material, which was partly decolorized to a yellow color, but which would not crystallize. This material was a barium salt of a sulfonic acid, presumably of acetamidothiophenesulfonic acid, but it was not characterized further.

The residue from the chloroform solution was crystallized from benzene; m.p. 109–112°. This was 2-thenomethylamide. That it was not 2-thienyl methyl ketoxime (m.p. 114°) was demonstrated, since a mixed m.p. determination of these two substances melted at 75–78°. Saponification of a 0.04-g. sample gave rise to 2-thenoic acid, m.p. and mixed m.p., 129°.

2-Thenomethylamide.—This material was prepared by interaction of methylamine and 2-thenoyl chloride. After crystallization from benzene, it melted at 113–114°.

Anal. Calcd. for C_6H_7NOS: N, 9.92. Found: N, 9.94.

2-Acetamido-3,5-thiophenedisulfonyl Chloride.—Aceto-2-thiophenamide (2.18 g.) was melted and allowed to solidify to a thin crust on the bottom of the flask. Then 26 ml. of chlorosulfonic acid was added. The flask was swirled in an ice-bath until solution was complete, then the mixture was heated 18 minutes on a steam-bath. The solution was poured into ice-water and the light brown, gummy sulfonyl chloride filtered off, dissolved in benzene, dried over sodium sulfate and the crude product decolorized once in benzene solution and then once in ether solution. It was then suspended in hot ligroin (b.p. 85–100°) and 15 ml. of benzene was added, which was just enough to dissolve all the material. On cooling, the solution deposited small hard crystals which were filtered off and desiccated overnight; m.p. 114° (uncor.); yield 2.18 g. or 44%.

Anal. Calcd. for $C_6H_5Cl_2NO_5S_2$: Cl, 22.01. Found: Cl, 22.44.

Summary

Several new reactions of aceto-2-thiophenamide are recorded.

EVANSTON, ILLINOIS RECEIVED JULY 28, 1950

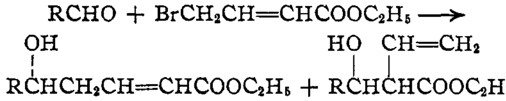
[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

The Synthesis of Some δ-Lactones of α,β,δ-Trihydroxy Acids[1]

BY JAMES ENGLISH, JR., J. DELAFIELD GREGORY AND JAMES R. TROWBRIDGE, II

The synthesis of α,β,δ-trihydroxy acids was undertaken in view of the fact that the structural formula of auxin *a*, as proposed by Kögl,[2] places it in this otherwise unencountered class of compounds. Several δ-hydroxy-α,β-unsaturated esters have previously been prepared by the Reformatsky reaction of ethyl γ-bromocrotonate with various aldehydes.[3] A former investigation revealed that performic acid prepared from 90% hydrogen peroxide was a convenient reagent for the hydroxylation of α-β unsaturated acids and esters.[4] In the work to be described, the hydroxylation of two δ-hydroxy-α,β-unsaturated esters with performic acid yielded, in each case, an isomeric mixture of α,β,δ-trihydroxy acids which were isolated as δ-lactones.

The initial investigation[3] of the Reformatsky reaction of ethyl γ-bromocrotonate with several cyclic aldehydes showed that the crude products contained substantial quantities of esters which boiled 20–35° lower than the desired δ-hydroxy-α,β-unsaturated esters at pressures of less than 1 mm. A similar reaction of heptaldehyde with ethyl γ-bromocrotonate yielded in addition to the expected product, ethyl 5-hydroxy-2-hendecenoate (I, R = *n*-hexyl), an isomeric lower-boiling ester, ethyl 3-hydroxy-2-vinylnonanoate (II, R = *n*-hexyl). The ester II, R = *n*-hexyl, was quantitatively hydrogenated over a platinum oxide catalyst to ethyl 3-hydroxy-2-ethyl-nonanoate. This latter ester was also obtained as the product of the Reformatsky reaction of heptaldehyde with ethyl α-bromo-*n*-butyrate. Samples of the ester which had been prepared by each of two synthetic routes were hydrolyzed to the free acids which were then converted to crystalline *p*-bromophenacyl esters. These derivatives were proved to be identical by a determination of the mixed melting point.



$$RCHO + BrCH_2CH{=}CHCOOC_2H_5 \longrightarrow \underset{\text{I}}{R\overset{OH}{\overset{|}{C}}HCH_2CH{=}CHCOOC_2H_5} + \underset{\text{II}}{R\overset{HO}{\overset{|}{C}}H\overset{CH=CH_2}{\overset{|}{C}}HCOOC_2H_5}$$

The analogous reaction of cyclopentanecarboxaldehyde and ethyl γ-bromocrotonate also yielded two isomeric esters, ethyl 5-cyclopentyl-5-hydroxy-2-pentenoate (I, R = cyclopentyl), and ethyl 3-cyclopentyl-3-hydroxy-2-vinylpropanoate (II, R = cyclopentyl). The lower-boiling type II esters readily decolorized a test solution of 1% bromine in carbon tetrachloride. The type I esters reacted much less rapidly with this reagent as expected

---

(1) This material is taken from dissertations submitted to the Faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the Ph.D. degree by J. Delafield Gregory, 1947, and James R. Trowbridge, II, 1950.

(2) Kögl, *Ber.*, **68A**, 16 (1945).

(3) English and Gregory, THIS JOURNAL, **69**, 2123 (1947).

(4) English and Gregory, *ibid.*, **69**, 2120 (1947).

in view of the known resistance of a double bond α-β to a carbethoxy group to bromine addition.[5] The type I esters were also distinguishable from the type II esters by their strong absorption of ultraviolet light in the region of 210–215 mμ.

In view of the fact that a number of examples have been reported in the literature of Reformatsky reactions of γ-bromocrotonic esters with various ketones and aromatic aldehydes,[6] it is quite surprising that only one group of investigators, Jones, O'Sullivan and Whiting,[7] have reported finding a rearrangement product corresponding to the type II ester. From a Reformatsky reaction of benzaldehyde with methyl γ-bromocrotonate, they isolated a small yield (2%) of methyl 3-phenyl-3-hydroxy-2-vinylpropanoate in addition to a 25% yield of the expected ester, methyl 5-phenyl-5-hydroxy-2-pentenoate. As is shown in Table I, the rearranged esters were the chief products obtained by us in analogous reactions with two aliphatic aldehydes.

TABLE I

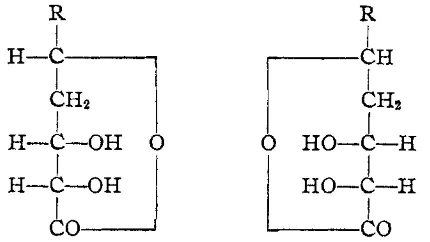
PER CENT. THEORETICAL YIELD OF ESTERS FROM REFORMATSKY REACTIONS OF ETHYL γ-BROMOCROTONATE

R	Type I	Type II
Cyclopentyl	19	49
n-Hexyl	13	29

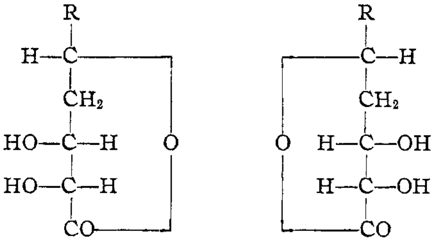
The allylic isomer of ethyl γ-bromocrotonate, ethyl α-bromovinylacetate, was prepared by the method of Rambaud.[8] The same pair of isomeric esters, I and II (R = *n*-hexyl), was obtained from a Reformatsky reaction of heptaldehyde with ethyl α-bromovinylacetate as had previously been obtained in the reaction of heptaldehyde with ethyl γ-bromocrotonate. There appears to be a similarity in the behavior of these bromo-esters in the Reformatsky reaction to that of the butenyl halides in the Grignard reactions which have been extensively investigated by Young and others.[9] Although these investigators were able to separate equilibrium mixtures of butenyl bromides by fractional distillation at reduced pressure, no ethyl α-bromovinylacetate was obtained by us in an attempted fractionation of ethyl γ-bromocrotonate. Rambaud[8] had previously observed a rearrangement of ethyl α-bromovinylacetate to ethyl γ-bromocrotonate upon distillation at 65–70°.

Hydroxylation Reactions

A prediction can be made with regard to the stereochemistry of the products obtained from the hydroxylation of the type I esters with performic acid. These esters are believed to have a *trans* configuration at the carbon to carbon double bond. This assumption is supported by the fact that it was not possible to form δ-lactones from the corresponding free acids.[3] Hydroxylation with performic acid in common with other peracids is known to give *trans* addition of hydroxyl groups.[4] Since the hydroxylation of a *trans* configuration at a double bond with a reagent which gives *trans* addition of hydroxyl groups leads to an *erythro* configuration of the adjacent hydroxyl groups,[10] the expected configurations of the products of the performic acid hydroxylation of I are then represented by the two *dl*-pairs, IIIa and IIIb (R = *n*-hexyl or cyclopentyl).



IIIa



IIIb

The performic acid hydroxylation of I, when R = *n*-hexyl or cyclopentyl, gave a product which proved to be a mixture of isomeric lactones. When the crude hydroxylation product from either the *n*-hexyl or cyclopentyl analog was fractionally sublimed at less than 1 mm. pressure, the least volatile portions of sublimate yielded in each case a less volatile fraction with a constant melting point, 124–125° and 164–165°, respectively, and a less pure volatile fraction. The crude lactone mixtures were more effectively separated by the aid of adsorption on Silene EF by continuous elution, with benzene as the eluting agent. These results are summarized in Table II.

The most volatile fractions obtained by fractional sublimation, which melted at 108–111° and 146–149° (III, R = *n*-hexyl and cyclopentyl, respectively), were also chromatographed on columns of Silene EF. The first fractions of solute obtained in the eluent again had constant melting points of 108–109° and 157–158.5°, but no succeeding fractions with constant melting properties were observed.

Preliminary studies of the oxidation of the constant-melting fractions of III (R = *n*-hexyl or cyclopentyl) with lead tetraacetate in glacial acetic acid show that they consume the expected equimolal quantity of this reagent at approximately

---

(5) Frognier and Van Goetsenhoven, *Bull. soc. chim. Belg.*, **42**, 391 (1933).

(6) (a) Fuson, Arnold and Cooke, THIS JOURNAL, **60**, 2272 (1938); (b) Ziegler, Späth, Schaaf and Schuman, *Ann.*, **551**, 80 (1942); (c) Cook and Schoental, *J. Chem. Soc.*, 288 (1945); (d) Karrer, Jucker and Schick, *Helv. Chim. Acta*, **29**, 704 (1946); (e) Ahrens and Van Dorp, *Rec. trav. chim.*, **65**, 338 (1946); (f) Heilbron, Jones and O'Sullivan, *J. Chem. Soc.*, 866 (1946); (g) Bachmann and Wendler, THIS JOURNAL **68**, 2580 (1946); (h) Ross, *J. Chem. Soc.*, 1367 (1947); (i) Stork, THIS JOURNAL, **69**, 2936 (1947); (j) Cook and Philip, *J. Chem. Soc.*, 162 (1948); (k) Bachmann and Dreiding, *J. Org. Chem.*, **13**, 317 (1948).

(7) Jones, O'Sullivan and Whiting, *J. Chem. Soc.*, 1415 (1949).

(8) Rambaud, *Bull. soc. chim.*, [5] **1**, 1317 (1934).

(9) (a) Young and Roberts, THIS JOURNAL, **67**, 148 (1945); **67**, 319 (1945); (b) Young, Winstein and Prater, *ibid.*, **58**, 104 (1936); **58**, 289 (1936).

(10) Braun, *ibid.*, **51**, 228 (1929).

TABLE II

MELTING POINTS OF FRACTIONS OBTAINED FROM MIXTURES OF δ-LACTONES OF α,β,δ-TRIHYDROXY ACIDS

Method of separation	III, R = *n*-hexyl	III, R = cyclopentyl
Fractional Sublimation		
(a) Least volatile	124–125	164–165
(b) Most volatile	108–111	146–149
(c) Minimum melting point of intermediate fractions	100–103	140–142
Chromatography		
(a) First fraction of solute in eluent	108–109	157–158.5
(b) Last fraction of solute in eluent	121–123[a]	164–165
(c) Minimum melting point of intermediate fractions	106–108	142–146

[a] The melting point was not depressed when this fraction was admixed with the fraction, m.p. 124–125°, obtained by fractional sublimation.

the same rate. Striking differences in the rates of reaction of lead tetraacetate with *cis* and *trans* configuration of adjacent free hydroxyl groups have been noted by others.[11] It is hoped that further investigation in this direction will provide experimental verification of the predicted *cis* configuration of the hydroxylated products.

Experimental

Cyclopentanecarboxaldehyde.[12]—A solution of 40 g. of concentrated sulfuric acid in 3 l. of water was placed in a five-liter flask equipped with a reflux condenser, thermometer, nitrogen gas inlet and an efficient mechanical stirrer, and 500 g. (1.70 moles) of mercuric sulfate was added. Continuous agitation maintained a uniform suspension of a fine, yellow precipitate of basic mercuric sulfate which formed during this addition. The contents of the flask were heated to 55° and 77 g. (0.95 mole) of freshly distilled cyclohexene was added at one time. While a nitrogen atmosphere was maintained, the reaction mixture was held at 55–60° for one hour. The angle of the condenser was then adjusted downward for distillation, and 400 ml. of distillate was collected during 2 hours time. The aqueous layer of the distillate was separated, extracted with ether and the extract combined with the separated layer of aldehyde and dried over sodium sulfate. Fractionation of the extract yielded 7.5 g. of recovered cyclohexene, b.p. 83–84°, and 48 g. of cyclopentanecarboxaldehyde, b.p. 136.5–137.5°, which represents a 52% yield (58% counting recovered cyclohexene).

Ethyl 5-Cyclopentyl-5-hydroxy-2-pentenoate (I, R = Cyclopentyl) and Ethyl 3-Cyclopentyl-3-hydroxy-2-vinylpropanoate (II, R = Cyclopentyl).—A Reformatsky reaction was carried out in a manner previously described,[3] employing 45 g. of cyclopentanecarboxaldehyde, 90 g. of ethyl γ-bromocrotonate, 50 g. of 20 mesh zinc and a solvent mixture of 150 ml. of benzene and 100 ml. of ether. After evaporation of the excess solvent, the crude hydrolysis product was rapidly distilled at 1 mm. pressure and yielded 79 g. of yellow liquid, b.p. 90–155°. The distilled material was carefully fractionated through a 75-cm. column of the Podbielniak type. Two distinct fractions were obtained.

The first fraction, b.p. 87–92° (0.5 mm.), n^{25}D 1.471, weighed 45.9 g., and represented a 49% yield of **ethyl 3-cyclopentyl-3-hydroxy-2-vinylpropanoate (II)**.

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.93; H, 9.43. Found: C, 67.70; H, 9.23.

The second fraction, b.p. 122–124° (0.5 mm.), n^{25}D 1.485, weighed 18.0 g. and corresponded to a 19% yield of the previously described[3] **ethyl 5-cyclopentyl-5-hydroxy-1-pentenoate.**

Ethyl 5-Hydroxy-2-hendecenoate (I, R = *n*-Hexyl) and Ethyl 3-Hydroxy-2-vinylnonanoate (II, R = *n*-Hexyl). A. —A Reformatsky reaction employing a freshly distilled sample of heptaldehyde, 57 g., b.p. 152.5–153°, 96 g. of ethyl γ-bromocrotonate, 50 g. of 20-mesh granulated zinc and a solvent mixture of 150 ml. of benzene and 150 ml. of ether again yielded two isomeric esters. The first fraction, 41.5 g., b.p. 101–104° (0.5 mm.), n^{25}D 1.448, represented a 29% yield of II, R = *n*-hexyl.

Anal. Calcd. for $C_{13}H_{24}O_3$: C, 68.42; H, 10.53. Found: C, 68.67; H, 10.52.

The second fraction, 18.3 g., b.p. 132–136° (0.5 mm.), n^{25}D 1.460, represented a 13% yield of I, R = *n*-hexyl.

Anal. Calcd. for $C_{13}H_{24}O_3$: C, 68.42; H, 10.53. Found: C, 68.21; H, 10.61.

B.—A sample of ethyl α-bromovinylacetate, b.p. 66–67° (12 mm.), n^{25}D 1.467, which had been prepared by the method of Rambaud, was calculated to contain 83% of this product on the basis of its bromine content.

Anal. Calcd. for $C_6H_9O_2Br$: Br, 41.40. Found: Br, 34.49.

The addition of a solution of 8.0 g. of ethyl α-bromovinylacetate (83% pure), 5.0 g. of heptaldehyde, 10 ml. of benzene and 10 ml. of ether to 10 g. of 20-mesh granulated zinc covered by 10 ml. of benzene in 20 minutes time resulted in a vigorous exothermic reaction. The reaction products were isolated in the usual manner and fractionated through a 20-cm. column of the Podbielniak type. Two fractions were obtained as follows: II (R = *n*-hexyl), 2.34 g., b.p. 100–104° (0.5 mm.), n^{25}D 1.448, and I (R = *n*-hexyl), 1.32 g., b.p. 130–134° (0.5 mm.), n^{25}D 1.461.

Ethyl 3-Hydroxy-2-ethylnonanoate. A. From Ethyl α-bromo-*n*-butyrate.—The product of a Reformatsky reaction of 40 g. of ethyl α-bromo-*n*-butyrate and 20 g. of heptaldehyde was 30 g. of a colorless liquid, b.p. 104–106° (0.5 mm.), n^{25}D 1.438.

Anal. Calcd. for $C_{13}H_{26}O_3$: C, 67.80; H, 11.39. Found: C, 67.86; H, 11.51.

B. **By Hydrogenation of II, R = *n*-Hexyl.**—A 12.2-g. sample of II, R = *n*-hexyl, in 10 ml. of absolute alcohol, absorbed the calculated quantity of hydrogen when hydrogenated at three atmospheres pressure over 0.1 g. of platinum oxide catalyst. The hydrogenated material was distilled and yielded 10.3 g. of ethyl 3-hydroxy-2-ethylnonanoate, b.p. 100–105° (0.5 mm.), n^{25}D 1.439.

Anal. Calcd. for $C_{13}H_{26}O_3$: C, 67.80; H, 11.39. Found: C, 68.14; H, 11.41.

A sample of this ester as prepared by method (B) was saponified to yield 3-hydroxy-2-ethylnonanoic acid. The free acid was converted to its *p*-bromophenacyl ester,[13] and the crude product was recrystallized several times from 95% ethanol to yield white crystals, m.p. 88–89°.

Anal. Calcd. for $C_{19}H_{27}O_4Br$: C, 57.18; H, 6.82; Br, 20.01. Found: C, 57.06; H, 6.97; Br, 20.13.

The ester prepared by method (A) was similarly converted to the *p*-bromophenacyl ester of 3-hydroxy-2-ethylnonanoic acid. The product, after several recrystallizations from 95% ethanol, melted at 88–89°, and its melting point was not depressed upon admixture with the sample previously prepared.

δ-Lactones of 5-Cyclopentyl-2,3,5-trihydroxypentanoic Acid.—A mixture of 35 g. of 98% formic acid, 9.5 g. of 90% hydrogen peroxide and 0.2 g. of sulfuric acid was allowed to stand for 20 minutes. Then 7.0 g. of ethyl 5-cyclopentyl-5-hydroxy-2-pentenoate was added at once to the prepared performic acid solution with agitation. The reaction mixture was warmed cautiously to 50°. Care was then taken to prevent the reaction mixture from exceeding 60° by the application of external cooling. When the initial exothermic reaction had subsided, the reaction mixture was held at 60° for an hour. Then the temperature was raised to 80° for an additional hour to decompose excess performic acid. The solution was then concentrated under reduced pressure at 30–40° to a volume of 10 ml. of straw-colored sirup. The sirupy residue was saponified on the steam-bath for 20

---

[11] (a) Criegee, Kraft and Frank, *Ann.*, **507**, 159 (1933); (b) Criegee, *ibid.*, **507**, 495, 211 (1932); (c) Hockett, Dienes and Ramsden, THIS JOURNAL, **65**, 1474 (1943); (d) Hockett, Nickerson and Raeder, *ibid.*, **66**, 472 (1944).

[12] This convenient procedure for the preparation of cyclopentanecarboxaldehyde is derived from U. S. Patent 2,429,501 (1947) issued to Yale and Hearne.

[13] Judefind and Reid, THIS JOURNAL, **42**, 1046 (1920).

minutes with 50 ml. of 10% aqueous sodium hydroxide, diluted with 50 ml. of water and extracted with ether. The solution was then acidified with 6 *N* sulfuric acid. The oily layer which separated at this point and the aqueous phase were then continuously extracted for 24 hours with 200 ml. of carbon tetrachloride. The cooled carbon tetrachloride extract deposited a crop of white crystals which was removed by filtration. An additional crop was collected from the concentrated mother liquor. The total product, m.p. 142–148°, after recrystallization from benzene, weighed 2.63 g.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.06. Found: C, 59.54; H, 8.20.

δ-Lactones of 2,3,5-Trihydroxyhendecanoic Acid.—The procedure employed in the hydroxylation of 7.6 g. of ethyl 5-hydroxy-2-hendecenoate was the same as described previously for ethyl 5-cyclopentyl-5-hydroxy-2-pentenoate. A total of 1.76 g. of white crystalline material, m.p. 108–112°, was collected from the carbon tetrachloride extract.

Anal. Calcd. for $C_{11}H_{20}O_4$: C, 61.08; H, 9.32. Found: C, 60.80; H, 9.54.

Fractional Sublimation.—The crude mixtures of isomeric δ-lactones, III (R = cyclopentyl) and III (R = *n*-hexyl) were sublimed at 100–110° (0.5–1.0 mm.) onto a water cooled condenser. The sublimation was interrupted at arbitrary intervals to collect portions of sublimate. Melting points were determined for the various fractions and the less volatile fractions with higher melting points were combined. This process was repeated four or five times until the least volatile fractions melted sharply at a constant value. The melting points of these latter fractions were unchanged by chromatography on columns on Silene EF. No similar constant-melting fractions were obtained from the more volatile fractions.

III, R = cyclopentyl, m.p. 164–165°. *Anal.* Calcd. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.06. Found: C, 59.76; H, 7.92.

III, R = *n*-hexyl, m.p. 124–125°. *Anal.* Calcd. for $C_{11}H_{20}O_4$: C, 61.08; H, 9.32. Found: C, 60.80; H, 9.27.

Chromatography.—The adsorbent employed was Silene EF mixed with Supercel in a 4:1 ratio. A quantity of solute which was 1% of the weight of the adsorbent was dissolved in a quantity of benzene small enough to give a nearly saturated solution. After addition of the solute solution, the column was eluted with additional benzene while successive fractions of eluent were collected and evaporated to dryness. In each case constant-melting products were obtained in the initial fractions of eluent containing solute.

III, R = cyclopentyl, m.p. 157–158.5°. *Anal.* Calcd. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.06. Found: C, 59.86; H, 7.92.

III, R = *n*-hexyl, m.p. 108–109°. *Anal.* Calcd. for $C_{11}H_{20}O_4$: C, 61.08; H, 9.32. Found: C, 61.04; H, 9.27.

Summary

1. A study has been made of the Reformatsky reaction of ethyl γ-bromocrotonate and two aliphatic aldehydes. The structure of the rearranged by-products has been investigated and determined.

2. The Reformatsky reactions of heptaldehyde with ethyl γ-bromocrotonate and its allylic isomer, ethyl α-bromovinylacetate, were found to yield the same pair of isomeric unsaturated hydroxyesters as products.

3. The stereoisomeric mixture of δ-lactones of α,β,δ-trihydroxy acids, obtained as products from the reaction of performic acid with two δ-hydroxy-α,β-unsaturated esters, has been analyzed by the use of fractional sublimation and chromatography. Two apparently homogeneous isomers have been obtained in each case.

NEW HAVEN, CONN. RECEIVED AUGUST 7, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE AND ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Decarbonylation of Diphenyl Triketone[1]

BY JOHN D. ROBERTS, DONALD R. SMITH AND C. C. LEE

One of the characteristic reactions of α-polycarbonyl compounds is their tendency to undergo "decarbonylation"[2] with the formation of a compound with one less carbon atom and carbon monoxide or carbon dioxide. An important synthetic example of this type of reaction is the thermal decomposition of oxalylacetic esters which yield the corresponding malonic esters and carbon monoxide. The related thermal decarbonylation of ethyl pyruvate has been studied by Calvin and Lemmon.[3] These workers found that ethyl pyruvate-2-C^{14} gave only non-radioactive carbon monoxide which result indicates that the ester carbonyl group is lost exclusively.

The decarbonylation reactions of diphenyl triketone (diphenylpropane-1,2,3-trione, I) are particularly interesting since they have been reported to be brought about by a wide variety of agents such as bases,[4] acids,[5] cupric acetate,[6] aluminum chloride[5] and sunlight.[7] In the present investigation, a study was made of some of these reactions using C^{14}-labeled diphenyl triketones in order to determine whether the center or side carbonyl groups are lost in the decarbonylation process.

Diphenyl-1,2,3-propanetrione-1-C^{14} (Ia) was synthesized from sodium acetate-1-C^{14} as follows.[8] Acetophenone-carbonyl-C^{14} was prepared by the procedure of Brown and Neville[9] and converted to dibenzoylmethane.[10] Although it involves more steps, the procedure of Kohler and Erickson[11] was found to be preferable to other reported methods[12] for the preparation of I from dibenzoylmethane.

---

[1] Supported in part by the joint program of the Office of Naval Research and the Atomic Energy Commission.

[2] In our definition, decarbonylation is the loss of a carbonyl group without reference to whether carbon monoxide or carbon dioxide is formed. Since the carbonyl group might be of any type, the decarboxylation of acids is considered to be included as a special case.

[3] Calvin and Lemmon, THIS JOURNAL, **69**, 1232 (1947).

[4] de Neufville and von Pechmann, *Ber.*, **23**, 3375 (1890).

[5] Schönberg and Azzam, *J. Chem. Soc.*, 1428 (1939).

[6] Blatt and Hawkins, THIS JOURNAL, **58**, 81 (1936).

[7] Schönberg and Mustafa, *J. Chem. Soc.*, 997 (1947).

[8] The sodium acetate-1-C^{14} was obtained from Tracerlab, Inc., on allocation from the United States Atomic Energy Commission.

[9] Brown and Neville, United States Atomic Energy Commission, MDDC 1168.

[10] "Organic Syntheses," Coll. Vol. I, 2nd ed., pp. 78, 205.

[11] Kohler and Erickson, THIS JOURNAL, **53**, 2301 (1931).

[12] (a) Wieland and Bloch, *Ber.*, **37**, 1524 (1904); (b) "Organic Syntheses," Coll. Vol. II, p. 244.