on pouring onto ice the product precipitated as brown, flat needles, 50 g. (65%). Recrystallization from Skellysolve B[32] gave only partial removal of the brown color, so the product was recrystallized from dilute ethanol (charcoal), giving 38 g. (49%) of N-(1-methylcyclohexyl)-acetamide, m.p. 84–85°.

Pyrolysis Procedure.—The apparatus and procedure for the pyrolysis were essentially the same as those described previously.[11] In the later experiments the temperature of the furnace was controlled by means of an Amplitrol (Thermo Electric Mfg. Co.) proportioning controller, which was found capable of maintaining the temperature within ±5° or less at 600°. The calibration of the instrument appeared to change with time so that use of a pyrometer and thermocouple as described previously was essential, the pyrometer being positioned to read the maximum temperature in the column (which was found to be as much as 60° above the temperature near the ends).

The addition of solid amides was facilitated by means of an electrically heated dropping funnel. A unique feature of the funnel used was a Teflon needle valve similar to that described by Nester.[33] An alternative design employed a heated Hershberg funnel.[34]

Two procedures were used in working up the pyrolysates. (a) The crude mixture was distilled through a short Vigreux column and all material boiling up to 10° above the boiling point of the expected olefin(s) was collected. Tap water (temperature *ca.* 12°) was used to cool the condenser and normally no effort was made to collect gaseous or very low boiling components. In the pyrolyses of N-cyclohexylacetamide and N-cyclohexyl-N-methylacetamide, however, the liquifiable product (in Dry Ice–ethanol) was transferred, with due regard for the very low boiling point of some components, to a simple distillation set-up and distilled. The low boiling components were collected in a receiver cooled in Dry Ice–ethanol. These are listed in Table I as the crude butadiene fraction. This fraction for run 14 was analyzed for actual butadiene content by gas chromatography. The fractions boiling from room temperature (*ca.* 30°) to 90° are listed in Table I as the crude cyclohexene fraction. The unreacted amide was recovered by recrystallization or fractional distillation under reduced pressure of the residue.

(b) The crude pyrolysate was taken up in a small amount of ethanol and the resultant solution was steam distilled. The water-insoluble portion of the steam distillate was mechanically separated and analyzed as described below. The steam non-volatile residue was distilled under reduced pressure or recrystallized. From the standpoint of convenience and ease of manipulation (especially with pyrolysates from solid amides) this procedure was preferable; however, water-soluble components of the pyrolysate were lost during the work-up. This procedure was used for all experiments listed in Table II.

The volatile fraction was analyzed by (1) fractional distillation through a Podbielniak column[35] and oxidation[1] of any olefin to the glycol in the early experiments, (2) infrared spectra in later experiments and (3) gas chromatography employing a Perkin–Elmer model 154-B vapor fractometer in the most recent experiments. Those volatile fractions which separated into two or more phases were mechanically separated and each phase was analyzed separately. For the analysis by gas chromatography, stainless steel columns (200–300 × 0.7 cm.) packed with Perkin–Elmer column packing B or 30% (by weight) of a saturated solution of silver nitrate in ethylene glycol on Celite 545 (100–200 mesh) were used with helium as the mobile phase. The weight percentage composition of each olefin mixture was obtained by determining the ratios of the individual peak areas (measured by use of a planimeter) to the sum of all the areas, each individual area being corrected by a multiplicative factor (determined from the analysis of mixtures of standard substances). The results are considered accurate to within ±1% (relative).

The gas chromatographic analyses of certain of the crude cyclohexene fractions (run nos. 14, 18, 19, 21) are given in Table III. In the analyses of runs 8 and 10 the fractions boiling from 30–110° were analyzed. In the analyses of runs 23–28 (Tables II and III) the entire steam volatile product was analyzed; only in run 28 were more than traces of products other than methylenecyclohexane and 1-methylcyclohexene obtained.

In order of increasing retention volumes, compounds resolved by the Perkin–Elmer B packing were: methylenecyclopentane, (1-methylcyclopentene, cyclohexane), cyclohexene, benzene, methylcyclohexane, (methylenecyclohexane, 3-methylcyclohexene, 4-methylcyclohexene), 1-methylcyclohexene, toluene. Compounds appearing within one set of parentheses were not resolved from each other. For the silver nitrate–glycol column: (cyclohexane, methylcyclohexane), (1-methylcyclopentene, benzene, 1-methylcyclohexene), toluene, (4-methylcyclohexene, cyclohexene, 3-methylcyclohexene), methylenecyclohexane.[36]

To identify ethylene as one product of the pyrolysis of N-cyclohexyl-N-methylacetamide a 0.20-mole portion of the amide was pyrolyzed at 575° (0.20 g./min.) with no nitrogen passing through the system and the gas evolved (*ca.* 2 l.) was collected over water. The gas was analyzed by infrared spectroscopy and found to consist largely of ethylene together with a small amount of butadiene and other substances. In general, however, the gaseous products were not collected.

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[33] R. G. Nester, *Anal. Chem.*, **28**, 278 (1956).

[34] E. B. Hershberg, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 129.

[35] J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1950, p. 237.

[36] This column will resolve 3-methylcyclohexene and 4-methylcyclohexene (E. Gil-Av, J. Herling and J. Shabtai, *Chemistry & Industry*, 1483 (1957)) but not in the presence of cyclohexene.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF BOSTON UNIVERSITY]

Synthesis of Unsaturated Fatty Acids: *dl*-Ricinoleic Acid[1]

BY WALTER J. GENSLER AND CAROLYN B. ABRAHAMS

RECEIVED MARCH 5, 1958

9-Chlorononyne-1, as its lithium derivative, adds to 1,2-epoxyoctane to give 1-chloro-11-hydroxyheptadecyne-8. The corresponding iodide with potassium cyanide gives 1-cyano-11-hydroxyheptadecyne-8, which on saponification leads to *dl*-ricinstearolic acid. Addition of one mole of hydrogen forms *dl*-ricinoleic acid. Further hydrogenation of methyl *dl*-ricinoleate gives methyl *dl*-12-hydroxystearate.

From the standpoint of synthesis, the significant structural feature in ricinoleic acid (VIII) is the β-hydroxy-*cis*-olefinic grouping. In earlier syntheses of ricinoleic acid, two different methods were employed for the formation of this grouping. In one scheme, the essential step was a Reformatsky condensation of propargyl bromide,[2] or of a γ-substituted propargyl bromide,[3] with an appropriate aldehyde. A second method centered around the

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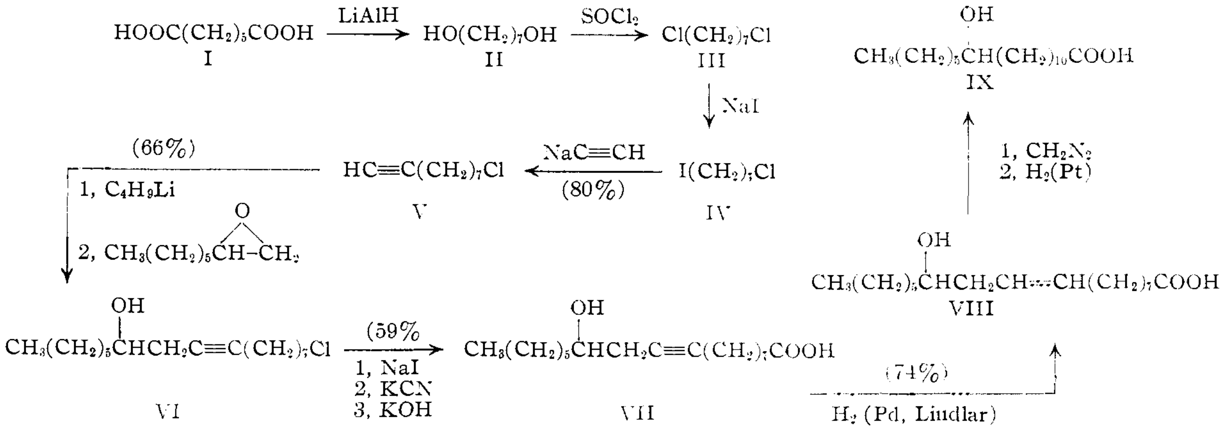
[1] Abstracted from the Dissertation submitted by Carolyn B. Abrahams to the Graduate School of Boston University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1957.

[2] L. Crombie and A. G. Jacklin, *Chemistry & Industry*, 1197 (1954); *J. Chem. Soc.*, 1740 (1955).

[3] L. Crombie and A. G. Jacklin, *ibid.*, 1622 (1957).



preparation of, and the addition of a Grignard reagent to, a β,γ-unsaturated aldehyde.[4] We wish to describe a new synthesis of ricinoleic acid, formulated as I-VIII, in which the β-hydroxy unsaturation is introduced by combination of a metal acetylide with an ethylene oxide.[5]

The required acetylene, 9-chlorononyne-1 (V), was synthesized from pimelic acid by reduction to 1,7-dihydroxyheptane (II), treatment of the glycol with thionyl chloride to form 1,7-dichloroheptane (III) and, after replacing one of the chlorine atoms with iodine, combination with sodium acetylide. The ethylene oxide, 1,2-epoxyoctane, was prepared by epoxidation of octene-1 either with perbenzoic acid[6] or with trifluoroperacetic acid.[7] Both reagents gave product in average yields of 75–80%. However, oxidation with trifluoroperacetic acid proved more convenient in several respects, and was preferred.

Addition of Grignard reagents, including acetylenic Grignard reagents, to epoxides is a familiar process,[8] the addition of lithium acetylides less so.[9] However, because of possible complications in the reaction of epoxides with Grignard reagents, the organolithium addition appeared more attractive, and was selected for investigation. Reaction conditions were found eventually by which the lithium derivative of 9-chlorononyne-1 (V) with 1,2-epoxyoctane in dioxane solvent afforded 1-chloro-11-hydroxyheptadecyne-8 (VI) in 66% yield. Structure VI was assigned rather than that of 11-chloro-1-hydroxy-2-hexylundecyne-3 on the basis of generalizations concerning the mode of nucleophilic addition to unsymmetrically substituted ethylene oxides,[10] and was confirmed when methyl *dl*-12-hydroxystearate (IX) emerged in the last step of the series.

Racemic ricinstearolic acid (VII) was obtained from chloride VI in 59% yield by allowing the corresponding iodide (prepared from chloride VI with sodium iodide) to react with potassium cyanide, and by saponifying the resulting racemic ricinstearolonitrile. The melting point of the crystalline synthetic *dl*-ricinstearolic acid (VII) agreed with the melting point reported before[2] for the same compound, and was close to the melting point of ricinstearolic from natural ricinoleic acid. Semihydrogenation[2] of the *dl*-ricinstearolic acid over Lindlar catalyst[11] gave *dl*-ricinoleic acid (VIII) melting at 9–15° before, and at 22–24° after, purification by chromatography. The purified material agreed in melting point and in index of refraction with previously reported samples of racemic ricinoleic acid.[2,4]

Diazomethane converted the synthetic ricinoleic acid to methyl *dl*-ricinoleate[2] with the same index of refraction as methyl ricinoleate from castor oil and with the same infrared absorption spectrum. The presence of one double bond, the absence of branching and the presence of hydroxyl at the 12-position were established by formation of the known compound, methyl *dl*-12-hydroxystearate (IX), on addition of one mole of hydrogen to methyl *dl*-ricinoleate.

Acknowledgment.—We wish to thank The Baker Castor Oil Co. for the grant under which this work was performed, and to acknowledge with pleasure the encouragement and assistance of Don S. Bolley, Technical Director, The Baker Castor Oil Co.

Experimental[12]

9-Chlorononyne-1 (V).—1,7-Dihydroxyheptane (II), n^{25}D 1.4522, was obtained from pimelic acid (I) by reduction with lithium aluminum hydride.[13] Continuous introduction of pimelic acid into the ethereal lithium aluminum hydride by an extraction procedure was preferred to addition through a dropping funnel. The reported values for the index of refraction are n^{25}D 1.4520[14] and n^{24}D 1.4527–1.4540.[3] The glycol was converted with thionyl chloride to 1,7-dichloroheptane (III) essentially according to directions

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[4] V. G. Kendall, P. B. Lumb and J. C. Smith, *Chemistry & Industry*, 1228 (1954); A. S. Bailey, V. G. Kendall, P. B. Lumb, J. C. Smith and C. H. Walker, *J. Chem. Soc.*, 3027 (1957).

[5] A preliminary report has appeared in *Chemistry & Industry*, 47 (1957).

[6] *Cf.* D. Swern in R. Adams, "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 378.

[7] W. D. Emmons and A. S. Pagano, THIS JOURNAL, **77**, 89 (1955).

[8] *Cf.* M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-metallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954; N. G. Gaylord and E. I. Becker, *Chem. Revs.*, **49**, 413 (1951).

[9] *Cf.* N. A. Milas, N. S. MacDonald and D. M. Black, THIS JOURNAL, **70**, 1829 (1948).

[10] *Cf.* S. Winstein and R. B. Henderson in R. C. Elderfield's "Heterocyclic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 32.

[11] H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

[12] Boiling points and melting points are uncorrected. Analyses were performed by Carol K. Fitz, 115 Lexington Ave., Needham Heights 94, Mass. Infrared absorption spectra were obtained with neat liquids using a single-beam spectrophotometer.

[13] *Cf.* R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 2548 (1947).

[14] W. F. Huber, *ibid.*, **73**, 2730 (1951).

in the literature.[3,15] Distilled, water-white material, b.p. 103–105° (8 mm.), $n^{25}\mathrm{D}$ 1.4560, was obtained in 80–90% yield. 1,7-Dichloroheptane has been reported before with b.p. 106–110° (15 mm.), $n^{19}\mathrm{D}$ 1.4591,[3] and with b.p. 124–125° (35 mm.), $n^{25}\mathrm{D}$ 1.4565.[14] The yield in the reaction of 1,7-dichloroheptane (III) with sodium iodide to give 1-chloro-7-iodoheptane (IV), b.p. 144–149° (6 mm.), $n^{25}\mathrm{D}$ 1.5178, was 39% (50–75% when corrected for recovered 1,7-dichloroheptane). The index of refraction observed before was $n^{23}\mathrm{D}$ 1.5136[3] and $n^{25}\mathrm{D}$ 1.5158.[14]

Conversion of 1-chloro-7-iodoheptane (IV) to 9-chlorononyne-1 (V) was modelled after earlier experiments with an homologous compound.[16–18] A rapid stream of acetylene was introduced into 1 liter of liquid ammonia containing pieces of clean sodium (7.00 g. or 0.305 g. at.). After the blue color was discharged (0.5 hour), addition of acetylene was continued for an additional hour. The acetylene, before reaching the reaction flask, was bubbled through concentrated sulfuric acid and then passed through an empty flask. 1-Chloro-7-iodoheptane (61.7 g. or 0.236 mole) was added dropwise over the course of 45 min. at a rate producing no flooding in the condenser. The last traces of 1-chloro-7-iodoheptane were rinsed into the reaction mixture with the help of 50 ml. of sodium-dried ether. After 5 hours of stirring and refluxing, 100 ml. of water was added at a rate compatible with the condenser capacity, and the mixture was allowed to stand until most of the ammonia had evaporated.

The yellow organic material was extracted into several portions of ether (total 700 ml.), and the combined ether solution washed several times with 100-ml. portions of water, twice with 50-ml. portions of 5% hydrochloric acid, and finally with water until the washings were neutral to litmus. Solvent was removed after drying the solution with sodium sulfate, and the residue was distilled. A small forerun was discarded, and 30 g. (80%) of 9-chlorononyne-1, $n^{25}\mathrm{D}$ 1.4511, was collected at b.p. 102–105° (19 mm.).

Anal. Calcd. for $C_9H_{15}Cl$: C, 68.1; H, 9.5. Found: C, 68.1; H, 9.5.

1-Chloro-11-hydroxyheptadecyne-8 (VI).—Commercial dioxane was refined[19] by stirring 2 kg. of dioxane for 1 hour with 200 ml. of 50% potassium hydroxide solution and 20 g. of pyrogallol. The dioxane, separated from the black sludge, was stirred with anhydrous calcium chloride for an hour, and finally boiled for one day with 40 g. of sodium.

9-Chlorononyne-1 (30.0 g. or 0.189 mole) and 630 ml. of purified dioxane were placed in a 2-liter three-necked flask fitted with stirrer, dropping funnel, condenser and gas inlet tube. The glassware had been carefully dried and nitrogen was used throughout to blanket the reaction mixture. Over the course of 10 min., 175 ml. of 0.0011 *M* ethereal butyllithium[20] (0.189 mole) was added, after which the milky solution was boiled for an hour.

1,2-Epoxyoctane[7] (38.5 g. or 0.30 mole) in 125 ml. of purified dioxane was added in one portion, residual material being washed in with an extra 25 ml. of dioxane. The yellow mixture was boiled for 18 hours.

After 400 ml. of solvent had been removed by distillation, the cooled concentrated mixture was poured over 1000 g. of ice and 100 ml. of glacial acetic acid. The yellow organic layer was taken up in 1 liter of ether, and the aqueous acid layer was extracted with four 100-ml. portions of ether. The combined ether solutions were washed with water until the wash-water showed *p*H 6, and then dried with sodium sulfate. Solvent was removed and the residue distilled in a Claisen flask. After a forerun (16.8 g.) of 1,2-epoxyoctane and 9-chlorononyne-1, 36 g. (66.5%) of faintly yellow 1-chloro-11-hydroxyheptadecyne-8 (VI), b.p. 165–166° (0.2 mm.) and $n^{25}\mathrm{D}$ 1.4714, was collected. Infrared absorption at 3401 cm.$^{-1}$ (2.94 μ) confirmed the presence of hydroxyl group.

Anal. Calcd. for $C_{17}H_{31}OCl$: C, 71.2; H, 10.9; Cl, 12.4. Found: C, 71.3; H, 10.8; Cl, 12.5.

1-Iodo-11-hydroxyheptadecyne-8.—A mixture of 36.0 g. (0.125 mole) of 1-chloro-11-hydroxyheptadecyne-8 (VI), 75.0 g. (0.50 mole) of sodium iodide and 1.25 l. of acetone (reagent grade, Merck) was stirred and boiled for 30 hours. The cooled mixture was filtered, boiled further for 15 hours, and filtered again. Boiling for an additional period of 5 hours failed to produce more precipitate. The weight of precipitated sodium chloride corresponded to an 85% conversion.

Distillation at atmospheric pressure followed by distillation at water-pump vacuum removed solvent. Ether (500 ml.) was added to the residue, and the mixture was shaken twice with 50-ml. portions of 5% sodium thiosulfate solution and three times with water. The solution, after drying with sodium sulfate, was warmed on the steam-bath under reduced pressure to remove ether. The residual oil (43.3 g.) was taken as 1-iodo-11-hydroxyheptadecyne-8, and was used without further treatment.

1-Cyano-11-hydroxyheptadecyne-8.—Using conditions suggested by the experiments of Fierz-David and Kuster,[21] a mixture of the above iodo compound with 16.3 g. (0.25 mole) of potassium cyanide, 304 ml. of absolute ethanol and 47 ml. of water was boiled and stirred in a nitrogen atmosphere for 15 hours. After 300 ml. of solvent had been removed by distillation, the oily residue was dissolved in 500 ml. of ether and was washed with water until neutral to litmus. The solution, dried with sodium sulfate, was distilled under reduced pressure to remove solvent, and the residual 1-cyano-11-hydroxyheptadecyne-8 (32.2 g.) was used directly in the next step.

***dl*-Ricinstearolic Acid (VII).**—A mixture of the cyano compound, 250 ml. of alcohol and 250 ml. of 20% aqueous potassium hydroxide solution was stirred and boiled under nitrogen for 72 hours. No ammonia was evolved after this time. Solvent (*ca.* 260 ml.) was removed by distillation on the steam until the vapor temperature reached 95°. The cooled material in the flask was washed with three 25-ml. portions of ether, and then acidified to *p*H 1 at ice-bath temperatures by dropwise addition of concentrated hydrochloric acid. The white product was extracted into ether (400 ml.) and the ether solution shaken with portions of water until the water was neutral. The solution was dried over sodium sulfate, the drying agent was removed by filtration, and the filtrate was distilled on the steam-bath under reduced pressures to remove solvent. The pale yellow residue (27.5 g.) after two crystallizations from hexane (50-ml. and 45-ml. volumes of solvent were used) afforded 21.9 g. of white crystalline *dl*-ricinstearolic acid, m.p. 53–54°. The yield from 1-chloro-11-hydroxyheptadecyne-8 (VI) was 59%.

Anal. Calcd. for $C_{18}H_{32}O_3$: C, 72.9; H, 10.9; neut. equiv., 296. Found: C, 72.8; H, 10.9; neut. equiv., 295.

Synthetic *dl*-ricinstearolic acid was reported before[2] with m.p. 53–53.5°. Ricinstearolic acid from natural ricinoleic has been obtained with m.p. 52°[2] and with m.p. 49–50°.[22]

***dl*-Ricinoleic Acid (VIII).**—*dl*-Ricinstearolic acid was hydrogenated over a palladium–calcium carbonate plus lead catalyst[11] in methanol containing some quinoline according to the procedure of Crombie and Jacklin.[2] Hydrogenation stopped spontaneously after 98% of the calculated amount of hydrogen had been absorbed. The *dl*-ricinoleic acid (m.p. 9–15°) so obtained in 88–91% yield was purified by chromatography.

Adsorbent was prepared by thoroughly mixing one part of decolorizing carbon (Norit) and two parts of diatomaceous earth (Hyflo). A chromatography column 14 mm. in diameter was formed using 4 g. of the adsorbent. *dl*-Ricinoleic acid (227 mg.) dissolved in 10 ml. of dry petroleum ether (30–60°) and dry ether (7 volumes to 1) was placed on the column, and the following solvents passed through the column: two 20-ml. portions of petroleum ether (30–60°)–ether (7:1), two 20-ml. portions of petroleum ether–ether (6:1), two 20-ml. portions of petroleum ether–ether (2:1), 80 ml. of petroleum ether–ether (1:1) and finally ether. Solvent was evaporated from the eluate fractions at room temperature by directing a jet of dry nitrogen

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(15) K. Ahmad, F. M. Bumpus and F. M. Strong, THIS JOURNAL, **70**, 3391 (1948).

(16) W. J. Gensler and G. R. Thomas, *ibid.*, **73**, 4601 (1950).

(17) R. A. Raphael and F. Sondheimer, *J. Chem. Soc.*, 2100 (1950).

(18) W. J. Gensler and H. N. Schlein, THIS JOURNAL, **77**, 4846 (1955); *cf.* H. N. Schlein, Doctoral Dissertation, Boston University, 1954.

(19) We are indebted to Dr. F. Johnson for the procedure.

(20) H. Gilman and J. W. Morton, Jr., in R. Adams, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 258.

(21) H. E. Fierz-David and W. Kuster, *Helv. Chim. Acta*, **22**, 82 (1939).

(22) J. Grigor, D. M. MacInnes, J. McLean and (in part) A. J. P. Hogg, *J. Chem. Soc.*, 1069 (1955).

at the surface. No material appeared in any of the fractions excepting that in the petroleum ether–ether 1:1 solvent (171 mg.) and that in the ether solvent (15 mg.). These two combined fractions (186 mg., 82% recovery), m.p. 22–24°, n^{25}_{D} 1.4702, were taken as pure *dl*-ricinoleic acid.

Anal. Calcd. for $C_{18}H_{34}O_3$: C, 72.4; H, 11.5; neut. equiv., 298.5. Found: C, 72.2; H, 11.3; neut. equiv., 298.1.

This synthetic ricinoleic acid showed intense hydroxyl absorption at 3401 cm.$^{-1}$ (2.94 μ) and carbonyl absorption at 1715 cm.$^{-1}$ (5.83 μ). The infrared absorption curve for this material had all the features of the curve for natural ricinoleic acid (see below), although the three minor peaks at 9.0–9.5 μ differed slightly in relative intensity. The melting points reported before for *dl*-ricinoleic acid are 23–24°[2] and 23–24.5°.[4] The index of refraction may be compared to the n^{25}_{D} 1.4698 value observed in this work (see below) for natural ricinoleic acid, and to the recorded values of n^{19}_{D} 1.4723[2] and n^{25}_{D} 1.4702[4] for racemic ricinoleic acid.

Natural Ricinoleic Acid.—Lithium ricinoleate,[23] m.p. 181–182.5°, was shaken vigorously for 15 min. with 50 ml. of ether and 50 ml. of ice-cold 5% hydrochloric acid. The separated aqueous phase was extracted with two 25-ml. portions of ether, and the combined ethereal solutions were washed free of mineral acid with water and were dried over sodium sulfate. The yellow oil (4.2 g.) remaining after removal of solvent at room temperature at reduced pressures showed m.p. 4–8° and n^{25}_{D} 1.4673. This material was purified by chromatography as described for the synthetic material. The resulting refined ricinoleic acid, m.p. 20–22°, n^{25}_{D} 1.4698, neut. equiv. 298.8, was obtained in 67% yield from the lithium salt.

Methyl *dl*-Ricinoleate.—A distilled ethereal solution of diazomethane, taken in excess, was added slowly to an ice-cold solution of 1.0 g. (0.003 mole) of unpurified *dl*-ricinoleic acid, n^{25}_{D} 1.4676. The yellow reaction mixture was swirled and allowed to stand overnight at room temperature. After addition of one drop of acetic acid, the solution was washed with three 20-ml. portions of water and then dried with sodium sulfate. Ether was removed, and the yellow residue was distilled in a short-path still formed from a creased test-tube. The initial distillate, n^{25}_{D} 1.4610, collected at bath temperature 155–157° (0.01 mm.), weighed 0.99 g. The colorless distillate from the second distillation weighed 0.75 g. and showed n^{25}_{D} 1.4608. A sample for analysis was taken from the third distillate, n^{25}_{D} 1.4603, b.p. (bath temperature) 164–166° (0.02 mm.), which weighed 0.60 g.

Anal. Calcd. for $C_{19}H_{36}O_3$: C, 73.0; H, 11.6. Found: C, 72.9; H, 11.5.

Methyl ricinoleate[23] from castor oil distilled at a bath temperature of 161–164° (0.02 mm.) and showed n^{25}_{D} 1.4602. The infrared spectra of synthetic and of castor oil methyl ricinoleate were superposable, both curves showing hydroxyl (3448 cm.$^{-1}$ or 2.90 μ) and carbonyl (1745 cm.$^{-1}$ or 5.73 μ) peaks. Methyl *dl*-ricinoleate has been reported before with n^{20}_{D} 1.4632[4] and n^{16}_{D} 1.4638.[2]

Methyl *dl*-12-Hydroxystearate (IX).—Methyl *dl*-ricinoleate (1.77 g. or 0.0060 mole), glacial acetic acid (25 ml.) and platinum oxide (0.20 g.) were stirred at room temperature under an atmosphere of hydrogen. The calculated amount of hydrogen was absorbed within 25 min., after which time hydrogen uptake stopped. The catalyst was removed by filtration, and the solvent by distillation at room temperature at reduced pressures. An ether solution of the residue was washed repeatedly with 20-ml. portions of water until the washings were neutral to litmus, and then was dried with sodium sulfate. The crystalline solid (1.50 g., m.p. 53–53.5°) remaining after removal of solvent *in vacuo* at room temperature was crystallized from acetone to give methyl *dl*-12-hydroxystearate (1.37 g., 77%), m.p. 55–55.5°. Two additional crystallizations from acetone did not change the melting point.

Anal. Calcd. for $C_{19}H_{38}O_3$: C, 72.6; H, 12.2. Found: C, 72.4; H, 12.3.

The same racemic material was reported before with m.p. 50–51°,[24] and m.p. 53.4–53.6°.[25] The optically active form has m.p. 57.5–58°.[26]

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[23] We are indebted to The Baker Castor Oil Co. for providing this material.

[24] C. G. Tomecko and R. Adams, THIS JOURNAL, **49**, 522 (1927).

[25] S. Bergström, G. Aulin-Erdtman, B. Rolander, E. Stenhagen and S. Östling, *Acta Chem. Scand.*, **6**, 1157 (1952).

[26] F. Straus, H. Heinze and L. Salzman, *Ber.*, **66**, 631 (1933).

[CONTRIBUTION FROM DEPARTMENT OF PHARMACEUTICAL CHEMISTRY, SCHOOL OF PHARMACY, THE HEBREW UNIVERSITY, HADASSAH MEDICAL SCHOOL]

The Stereochemistry and Mechanism of Reversible Polymerization of 2,2-Disubstituted 1,3-Propanediol Carbonates

BY SHALOM SAREL[1] AND LEO A. POHORYLES

RECEIVED JANUARY 25, 1958

The effect of alkyl substituents positioned at carbon atoms 1 and 2 in 1,3-propanediol carbonates upon their tendencies to undergo reversible polymerization is described. Polyneopentylene carbonate displays thermal transformation in the solid state. A tentative spiral structure having a six-membered ring fold is proposed for the polymer chain. The existing physical and chemical properties of the polymeric material can reasonably be correlated with the structural picture presented. The stereochemical course and mechanism of reversible polymerization are discussed.

Introduction

In the course of synthetic work aimed at preparing some cyclic carbonates of 2,2-disubstituted 1,3-propanediols (I), needed for another research program,[2] we observed that, depending on reaction conditions and molecular structure, some carbonates are obtained only in a polymeric form (II). Thus, when 2,2-dimethyl-, 2-methyl-2-*n*-propyl- and 2-methyl-2-isoamyl-1,3-propanediol are treated with diethyl carbonate in the presence of catalytic amounts (0.5% mole) of sodium methoxide, only polycarbonates (IIb-IId) are produced in high yield. On the other hand, six-membered cyclic carbonates (Ie-If) are exclusively produced when 2,2-diethyl-, 2-ethyl-2-phenyl-1,3-propanediol and 2,4-pentanediol and 1,3-butanediol are subjected to the above ester-interchange reaction conditions.[3] Compounds Ib, Ic and Id, also could be obtained by using larger amounts of catalyst (2.5%–5% mole) and controlling the elimination of ethanol produced during the above-mentioned ester-interchange reaction, or through thermal depolymerization of the polymeric products. Compound IIb, in analogy

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[1] Formerly Shalom Israelashvili.

[2] L. A. Pohoryles and S. Sarel, *Compt. rend.*, **245**, 2321 (1957).

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