Anal. Calcd. for $C_{10}H_{12}O_6N_4$: N, 19.72. Found: N, 19.61.

Summary

1. Compounds identical with derivatives of dimeric glycolaldehyde have been prepared from dioxadiene.

2. The dioxane structure for dimeric glycolaldehyde and its derivatives is given synthetic experimental confirmation.

3. Attempts to prepare diglycolaldehyde or its *p*-nitrophenylhydrazone were unsuccessful under the conditions studied.

4. Hydrolysis of dioxene results in the formation of an aldehyde, probably 5-hydroxy-3-oxapentanal, of which the *p*-nitrophenylhydrazone and the 2,4-dinitrophenylhydrazone have been isolated.

5. Ether bonds beta to a functional group may be split by comparatively mild reagents. Hydrogen ions seem to be particularly important.

EVANSTON, ILLINOIS RECEIVED SEPTEMBER 11, 1941

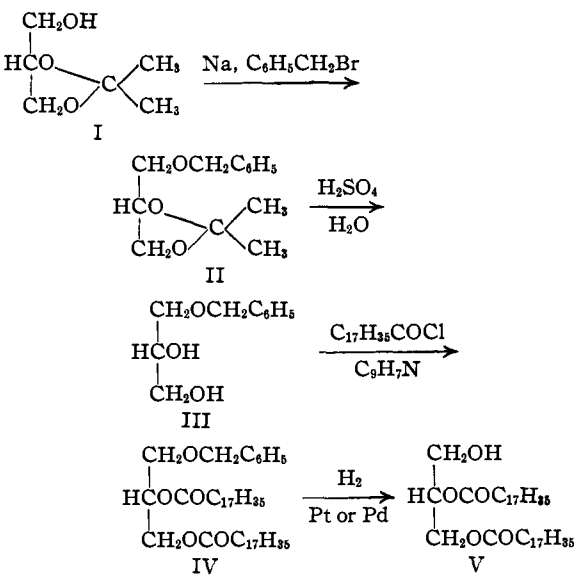
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BANTING INSTITUTE, UNIVERSITY OF TORONTO]

Optically Active α,β-Diglycerides

BY JOHN C. SOWDEN AND HERMANN O. L. FISCHER

In previous publications from this Laboratory, it has been shown that the enantiomorphic 1,2-acetone-glycerols[1,2] are convenient starting materials for the synthesis of optically active α-monoglycerides,[3] α-glycerophosphates,[4] and mixed acid triglycerides.[3] The methods involved in preparing these glycerol derivatives were such that no change in configuration could occur and the steric relationship of the products to *d*- and *l*-acetone-glycerol, and hence to *d*- and *l*-glyceraldehyde, was known.

A method has now been developed whereby these same starting materials, the stereoisomeric acetone-glycerols, may be employed to prepare optically active α,β-diglycerides of known configuration. The synthesis of *d*-α,β-distearin from *d*(+)-acetone-glycerol, represented in formulas I to V, illustrates the reactions involved.



The sequence of the above reactions is such that the asymmetry of the substituted glycerol molecule is maintained throughout.

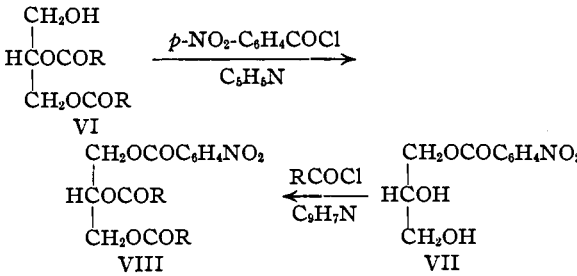
The benzyl group was introduced, I → II, by the reaction of benzyl chloride or benzyl bromide with the sodium salt of *d*(+)-acetone-glycerol, a reaction which had been reported previously for racemic acetone-glycerol by Lorenz Ach.[5] In order to demonstrate that the reaction with sodium had no racemizing effect, the known α'-methyl ether of *d*(+)-acetone-glycerol[6] was also prepared through the sodium salt, and found to be of good optical purity. The benzyl ether is especially suitable for the preservation of the asymmetry of the glycerol molecule, since in contrast to the trityl ether, for instance, it is relatively stable toward acid and alkali but can be cleaved readily by catalytic hydrogenation to produce the original alcohol group.[7] Moreover, to avoid racemization, the free α,β-diglycerides must at no time be subjected to the action of mineral acids, since these have been observed to cause migration of aliphatic residues in β-substituted mono- and diglycerides.[8] Since the

(1) E. Baer and H. O. L. Fischer, *J. Biol. Chem.*, **128**, 463 (1939).
(2) E. Baer and H. O. L. Fischer, THIS JOURNAL, **61**, 761 (1939).
(3) E. Baer and H. O. L. Fischer, *J. Biol. Chem.*, **128**, 475 (1939).
(4) E. Baer and H. O. L. Fischer, *ibid.*, **128**, 491 (1939); **135**, 321 (1940).
(5) German Patent 403,050 (*cf. Chem. Zentr.*, **96**, I, 293 (1925)).
(6) H. O. L. Fischer and E. Baer, *Naturwiss.*, **36**, 588 (1937).
(7) K. Freudenberg, W. Dürr and H. Hochstetter, *Ber.*, **61**, 1735 (1928); H. O. L. Fischer and B. Gohlke, *Helv. Chim. Acta*, **31**, 1130 (1933).
(8) E. Fischer, *Ber.*, **53**, 1621 (1920); M. Bergmann and N. M. Carter, *Z. physiol. Chem.*, **191**, 211 (1930); D. T. Jackson and C. G. King, THIS JOURNAL, **55**, 678 (1933).

cleavage of the benzyl ether in the present synthesis, IV → V, takes place under relatively mild conditions (in glacial acetic acid at room temperature), this danger of acyl migration is largely overcome.

In some instances, attempts to cleave the benzyl ether group with platinic oxide ("Adams catalyst") and hydrogen were unsuccessful, and hydrogenation of the aromatic ring, without cleavage, was found to have occurred. This is in agreement with the observations of Freudenberg, Dürr and Hochstetter,[7] who found that no cleavage occurs in the case of the benzyl ether of diacetone glucose, in ethyl alcohol, using platinum and hydrogen. However, palladium black appears to be a reliable catalyst for the removal of the benzyl group by hydrogen.

In order to demonstrate that the optical purity of the *aliphatic* α,β-diglycerides is comparable to that of the known *aromatic* α-monoglycerides,[3] their *p*-nitrobenzoates were prepared, as illustrated in VI, VII, VIII, starting from the free diglycerides and also from the known *l*-α-*p*-nitrobenzoyl glycerol.[3] The optical rotation of the resulting mixed triglyceride, VIII, was found to be the same when prepared either from the aliphatic diglyceride, VI, or from the aromatic monoglyceride, VII.



Acetylation of *d*-α,β-distearin produced an optically inactive acetate. This is in agreement with the observation of Baer and Fischer[3] that in no instance up to the present time have asymmetric triglycerides containing only aliphatic acid residues been found to possess a detectable optical rotation.

The α,β-diglycerides, prepared from *d*(+)-acetone-glycerol by the method described herein, are assigned to the *d*-series by applying the rules of classification already developed by Baer and Fischer[3] for the α-monoglycerides. Thus, an enantiomorphic α,β-diglyceride is to be regarded as having the same steric classification as that enantiomorphic glyceraldehyde from which it would result by esterification of the two hydroxyls followed by reduction of the aldehyde group to the primary alcohol.

Experimental

***d*(+)-Acetone-glycerol α′-Benzyl Ether.**—A mixture of 3.37 g. of *d*(+)-acetone-glycerol (1), 0.58 g. of powdered sodium and 50 cc. of anhydrous ethyl ether was refluxed, in the absence of moisture, for twenty hours. Benzyl chloride (8.8 cc., 3 moles) was added and the refluxing continued for seventy hours. The precipitated sodium chloride was removed by filtration and washed with anhydrous ethyl ether. After concentration of the filtrate, distillation at reduced pressure produced 3.74 g. (66%) of *d*(+)-acetone-glycerol α′-benzyl ether, b. p. (0.3 mm.) 95–97°; $n^{16}D$ 1.4970; d^{16}_4 1.060.

Anal. Calcd. for $C_{13}H_{18}O_3$ (222.3): C, 70.2; H, 8.16; molecular refractivity, *MR*, 61.36. Found: C, 70.2; H, 8.18; molecular refractivity, *MR*, 61.36.

Optical rotation. In substance, 1-dm. tube; α_D +17.8°, $[\alpha]_D$ +16.8°.

In subsequent preparations of the α′-benzyl ether, the excellent sodium naphthalene reagent of Scott, Walker and Hansley[9] which has recently been utilized in this Laboratory in the synthesis of natural batyl and chimyl alcohols,[10] was employed, to obviate the long refluxing necessary to form the sodium salt of *d*(+)-acetone-glycerol in the above prescription. In a typical preparation, 4.0 cc. of *d*(+)-acetone-glycerol was added to the sodium naphthalene solution prepared from 0.7 g. of sodium and 35 cc. of a molal solution of naphthalene in glycol dimethyl ether.[11] The resulting gel was shaken vigorously for a few minutes until all the green color due to sodium naphthalene had been discharged. Benzyl bromide (11 cc., 3 moles) was then added and the mixture refluxed gently, in the absence of moisture, for twenty hours. After filtration, the glycol dimethyl ether, naphthalene, and excess benzyl bromide were removed by distillation up to a bath temperature of 110° at 10 mm. pressure. Distillation of the residue at reduced pressure then produced 70% of the theoretical amount of *d*(+)-acetone-glycerol α′-benzyl ether.

***d*(+)-Acetone-glycerol α′-Methyl Ether.**—A mixture of 3.37 g. of *d*(+)-acetone-glycerol, 0.58 g. of sodium (slices) and 50 cc. of anhydrous ethyl ether was refluxed, in the absence of moisture, for eighteen hours. Methyl iodide (8 cc., *ca.* 5 moles) was then added and the refluxing continued for twenty-three hours. After filtration, the ether solution was concentrated and the product distilled at reduced pressure. There was obtained 1.5 g. (40%) of *d*(+)-acetone-glycerol α′-methyl ether, b. p. (10 mm.) 45–47°; optical rotation (in substance) α_D +22.1°; $[\alpha]_D$ +22.5°. Fischer and Baer[6] report for this compound b. p. 43–44° (10.5 mm.); optical rotation (in substance) $[\alpha]_D$ +20.1°.

***l*-α-Benzyl Glycerol Ether.**—A mixture of 15.0 g. of *d*(+)-acetone-glycerol α′-benzyl ether and 350 cc. of 0.2 *N* sulfuric acid was refluxed gently overnight. The result-

(9) N. D. Scott, J. F. Walker and V. L. Hansley, THIS JOURNAL, **58**, 2442 (1936); J. F. Walker and N. D. Scott, *ibid.*, **60**, 951 (1938).

(10) E. Baer and H. O. L. Fischer, *J. Biol. Chem.*, **140**, 397 (1941).

(11) Furnished through the courtesy of Mr. P. L. Magill of E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware.

ing clear solution was made alkaline by the addition of sodium bicarbonate, then saturated with sodium chloride and extracted three times with ethyl ether. The extract was washed with water, dried over sodium sulfate, and concentrated at reduced pressure. Two distillations of the residue produced 10.0 g. (81%) of pure *l*-α-benzyl glycerol ether, b. p. 138–139° (0.3 mm.); $n^{16}D$ 1.5342; d^{16}_4 1.143.

Anal. Calcd. for $C_{10}H_{14}O_3$ (182.2): C, 65.9; H, 7.74; molecular refractivity, *MR*, 49.47. Found: C, 66.1; H, 7.94; molecular refractivity, *MR*, 49.56.

Optical rotation. In substance, 1-dm. tube; α_D +6.1°; $[\alpha]_D$ +5.3°.

Glycol titration. The ether was titrated quantitatively for 1,2-glycol content by the method of Criegee.[12] It was observed that the ether consumed 110% of the theoretical amount of lead tetraacetate during twenty hours at room temperature, and 131% of the theoretical amount during forty-four hours. This anomalous behavior may be due to slow oxidation of the methylene group in the benzyl portion of the molecule by the lead tetraacetate.

An attempt was made to hydrolyze the *d*(+)-acetone-glycerol α'-benzyl ether by refluxing for two hours with 90% acetic acid. However, the product obtained showed constants quite different from those of the pure *l*-α-benzyl glycerol ether described above, and the Criegee glycol titration of this product showed consumption of only 50% of the theoretical amount of lead tetraacetate.

d-α,β-Distearin α'-Benzyl Ether.—A solution of 2.28 g. of *l*-α-benzyl glycerol ether in 15 cc. of absolute chloroform was added to a solution containing 7.59 g. of stearyl chloride, 12 cc. of absolute chloroform and 6 cc. of quinoline. The mixture was kept at 37° for forty hours. Ethyl ether was then added and the solution was washed rapidly with 1% hydrochloric acid, water, saturated sodium bicarbonate solution and water. After drying over sodium sulfate, the ether solution was concentrated at reduced pressure to a crystalline mass. Recrystallization from ethyl ether yielded 6.7 g. (75%) of pure *d*-α,β-distearin α'-benzyl ether, m. p. 50.5–51°.

Anal. Calcd. for $C_{46}H_{82}O_5$ (715): C, 77.2; H, 11.55; Found: C, 77.0; H, 11.44.

Optical rotation. In absolute $CHCl_3$, 1-dm. tube, *c* 7.48; α_D +0.46°; $[\alpha]_D$ +6.1°.

d-α,β-Dipalmitin α'-Benzyl Ether.—This compound was prepared (yield, 72%) in a manner similar to that described for the distearin benzyl ether. Recrystallization from anhydrous ethyl ether yielded pure *d*-α,β-dipalmitin α'-benzyl ether, m. p. 42–42.5°.

Anal. Calcd. for $C_{42}H_{74}O_5$ (659); C, 76.5; H, 11.32. Found: C, 76.4; H, 11.25.

Optical rotation. In absolute $CHCl_3$, 1-dm. tube, *c* 8.53; α_D +0.54°; $[\alpha]_D$ +6.3°.

d-α,β-Dibutyrin α'-Benzyl Ether.—To a solution of 7.37 g. of *l*-α-benzyl glycerol ether in 40 cc. of absolute pyridine at 0° was added gradually 10.5 cc. of butyryl chloride. The mixture was allowed to stand for forty-eight hours at room temperature and the product was isolated in the usual manner. Distillation of the product from a Hickman type still at a bath temperature of 140° at 0.005 mm. yielded 9.14 g. (70%) of *d*-α,β-dibutyrin-α'-benzyl ether; $n^{20}D$ 1.4800; d^{20}_4 1.055.

Anal. Calcd. for $C_{18}H_{26}O_5$ (322.4): C, 67.1; H, 8.13. Found: C, 67.2; H, 8.48.

Optical rotation. In substance, 1-dm. tube; α_D +16.33°; $[\alpha]_D$ +15.5°.

d-α,β-Dimethyl α'-Benzyl Glycerol Ether.—A solution of 10.0 g. of *l*-α-benzyl glycerol ether in 100 cc. of methyl iodide was refluxed with 25 g. of silver oxide and 25 g. of powdered "Drierite" for twenty-three hours. An additional 25 g. of silver oxide was then added and the refluxing continued for twenty-one hours. The mixture was cooled, diluted with absolute ethyl ether, filtered, and concentrated *in vacuo*. Fractionation at reduced pressure produced 8.0 g. (70%) of the methylated α-benzyl glycerol ether, b. p. 147–148° (13 mm.); $n^{17}D$ 1.4932; d^{17}_4 1.034.

Anal. Calcd. for $C_{12}H_{18}O_3$ (210.3): C, 68.5; H, 8.63. Found: C, 68.1; H, 8.26.

Optical rotation. In substance, 1-dm. tube; α_D +4.26°; $[\alpha]_D$ +4.1°.

d-α,β-Distearin.—A suspension of 1.0 g. of platinic oxide monohydrate ("Adams catalyst")[13] in 10 cc. of glacial acetic acid was shaken with hydrogen at slightly greater than atmospheric pressure until reduction of the catalyst was complete. A suspension of 1.9 g. of *d*-α,β-distearin α'-benzyl ether and 20 cc. of glacial acetic acid was then added and the shaking continued at room temperature. After two and three-quarters hours the absorption of hydrogen (*ca.* $4H_2$) had practically ceased. Both the distearin α'-benzyl ether and the distearin are sparingly soluble in glacial acetic acid at room temperature, and the mixture remained heterogeneous throughout the reduction. Sufficient ethyl ether was added to dissolve the distearin, and the catalyst was centrifuged off. The ether–acetic acid solution of the product was concentrated at room temperature under reduced pressure to a volume of about 150 cc. The resulting crystalline precipitate (1.24 g. or 70%, m. p. 72–74°) was filtered off and dried at reduced pressure over potassium hydroxide. Two recrystallizations from a mixture of chloroform and low-boiling petroleum ether produced pure *d*-α,β-distearin, m. p. 74.5–75°.

Anal. Calcd. for $C_{39}H_{76}O_5$ (625): C, 74.9; H, 12.26. Found: C, 74.7; H, 12.13.

Optical rotation. In absolute $CHCl_3$, 1-dm. tube, *c* 6.18; α_D −0.17°; $[\alpha]_D$ −2.7°.

When ethyl acetate was substituted for acetic acid in the above procedure, no apparent reduction took place and the starting material was recovered unchanged.

d-α,β-Distearin *p*-Nitrobenzoate.—To demonstrate the optical purity of the *d*-α,β-distearin, it was converted to the *p*-nitrobenzoate and this compound was compared with the product from the reaction of *l*-α-*p*-nitrobenzoyl glycerol,[3] and stearyl chloride.

1. A solution of 0.42 g. of *d*-α,β-distearin in 7 cc. of absolute chloroform was added to 0.13 g. of *p*-nitrobenzoyl chloride in 1 cc. of absolute pyridine. After standing for forty hours at room temperature, ethyl ether was added and the ether solution was washed rapidly with 1% hydrochloric acid, water, saturated sodium bicarbonate solution and water. The extract was dried over sodium sulfate

(12) R. Criegee, *Ber.*, **64**, 260 (1931).

(13) "Organic Syntheses," Collective Vol. I, 1932, p. 452.

and concentrated at room temperature to about 20 cc. On cooling, there was obtained 0.46 g. (89%) of *d*-α,β-distearin *p*-nitrobenzoate, m. p. 63–66°. After two recrystallizations from ethyl ether, the melting point was constant at 67–67.5°.

Anal. Calcd. for $C_{46}H_{79}O_8N$ (774): C, 71.4; H, 10.29; N, 1.81; 3.88 cc. of 0.1 *N* NaOH per 100 mg. Found: C, 71.4; H, 10.05; N, 1.89; 3.93 cc. of 0.1 *N* NaOH per 100 mg.

Optical rotation. In absolute $CHCl_3$, 1-dm. tube, *c* 9.23; α_D −0.13°; $[\alpha]_D$ −1.4°.

2. To 1.0 g. of *l*-α-*p*-nitrobenzoyl glycerol ($[\alpha]_D$ −17.1°, C_2H_5OH) in 5 cc. of quinoline was added 2.55 g. of stearyl chloride in 5 cc. of quinoline. After standing at room temperature for five days, ethyl ether was added and the solution was washed in rapid succession with 3% hydrochloric acid, water, saturated sodium bicarbonate solution and water. The solution was dried over sodium sulfate and concentrated to dryness at room temperature. Four recrystallizations of the residue from ethyl ether yielded 1.03 g. of pure *d*-α,β-distearin *p*-nitrobenzoate, m. p. 67–67.5°. A mixed melting point with the compound above, from *d*-α,β-distearin and *p*-nitrobenzoyl chloride, was undepressed.

Anal. Calcd. for $C_{46}H_{79}O_8N$ (774): C, 71.4; H, 10.29; N, 1.81. Found: C, 71.2; H, 10.32; N, 1.83.

Optical rotation. In absolute $CHCl_3$, 1-dm. tube, *c* 9.08; α_D −0.12°; $[\alpha]_D$ −1.3°.

d-α,β-Distearin Acetate.—To 0.53 g. of *d*-α,β-distearin in 10 cc. of absolute chloroform was added 1.0 cc. of acetic anhydride and 2.0 cc. of pyridine. After standing at room temperature for forty-eight hours, the resulting solution was concentrated to dryness at reduced pressure and the residue was recrystallized from a mixture of chloroform and low-boiling petroleum ether. There was obtained 0.48 g. (85%) of *d*-α,β-distearin acetate. After several recrystallizations, the pure triglyceride melted at 56.5–57°.

Anal. Calcd. for $C_{41}H_{78}O_6$ (667); C, 73.8; H, 11.79; 4.50 cc. of 0.1 *N* NaOH per 100 mg. Found: C, 73.7; H, 11.89; 4.33 cc. of 0.1 *N* NaOH per 100 mg.

Optical rotation. In absolute $CHCl_3$, 1-dm. tube, *c* 11.5; α_D 0.0°.

The acyl analyses of *d*-α,β-distearin *p*-nitrobenzoate and *d*-α,β-distearin acetate were carried out by refluxing 0.2 to 0.3 g. of the triglyceride in 60 cc. of absolute ethanol with 15 cc. of 0.1 *N* sodium hydroxide for one hour, cooling, and back-titrating with 0.1 *N* sulfuric acid, using thymol blue as indicator.

d-α,β-Dipalmitin.—The hydrogenation of *d*-α,β-dipalmitin α′-benzyl ether (3.43 g., 70 cc. of glacial acetic acid) was carried out in the same manner as that already described for the distearin benzyl ether, except that palladium black[14] (1.17 g.) was used as the catalyst instead of platinic oxide. The hydrogenation was complete in two and one-half hours, after one mole of hydrogen had been absorbed. Recrystallization of the crude crystalline product (2.63 g., 89%) from low-boiling petroleum ether, yielded pure *d*-α,β-dipalmitin, m. p. 67–67.5°.

Anal. Calcd. for $C_{42}H_{74}O_5$ (568.9): C, 73.9; H, 12.05. Found: C, 74.2; H, 12.29.

(14) J. Tausz and N. Putnoky, *Ber.*, **52**, 1573 (1919).

Optical rotation. In absolute $CHCl_3$, 1-dm. tube, *c* 8.00; α_D −0.18°; $[\alpha]_D$ −2.3°.

d-α,β-Dipalmitin *p*-Nitrobenzoate.—The *p*-nitrobenzoate was prepared from *d*-α,β-dipalmitin and from *l*-α-*p*-nitrobenzoyl glycerol in exactly the same way as described above for the distearin *p*-nitrobenzoate.

1. From *d*-α,β-dipalmitin: yield 79%; m. p., after recrystallization from a mixture of ethyl ether and methanol, 60–60.5°.

Anal. Calcd. for $C_{42}H_{71}O_8N$ (718): C, 70.3; H, 9.97. Found: C, 70.2; H, 9.77.

Optical rotation. In absolute $CHCl_3$, 1-dm. tube, *c* 10.7; α_D −0.15°; $[\alpha]_D$ −1.4°.

2. From *l*-α-*p*-nitrobenzoyl glycerol: m. p. 60–60.5°, mixed m. p. with the preparation from *d*-α,β-dipalmitin, 60–60.5°.

Anal. Calcd. for $C_{42}H_{71}O_8N$ (718): C, 70.3; H, 9.97; N, 1.95. Found: C, 70.2; H, 9.66; N, 1.97.

Optical rotation. In absolute $CHCl_3$, 1-dm. tube, *c* 11.9; α_D −0.19°; $[\alpha]_D$ −1.6°.

d-α,β-Dibutyrin.—The benzyl ether of *d*-α,β-dibutyrin (5 g.) was reduced in glacial acetic acid (65 cc.) using palladium black (1.2 g.) as catalyst. The reduction required five hours, after which time one mole of hydrogen had been absorbed. After centrifuging off the catalyst, the acetic acid was distilled at reduced pressure. Distillation of the residue from a small Hickman type still, at a bath temperature of 95° and 0.001 mm. pressure, yielded 3.1 g. (86%) of *d*-α,β-dibutyrin; $n^{20}D$ 1.4422; d^{20}_4 1.066.

Anal. Calcd. for $C_{11}H_{20}O_5$ (232.3): C, 56.9; H, 8.68. Found: C, 56.8; H, 8.85.

Optical rotation. In substance, 1-dm. tube; α_D +0.73°; $[\alpha]_D$ +0.69°. In absolute $CHCl_3$, 1-dm. tube, *c* 9.77; α_D ±0.0°. In absolute C_5H_5N, 1-dm. tube, *c* 7.08; α_D +0.12°; $[\alpha]_D$ +1.7°.

It is not certain that the distillation of the dibutyrin, even at the comparatively low temperature of 95°, does not bring about some racemization. Moreover, the proof of optical purity through the *p*-nitrobenzoate was not successful because of the difficulty encountered in purifying this low-melting, easily-soluble triglyceride. Therefore, the optical constants of the *d*-α,β-dibutyrin are submitted with these reservations.

d-α,β-Dimethyl α′-Cyclohexylmethyl Glycerol Ether.—The benzyl ether of *d*-α,β-dimethyl glycerol ether (7.7 g.) was reduced in acetic acid (70 cc.) using platinic oxide (4.0 g.) as catalyst. Reduction was complete after two hours. Fractionation of the product yielded 1.5 g. of the cyclohexylmethyl ether of *d*-α,β-dimethyl glycerol ether, (b. p. 135–138° (14 mm.); $n^{20}D$ 1.4478; d^{20}_4 0.9592) and only a negligible trace of lower-boiling material.

Anal. Calcd. for $C_{12}H_{24}O_3$ (216.3): C, 66.6; H, 11.18; molecular refractivity, *MR*, 60.34. Found: C, 66.6; H, 10.96; molecular refractivity, *MR*, 60.35.

Optical rotation. In substance, 1-dm. tube; α_D +4.72°; $[\alpha]_D$ +4.9°.

Summary

A method has been developed for the preparation of optically pure enantiomorphic α,β-diglycerides. Starting with optically active acetone-glycerol,

the method involves the following sequence of reactions: acetone-glycerol → acetone-glycerol α'-benzyl ether → glycerol α-benzyl ether → α,β-diglyceride α'-benzyl ether → α,β-diglyceride.

The procedure has been applied for the synthesis of optically pure d-α,β-distearin and d-α,β-dipalmitin.

TORONTO, CANADA RECEIVED SEPTEMBER 6, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WESTERN RESERVE UNIVERSITY]

Kinetics of the Thermal Decomposition of Straight Chain Paraffins[1]

BY R. E. BURK, LEONA LASKOWSKI AND H. P. LANKELMA

Several conflicting theories have been proposed for the mechanism of the thermal decomposition of straight chain paraffins. F. O. Rice[2] assumes that free radicals are formed in the initial step of the reaction. These free radicals are then able to undergo two types of reaction

$$C_nH_{2n+2} + C_{n_a}H_{2n_a+1} = C_{n_c}H_{2n_c+2} + C_{n_d}H_{2n_d+1}$$

or a further decomposition to give another radical

$$C_nH_{2n+1} = C_{n_b}H_{2n_b} + C_{n_c}H_{2n_c+1}$$

The relative proportion of each type of reaction is thought to be dependent upon probabilities which involve both energetic and structural factors. Rice has estimated the proportions of the various products which are to be expected on the basis of free radicals. Some observations have supported,[3] others have denied, such a mechanism.[4,5]

One of us[6] has developed an alternate theory based on initial decomposition to an olefin and a paraffin rather than free radicals. By assuming that every carbon–carbon bond is equivalent (with the possible exception of the end C atoms) and that reaction occurs when a given amount of energy, namely, the energy of activation, is accumulated in a single carbon–carbon bond, this theory is expressed by the following equation for the rate of decomposition (exclusive of dehydrogenation) of a straight chain paraffin

$$-dN/dt = N(n-1)ve^{-E/RT} = Nk$$

where N is the total number of moles of reactant, n is the number of carbon atoms in the decomposing hydrocarbon, v is the vibration frequency of the carbon atoms composing a bond and is equal to about 3.45×10^{13}/sec., E is the energy of activation, and k is the reaction velocity constant. If the assumptions made to obtain this rate equation are tenable, the energy of activation, E, should be a constant regardless of the number of carbon atoms in the decomposing hydrocarbons.

When this equation was first proposed, data adequate for testing it were not available. Since that time, however, numerous investigations[3,7–16] have supplied test material resulting in the energies of activation shown in the accompanying graph. These values of the energies of activation were calculated from the experimentally determined reaction velocity constants using the Burk[6] equation for the rate of decomposition of a straight chain paraffin from which

$$E = 2.303RT[\log k - \log v\,(n-1)]$$

All the values calculated have been plotted against the temperatures at which they were measured, using the same symbol for each value of E pertaining to a specified hydrocarbon. The reference is given alongside each symbol. No trend is evident for a functional relationship between the energy of activation and the particular hydrocarbon decomposing.

These values of the energy of activation vary from 59,000 to 65,000 g. calories per g. molecule. An average value of E cannot be obtained by the usual method of taking an arithmetic mean since the experiments are not equivalent. An error in temperature causes a proportional change in the energy of activation and an error in measuring the per cent. conversion occurs logarithmically. It seems more probable, however, that each experi-

(1) Original manuscript received August 16, 1939.
(2) Rice and Rice, "The Aliphatic Free Radicals," John Hopkins Press, Baltimore, Md., 1935.
(3) Frey, *Ind. Eng. Chem.*, **26**, 198 (1934).
(4) Patat, *Z. physik. Chem.*, **B32**, 274 (1936).
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