TABLE II

VAPOR PHASE CHROMATOGRAPHY RETENTION TIMES AND INFRARED SPECTRA FOR ETHYLCYCLOHEXANOLS

V.p.c. band	Retention time, min.	%	Compound	Characteristic absorption bands, cm.$^{-1}$
1	12	3		
2	16	4		
3	18	1	2-Ethylcyclohexanol (*cis*- and *trans*-)	880, 845, 820
4	20.5	7		
5	23.5	44	*trans*-3-Ethylcyclohexanol *cis*-4-Ethylcyclohexanol	1036, 1014, 968, 857, 815 1144, 990, 952, 897
6	26.5	41	*trans*-4-Ethylcyclohexanol *cis*-3-Ethylcyclohexanol	1090, 1052, 965, 897 1111, 1049, 957, 839

hexanol, *cis,trans*-4-ethylcyclohexanol, *cis,trans*-2-ethylcyclohexanol, 2-methyl-1-ethylcyclohexane, 3-methyl-1-ethylcyclohexane, 4-methyl-1-ethylcyclohexane, and ethylcyclohexane. Each was obtained by a method reported in the literature. The physical properties were in agreement with the reported values.

Analysis of the Residue.—Approximately 25 g. of the residue was placed in the bulb of a small modified retort and heated in a 60° oil bath for 24 hr. under vacuum (0.5 mm.). The volatile material (5.6 g.) was trapped in a second bulb contained in a Dry Ice–acetone bath. When the volatile material was chromatographed it gave two peaks with only minor impurities (less than 3%). This material was identified by means of infrared as the dehydro dimer.[2]

The remaining viscous residue was chromatographed using the thin layer technique (t.l.c.). The adsorbant was silica gel g and the eluent benzene (or petroleum ether, b.p. 30–60°). Two spots were observed when the plate was treated with iodine. One of these had an R_f value identical with that of the dehydro dimer. By v.p.c. it was shown that this viscous residue still contained 5.3 g. of dehydro dimer. The original 33 g. of residue, therefore, was composed of 14.5 g. (0.068 mole based on perester) of dehydro dimer and 18.5 g. of higher molecular weight material. Infrared of the entire residue showed it to be very much like the dehydro dimer but contaminated with acetate esters.

Acknowledgment.—This work was supported in part by the National Science Foundation through the Research Participation for College Teachers Program. The authors are grateful to Mr. D. LaFollette for his assistance in the early part of this work.

The Isomerization of 1,2-Di-*n*-octylcyclopropene with Alumina

TOSHISADA SHIMADATE, HENRY W. KIRCHER,
JAMES W. BERRY, AND ARCHIE J. DEUTSCHMAN, JR.

*Department of Agricultural Biochemistry,
The University of Arizona, Tucson, Arizona*

Received July 16, 1963

The fatty acids that contain a cyclopropene ring, sterculic acid and malvalic acid, are formed as triglycerides in *Sterculia foetida* oil and in cottonseed oil and are remarkable both for their unique chemical structure and for the physiological effects that have been observed when they are included in poultry diets.[1-4] Because destruction of the cyclopropene ring by hydrogenation,[2] rearrangement,[5] or reaction with gaseous hydrogen chloride or sulfur dioxide[6] eliminates the biological effects, we have been interested in the structures of the products that are formed by these procedures.

This paper concerns the nature of the products formed when the cyclopropene ring is destroyed by rearrangement with alumina. The simplicity of sterculene (I, 1,2-di-*n*-octylcyclopropene) together with its ready availability[7a] led to its choice as a model compound for the isomerization.

Sterculene was stirred at room temperature under nitrogen with an equal weight of activated alumina in ten volumes of petroleum ether (b.p. 30–60°). During the reaction its characteristic cyclopropene infrared bands at 5.38 and 9.92 μ[7b] gradually diminished in size and were replaced by bands at 6.13 and 11.15 μ (unsymmetrical disubstituted olefin) and 10.37 μ (*trans* double bond).

After 35 hr. the cyclopropene infrared bands had disappeared and the reaction mixture no longer gave the Halphen test,[8] an empirical test for sterculic and malvalic acid derivatives. The solution was filtered and distilled to give a 72% yield of a clear colorless oil having the same boiling point as I; redistillation showed the same boiling point and did not yield any residue.

A portion (12%) of the product polymerized during the isomerization, and the remainder (16%) could not be extracted from the alumina with petroleum ether.

The isomerized material smoothly consumed 1.7 moles of hydrogen per $C_{19}H_{36}$, which suggested that it is a mixture of compounds, 30% of the material containing one double bond and 70% containing two double bonds. Under the same conditions, I consumed 0.95 mole of hydrogen per $C_{19}H_{36}$.

The ultraviolet spectrum of the isomerized material showed an absorption peak with a maximum at 232 mμ. By assuming a molar extinction coefficient of 22,000[9] the material was calculated to contain 64% of compounds having conjugated double bonds.

The isomerized material reacted with maleic anhydride in refluxing xylene. After removal of solvent and saponification, 36% of the starting material was ex-

---

(1) F. S. Shenstone and J. R. Vickery, *Nature*, **190**, 168 (1961).

(2) J. C. Masson, M. G. Vavich, B. W. Heywang, and A. R. Kemmerer, *Science*, **126**, 751 (1957).

(3) J. R. Evans, J. A. Davidson, and S. L. Bandemer, *J. Nutr.*, **73**, 282 (1961).

(4) D. L. Schneider, M. G. Vavich, A. A. Kurnick, and A. R. Kemmerer, *Poultry Sci.*, **40**, 1644 (1961).

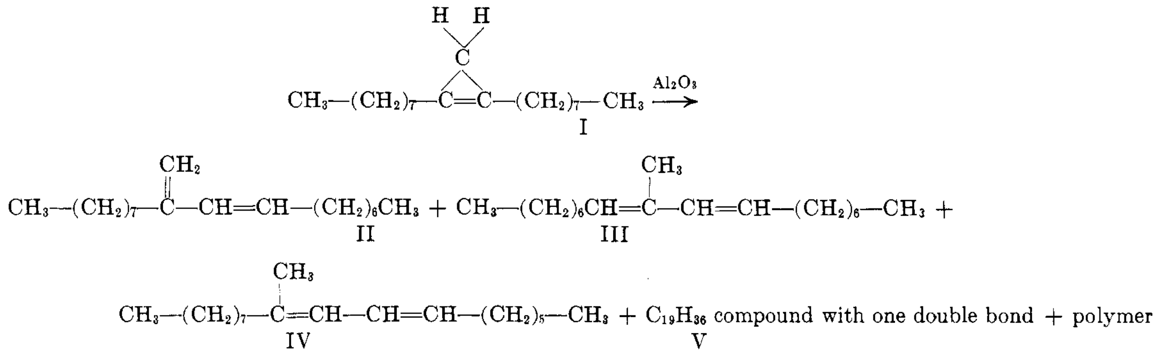
(5) W. A. Pons, Jr., J. C Kuck, and V. L. Frampton, *J. Am. Oil Chemists' Soc.*, **40**, 1644 (1961).

(6) A. J. Deutschman, Jr., B. L. Reid, H. W. Kircher, and A. A. Kurnick, *Poultry Sci.*, **40**, 1305 (1961).

(7) (a) H. W. Kircher, *J. Am. Oil Chemists' Soc.*, in press; (b) H. E. Nordby, B. W. Heywang, H. W. Kircher, and A. R. Kemmerer, *ibid.*, **39**, 182 (1962).

(8) A. J. Deutschman, Jr., and I. S. Klaus, *Anal. Chem.*, **32**, 1809 (1960).

(9) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," 2nd Ed., Edward Arnold Ltd., London, 1957, p. 93.



tracted from the alkaline saponification liquors. This suggested that 64% of the isomerized sterculene contained conjugated double bonds. The infrared spectrum of the material not reacting with maleic anhydride showed no characteristic bands for unsaturation.

A portion of the isomerized material was ozonized in methylene chloride at −50°. The ozonide was decomposed with zinc and aqueous acetic acid and separated into water-soluble, acidic, and neutral components. Formaldehyde was identified in the aqueous solution by its dimedone derivative.

The acid fraction, comprising 35% of the isomerized material ozonized, was methylated with 7% boron trifluoride in methanol and the methyl esters separated into three fractions by distillation. The fractions were analyzed by gas–liquid chromatography (g.l.c.) and the relative amount of methyl enanthate, caprylate, and pelargonate in each estimated from the areas under the peaks of the chromatogram and are given in Table I. The pure esters were separated on a preparative column, saponified, and the three acids positively identified as their crystalline *p*-toluidides.

Table I

Products Obtained from Ozonolysis of Isomerized Sterculene

Acidic		Neutral	
Compound	Yield,[a] %	Compound	Yield,[a] %
Methyl enanthate	2[b]	Enanthaldehyde	1[b]
Methyl caprylate	11[b]	Caprylaldehyde	21[b]
Methyl pelargonate	16[b]	2-Decanone	2[b]
Distillation residue	6	C_{19} compounds	6
		Distillation residue	19

[a] Expressed as per cent of the isomerized sterculene ozonized.
[b] Calculated from g.l.c. data.

The neutral fraction comprised 49% of the isomerized sterculene ozonized and was separated into four fractions by distillation. Enanthaldehyde, caprylaldehyde, and 2-decanone were recognized by g.l.c.; the amounts of each were estimated from the chromatograms and are given in Table I. The latter two compounds were identified by their crystalline 2,4-dinitrophenylhydrazones.

From the spectral, hydrogenation, maleic anhydride adduction, and ozonolysis data, the scheme, at the top of this page, for the isomerization of I is suggested.

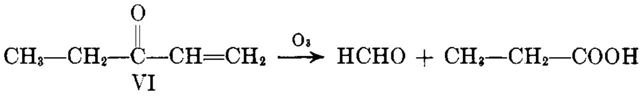
Under the conditions of the reaction about 28% of I or its isomerization products polymerize or cannot be removed from the alumina for other reasons. About 20–25% of I rearranges to substances whose structure is unknown. Presumably this is the portion of the distillate that absorbs 1 mole of hydrogen, does not react with maleic anhydride, and forms high molecular weight compounds on ozonolysis. At the present time, no further work is contemplated on this fraction.

The remaining 50–55% of I isomerizes to 9-methylene-10-octadecene (II), 9-methyl-8,10-octadecadiene (III), and 9-methyl-9,11-octadecadiene (IV). The latter is formed only to a small extent, 2–3%, for only that quantity of enanthaldehyde, enanthic acid, and 2-decanone were found in the ozonolysis mixture (Table I).

The relative quantities of the major isomerization products II and III can be calculated from the ratios of the C_8 and C_9 compounds obtained by ozonolysis. Compound II should give 1 mole each of C_8 and C_9 compounds and compound III should give 2 moles of C_8. It was observed (Table I) that twice as much C_8 as C_9 material is obtained; therefore, twice as much II is present in the isomerization mixture as III.

Theoretically, ozonolysis of structure II should give α-ketodecanoic acid or α-ketodecanal. Neither of these compounds were observed. The large quantity of pelargonic acid obtained arose from overoxidation of the primary ozonolysis products of II.

To test this theory, ethyl vinyl ketone (VI) was ozonized and the ozonide decomposed with zinc and acetic acid. Formaldehyde was identified as its dimedone derivative and propionic acid was the only other fragment found.



$$CH_3{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH{=}CH_2 \xrightarrow{O_3} HCHO + CH_3{-}CH_2{-}COOH$$

VI

Experimental

Sterculene (I) was prepared as described previously,[7a] b.p. 99–104° (0.05 mm.), n^{20}_{D} 1.4543, infrared at 5.38, 9.92 μ; lit.[7b] b.p. 102° (0.04 mm.), n^{20}_{D} 1.4540, infrared at 5.38, 9.92 μ. The alumina (Aluminum Company of America, Alcoa, grade F-6, mesh 8-14) was activated at 200 to 220° under nitrogen. Gas–liquid chromatography (g.l.c.) was performed with the Aerograph A-90-C apparatus. Ten-foot analytical columns with 30% diethylene glycol succinate or with 10% ethylene glycol succinate, and a 5-ft. preparative column with 20% diethylene glycol succinate were used.

Isomerization Reaction.—I (48.2 g.) was dissolved in 500 ml. of petroleum ether (b.p. 30–60°) and added to the activated alumina (50 g.). The mixture was stirred under nitrogen at room temperature for 35 hr. The mixture was filtered, the alumina extracted several times with fresh petroleum ether, and the combined filtrates evaporated *in vacuo* to leave 40.7 g. (84%) of an oil. The product was distilled, b.p. 100–118° (0.07 mm.), to give 35.1 g. (72.3% of I) of a colorless oil. This distillate was used for all further characterization studies.

Hydrogenation.—Two samples of 0.2881 g. and 0.2736 g. of the distillate were hydrogenated in absolute ethanol (15 ml.) over 5% palladium on charcoal (0.1 g.) at atmospheric pressure and room temperature in a standard Hershberg apparatus; 1.71 and 1.72 moles of hydrogen per $C_{19}H_{36}$ were consumed, respectively.

Maleic Anhydride Addition.—The distillate (2.5 g.) was refluxed for 5 hr. with maleic anhydride (3.0 g.) in xylene (10 ml.). After cooling, petroleum ether was added and the mixture extracted with water to remove unchanged maleic anhydride. The residue after removal of solvent (3.08 g.) was refluxed with sodium hydroxide (2.0 g.) in methanol (25 ml.) overnight. Water was added and the alkaline solution extracted with petroleum ether to yield an oil (0.9 g.) representing 36% of the distillate used in the experiment.

In a second run, the distillate (2.18 g.) was refluxed with maleic anhydride (2.00 g.) in xylene (10 ml.) overnight. Petroleum ether was added and the unchanged maleic anhydride extracted with water. Evaporation of the solvent left an oil (2.66 g.) which was distilled. A product (0.77 g., 35% of starting material) was obtained at 107° (0.05 mm.) whose infrared spectrum was the same as the neutral fraction obtained from the first run.

Ozonolysis.—The distillate (33.0 g.) of isomerized sterculene in dry methylene chloride (250 ml.) was cooled to −50° and ozone (3.36 g./hr.) was passed through the solution for 7 hr. The solution was allowed to warm to room temperature and was added to a suspension of zinc dust (16.0 g.) in 50% aqueous acetic acid (150 ml.) in a 1-l. flask fitted with stirrer, dropping funnel, and Vigreux condenser. Considerable heat was evolved during the addition, enough to distil most of the methylene chloride. The mixture was stirred overnight, refluxed an hour, filtered, and extracted three times with petroleum ether.

A portion of the aqueous layer was added to a solution of 10% dimedone in ethanol. White crystals were obtained, m.p. 190–191°, unchanged on admixture with an authentic sample of the dimedone derivative of formaldehyde, lit.[10] m.p. 187°.

The petroleum ether solution was extracted twice with 5% aqueous sodium hydroxide, dried over sodium sulfate, and evaporated to leave the neutral oxidation products (16.2 g.). G.l.c. showed four peaks and three of them corresponded to enanthaldehyde, caprylaldehyde, and 2-decanone. The aqueous solution was acidified and extracted to yield the acidic oxidation products (11.5 g.). These were esterified with a solution (80 ml.) of 7% boron trifluoride in methanol. G.l.c. showed three peaks corresponding to methyl enanthate, caprylate, and pelargonate. The neutral fraction was distilled. Four fractions were obtained: N-1, 5.50 g., b.p. 90–120° (45 mm.); N-2, 1.85 g., b.p. 60–100° (0.10 mm.); N-3, 2.62 g., b.p. 100–148° (0.10 mm.); N-4, residue, 6.20 g.

The methyl esters of the acidic fraction were distilled to yield three fractions: A-1, 8.45 g., b.p. 110–124° (45 mm.); A-2, 1.00 g., b.p. 60° (0.05 mm.); A-3, residue, 2.00 g.

Identification of Neutral Constituents.—A sample (0.6 g.) of N-1 was treated with 2,4-dinitrophenylhydrazine (0.4 g.) in ethanol (20 ml.). Yellow crystals were obtained, m.p. 104–105°, unchanged upon admixture with an authentic sample of caprylaldehyde 2,4-dinitrophenylhydrazone, lit.[11] m.p. 106°.

Fraction N-2 on similar treatment yielded the 2,4-dinitrophenylhydrazone of 2-decanone, m.p. and m.m.p. 73–74°, lit.[12] m.p. 73–74°.

Fraction N-3 on g.l.c. showed a small peak corresponding to 2-decanone and a large peak of long retention time, similar to that observed for 9,11-nonadecadione obtained by ozonolysis of sterculene (see below). It did not yield any crystalline carbonyl derivatives or a chelate with cupric acetate. It is presumed to be a dicarbonyl compound arising from structure V.

9,11-Nonadecadione.—I (10.0 g.) was ozonized as were the rearrangement products above and worked up in the same way. The product was distilled, b.p. 130–140° (0.10 mm.), to give 7.9 g. (70% of I) of a pale yellow sirup.

Anal. Calcd. for $C_{19}H_{36}O_2$: C, 76.97; H, 12.24. Found: C, 76.85; H, 12.39.

A sample of this compound yielded readily a bluish precipitate, m.p. 104–105°, on treatment with cupric acetate in ethanol.

Anal. Calcd. for $Cu(C_{19}H_{35}O_2)_2$: C, 69.74; H, 10.78. Found: C, 69.83; H, 11.05.

Identification of Acidic Constituents.—Fraction A-1 showed peaks on g.l.c. corresponding to the methyl esters of enanthic, caprylic, and pelargonic acid. Fraction A-2 contained only methyl pelargonate. Fraction A-1 was separated on a preparative g.l.c. column into its constituents.

Each was saponified and the *p*-toluidides of the acids prepared by the method given in Shriner and Fuson.[13] In this way, the *p*-toluidides of enanthic acid (m.p. 79–80°, lit.[13] m.p. 80°), caprylic acid (m.p. 69°, lit.[13] m.p. 70°), and pelargonic acid (m.p. 82°, lit.[13] m.p. 84°) were obtained. The melting points of the derivatives were not depressed upon admixture with authentic samples.

Ozonolysis of Ethyl Vinyl Ketone (VI).—A solution of ketone VI (10.5 g.) in methylene chloride (200 ml.) was cooled to −50° and ozone (2.88 g./hr.) was passed through it for 5.5 hr. The solution was allowed to warm to room temperature and added to zinc dust (11 g.) in 50% acetic acid (60 ml.).

The mixture was extracted with petroleum ether to yield an acid that was esterified with the 7% boron trifluoride in methanol reagent (70 ml.). Methylene chloride was added to the esterification medium and the solution washed several times with water, dried, and distilled. When about 30 ml. of material were left in the distillation flask, 20 ml. of bromobenzene were added and the distillation resumed. A fraction was collected, b.p. 75–78° (3.5 g.). It was saponified and its *p*-toluidide prepared. The melting point of the derivative, 123°, was unchanged on admixture with the *p*-toluidide of propionic acid, lit.[13] m.p. 124°.

The dimedone derivative of formaldehyde was obtained from the aqueous layer as before, m.p. and m.m.p. 190–191°, lit.[10] m.p. 187°.

---

[10] W. Weinberger, *Ind. Eng. Chem., Anal. Ed.*, **3**, 365 (1931).

[11] C. F. H. Allen, *J. Am. Chem. Soc.*, **52**, 2955 (1930).

[12] C. Jutz, *Ber.*, **91**, 1867 (1958).

[13] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 200, 276.

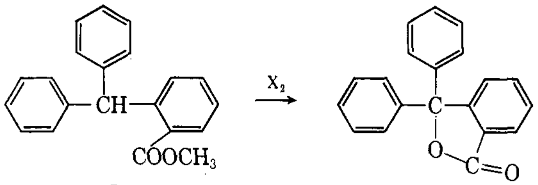
Steric Hindrance to Halogenation and Oxidation at the Tertiary Carbon of *o*-Carbophenoxytriphenylmethane

R. E. Lovins and L. J. Andrews

Department of Chemistry, University of California, Davis, California

Received September 3, 1963

In connection with another investigation, various substituted trityl halides have been prepared by free-radical halogenation of the corresponding triphenylmethanes. An interesting example of the steric protection of the tertiary position of the triphenylmethane molecule by a bulky *ortho* substituent has been encountered in the course of this synthetic work. Generally, trityl halides can be prepared in good quantity from the corresponding triphenylmethanes by photochemical methods or by reaction with N-bromosuccinimide. For example, a pure sample of trityl chloride itself has been obtained in 67% yield through photochlorination of triphenylmethane. Methyl *o*-benzhydrylbenzoate readily undergoes radical-type halogenation to give 3,3-diphenylphthalide (eq. 1). Presumably the tertiary halide derived from the ester is highly unstable with respect to lactone formation. No reaction occurs, however, when phenyl *o*-benz-



I II (1)