Anal. Calcd. for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.61; H, 5.61; N, 5.25.

The remaining crude neutral product (XXXIII) could not be induced to crystallize.

4-Phenyl-4-(β-carboxyethyl)-3,4-dihydro-2-quinolone (XXXIV).—The crude, neutral product remaining from the preceding experiment was dissolved in 25 ml. of glacial acetic acid and 50 ml. of concentrated hydrochloric acid. The solution was refluxed 5 hr. After dilution of the cooled solution, the crude material was taken into ether solution; the ether solution was washed with several portions of water and extracted with 5% sodium hydroxide solution. The alkaline solution was acidified with hydrochloric acid, and the crude acid was again extracted with ether. After the ether solution had been washed with water, dried over magnesium sulfate, and evaporated, the acid crystallized. There was obtained, after ether trituration, *ca.* 0.4 g. of crystals: m.p. 259–260°, raised to 262–263° by recrystallization from methanol; $\lambda_{\max}^{\mathrm{Nujol}}$ broad, bonded NH bands at 3.12–3.27 μ, intense doublet at 5.86 and 6.05 μ, and sharp, moderate peak 6.25 μ; $\lambda_{\max}^{\mathrm{EtOH}}$ 251 mμ (ε 11,090) with inflections at 263 and 280 mμ (ε 7800 and 2320, respectively).

Anal. Calcd. for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74. Found: C, 73.50; H, 5.86; N, 4.79.

Repetition of the steps, beginning with Beckmann rearrangement, leading to this compound did not significantly improve the yield. Attempted spirocyclization of this dihydroquinolone acid (0.4 g.), with polyphosphoric acid at 115–125° as usual, afforded less than 0.1 g. of neutral product consisting, after recrystallization from ether (Norit), of colorless crystals, m.p. 195–200° (softening 154°), evidently a mixture, $\lambda_{\max}^{\mathrm{Nujol}}$ 5.92–5.97 μ (unresolved doubled) and no peak *ca.* 700 cm.$^{-1}$, indicating that the material may have been an impure sample of spirotetralone.

1-Methyl-4-phenyl-4-(β-carbethoxyethyl)-3,4-dihydro-2-quinolone (XXXV). **A.**—Esterification of 0.25 g. of dihydroquinolone acid from the preceding experiment with a solution of 10 ml. of concentrated sulfuric acid in 200 ml. of ethanol gave, after usual isolation, 0.25 g. of neutral oil which did not crystallize.

B.—N-Methylation of 0.25 g. of ester from A, by refluxing and stirring with 1 g. of sodium hydride and 10 ml. of methyl iodide in 150 ml. of toluene for 7 hr., gave, after treatment with water and isolation of neutral product, 0.2 g. of noncrystalline material.

C.—Hydrolysis of crude product from B, by refluxing 3 hr. with 50 ml. each of glacial acetic and concentrated hydrochloric acids, and isolation of acid by extraction of an ether solution of crude material with dilute base and reacidification, gave crude acid which crystallized and, after filtration with the aid of ether, afforded 0.16 g. of material, m.p. 195–196°. Recrystallization from ether gave a pure sample: m.p. 198.5–199.5°; $\lambda_{\max}^{\mathrm{Nujol}}$ 5.77 and 6.13 μ (intense), as well as a bonded OH, a sharp peak at 6.27 μ and a sharp 701-cm.$^{-1}$ peak; $\lambda_{\max}^{\mathrm{EtOH}}$ 254 mμ (ε 10,460) with inflection at 262 mμ (ε 8820).

Anal. Calcd. for $C_{19}H_{19}NO_3$: C, 73.76; H, 6.19; N, 4.53. Found: C, 73.99; H, 6.19; N, 4.51.

Acknowledgment.—We are indebted to Mr. Louis Dorfman, Mr. George Robertson, Mr. Rudolf Oeckinghaus, Mr. James Mitchell, and Mrs. Carol Rodely for microanalytical data, to other members of Mr. Dorfman's staff, Miss Natalie Cahoon, Mrs. Margaret Mulligan, Miss Diane Bonney, and Mr. Charles Navarro for spectrophotometric results, and to Mrs. Angela Aretakis for aid in literature surveys.

Prototropic Rearrangement of a 1,4-Enyne. Products and Mechanism

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The alkaline rearrangement of methyl crepenynate (methyl *cis*-9-octadecen-12-ynoate) proceeds through a *cis*-enallenic intermediate to *trans,cis,trans*- and *trans,cis,cis*-8,10,12-octadecatrienoic acids in 70% yield. The formation of the isolable enallene is base catalyzed, but the second step, resulting in conjugated trienes, is thermal. These conjugated trienoic acids have been cyclized thermally to a disubstituted cyclohexadiene in good yield. The mechanism by which the Δ^{10} double bond of the conjugated triene becomes exclusively *cis* is probably an intramolecular 1,5-proton transfer *via* a cyclic transition state.

In a recent publication from this laboratory,[3] we reported isolation of a new polyunsaturated fatty acid, crepenynic acid, from the seed oil of *Crepis foetida* (family *Compositae*). This new acid was shown to have the structure of *cis*-9-octadecen-12-ynoic acid. In a subsequent publication,[4] we reported that methyl crepenynate (**1**) is readily isomerized by potassium hydroxide in ethylene glycol to an 8,10,12-octadecatrienoic acid (**2a**) in 70% yield. The nonconjugated enyne system was apparently converted completely to conjugated triene systems (**2a**–**3**) when heated with 10% base for 1 hr. at 120°.[4] The conjugated trienes had an infrared spectrum, characterized by maxima at 10.1 and 10.4 μ, different from any of the known geometric isomers of this system. Gas–liquid chromatography (g.l.c.) of the isomerization products showed, in addition to conjugated triene, an unknown peak which had retention characteristics[5] different from those of **2a** and **1**.

It became of interest to explore the mechanism by which this preponderance of one positional isomer is formed, to determine the geometric configuration of the conjugated trienoic acids formed, and to determine the structure of the unknown component which appeared on the gas chromatogram of the isomerization products. Results of such studies provide the basis of the work reported here.

Rearrangement of various types of acetylenic compounds under the influence of alkali has been observed by several groups of workers.[6–10] Allenes and isomeric acetylenes typically have been found as products. The alkali-catalyzed rearrangement of 1,4-enynes has been

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(2) A laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. Article is not copyrighted.

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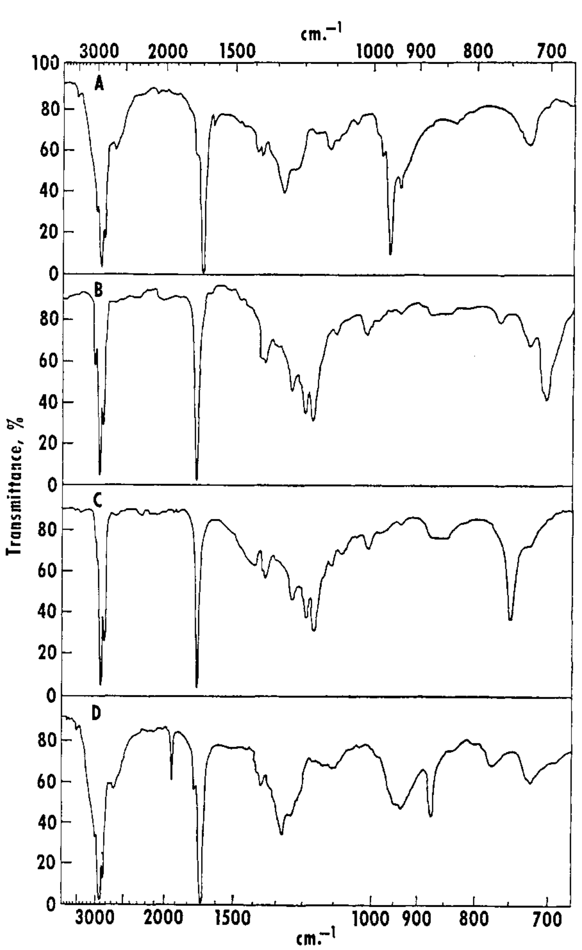

Figure 1.—Infrared spectra (CS_2 solutions) of (A) conjugated octadecatrienoic acids **2a–3**; (B) disubstituted cyclohexadiene ester **4**; (C) aromatic ester **5**; and (D) conjugated *cis*-enallenic acid **7**.

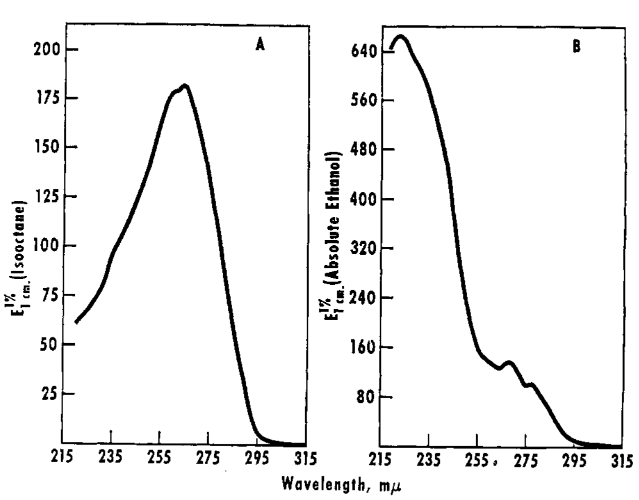

Figure 2.—Ultraviolet spectra of (A) disubstituted cyclohexadiene ester **4**; and (B) conjugated *cis*-enallenic acid **7**.

studied to a limited extent by Oroshnik and co-workers[9] and also by Bertrand.[10] They observed formation of conjugated allenes as end products rather than conjugated trienes. However, their preparative methods indicate that both were working with *trans*-enynes instead of *cis*-enynes as represented here by crepenynic acid.

Results

Cyclization of Conjugated Trienes.—When the conjugated trienes **2a–3** obtained from isomerization of methyl crepenynate were injected into an Apiezon L[11] g.l.c. column at 250°, 70% was converted into the new compound **4** (Scheme I) compared with 45% obtained with a polyester (LAC-2-R 446) column at 196°.[4] A quantity of **4** sufficient for characterization was isolated by preparative g.l.c. Spectral evidence obtained (Figures 1B and 2A) is consistent with a disubstituted cyclohexadiene structure.[12] Product **4** consumed 1.9 moles of hydrogen/mole of ester (calculation based on the molecular weight of a cyclohexadiene ester containing 19 carbon atoms). It was also found that **4** could be prepared by heating **2a–3** at 235° for 45 min., but the product contained polymeric material.

Aromatization of **4** was readily accomplished by heating with palladium on charcoal.[13] The aromatized product **5** shows the characteristic absorption bands (Figure 1C) of *ortho*-disubstituted benzenes.[14]

The mass spectrum of the aromatized cyclic ester suggests that it is mainly **5** ($n = 4$). Aromatic alkyl fragments obtained were 91, 105 (most intense), 147, 161, and 175. Aromatic carboxyl fragments were $M - 71$ and $M - 57$. Then a departure from this pattern was noted, and a different series of $M - 147$, $M - 161$, and $M - 175$ was observed. These fragments are in accord with the discussion of alkylbenzenes by Beynon[15] when $n = 4$. Oxidative degradation of the aromatic ester **5** by alkaline permanganate[12] followed by sublimation of the product gave a good yield of phthalic anhydride (**6**).

The facility with which **2a–3** undergoes thermal isomerization to **4** indicates that the main isomer, **2a**, must have a geometric configuration that is conducive to cyclization. It appears that the center double bond of the 8,10,12-conjugated triene is probably *cis*.[16]

Infrared Spectra of Conjugated Trienes.—The infrared spectra of the rearrangement products **2a–3** and of their esters prepared by diazomethane are similar in the 900–1000-cm.⁻¹ region. They show a strong band at 960 cm.⁻¹ (Figure 1A) and no absorption near 990 cm.⁻¹, indicating the absence of two adjacent *trans* double bonds.[17] However, acid-catalyzed esterification of **2a–3** probably effects some geometric isomerization of double bonds, since these esters do absorb at 990 cm.⁻¹ and, unlike the free acids, form adducts with maleic anhydride.[4,18]

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[11] The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

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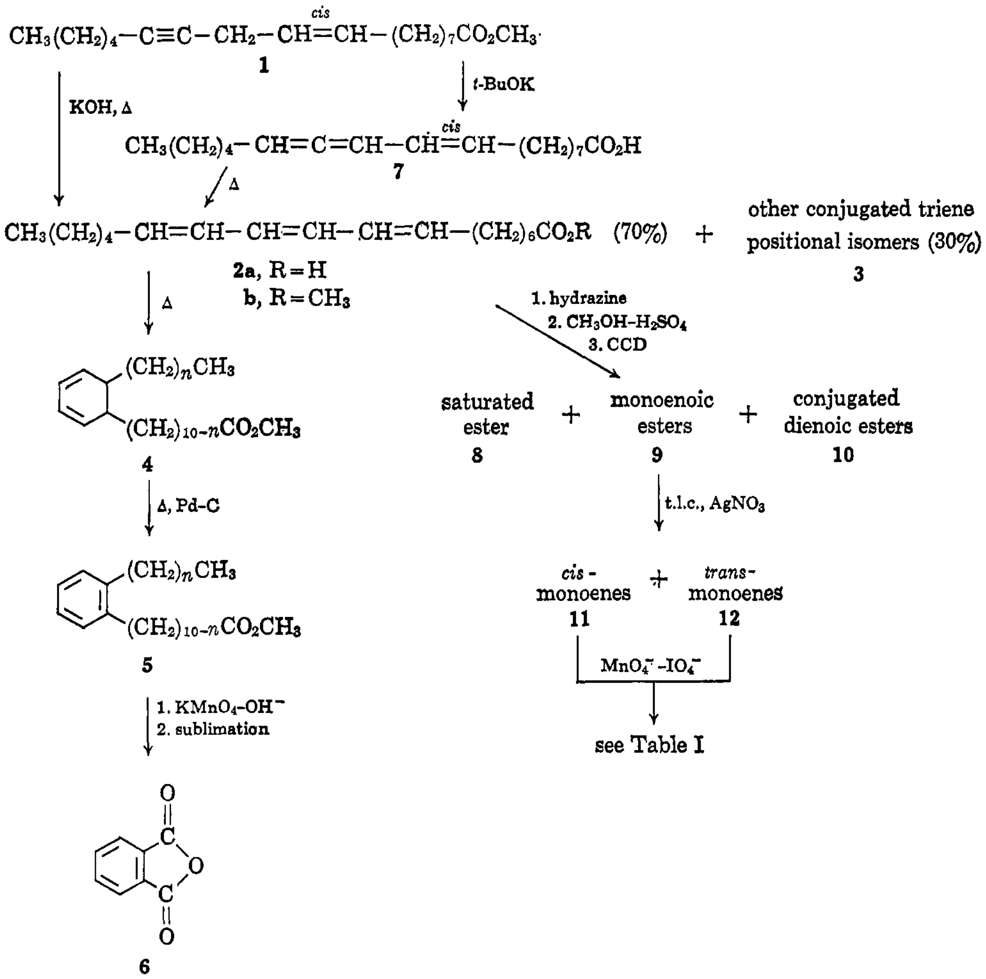
SCHEME I



Configuration of Conjugated Trienes.—A partial reduction of **2a**–**3** with hydrazine[19,20] was carried out to obtain direct evidence concerning the configuration of the individual double bonds. We had previously established the applicability of this method by partial reduction of α-eleostearic acid, a conjugated triene of known geometric configuration.[21]

The partial reduction products were esterified and separated by countercurrent distribution (c.c.d.) into saturated (**8**), monoenoic (**9**), conjugated dienoic (**10**), and conjugated trienoic ester fractions.[21]

The conjugated dienoic fraction was composed of 69% *cis,trans* (*trans,cis*), 16% *cis,cis*, and 11% *trans,trans* isomers as determined by g l.c. These isomers are relatively stable to g.l.c. conditions and are quite readily separated.[22] No separation of positional isomers was obtained. The oxidative cleavage of these conjugated dienes followed by analysis of the esterified products by g.l.c. showed that the predominant positional isomers present were the 8,10- and 10,12-octadecadienoates. The percentages of octanedioate (34%) and of decanedioate (42%) in the methyl esters of the oxidation mixture indicated that the 10,12-diene was present in larger quantity than the 8,10-diene.

The monoene fraction **9** was shown by quantitative infrared analysis[23] to contain 19.6% isolated *trans* double bonds. These monoenes were separated into a *cis* and a *trans* fraction by preparative thin layer chromatography (t.l.c.) on silver nitrate impregnated silica gel G plates as described earlier.[21] The *cis* fraction was obtained nearly pure, but the *trans* fraction was contaminated by 15% of *cis* monoenes because the complex mixture was not completely resolved. The percentages of the various monoene isomers in each fraction are shown in Table I. The

TABLE I

COMPOSITION OF MONOENES FROM HYDRAZINE REDUCTION[a]

C_{18} monoene isomer	% found in *cis*-Monoenes **11**	*trans*-Monoenes **12**[b]	% calcd. in monoene mixture **9**
Δ^7	. . .	0.9	0.3
Δ^8	2.3	35.5	11.7
Δ^9	8.2	2.6	6.6
Δ^{10}	64.4	6.1	47.8
Δ^{11}	11.8	1.5	8.8
Δ^{12}	12.0	44.8	21.4
Δ^{13}	1.3	7.9	3.2
Δ^{14}	. . .	0.7	0.2

[a] Determined by g.l.c. analysis of dibasic fragments from oxidative cleavage. [b] Contains 15% *cis* components by quantitative infrared analysis.

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calculated composition of **9** was derived by combining the results obtained for the *cis* and *trans* fractions.

These data show conclusively that most of the Δ^8 double bond in the original 8,10,12-triene **2a** has a *trans* configuration and that the Δ^{10} double bond is almost exclusively *cis*. The Δ^{12} double bond is a mixture of *cis* (*ca.* 40%) and *trans* configurations. Thus the original 8,10,12-octadecatrienoic acid (**2a**) is a mixture of *trans,cis,trans* and *trans,cis,cis* isomers.

The exact ratio of these two isomers originally present in the rearrangement mixture cannot be determined by any methods we used. The apparent amount of *cis*-Δ^{12}-monoene in the reduction products has probably been enhanced because the *trans* double bond of a *cis,trans*- or *trans,cis*-conjugated diene is reduced somewhat faster than the *cis* double bond. This rate difference was apparent in our earlier work with α-eleostearic (*cis,trans,trans*-9,11,13-octadecatrienoic) acid.[21] The small amount of the Δ^8-monoene in the reduction mixture compared with the amount of the Δ^{12}-monoene is also probably due to this rate difference because a large part of the Δ^{12}-monoene remaining would originate with the *cis,cis*-10,12-conjugated diene, whereas nearly all the Δ^8-monoene would be derived from the *trans,cis*-8,10-conjugated diene. The small amounts of conjugated trienes (**3**) other than the 8,10,12 isomer appear to be a complex mixture of geometric isomers.

Potassium *t*-Butoxide Rearrangement of Methyl Crepenynate.—The rearrangement of methyl crepenynate with potassium hydroxide at 120° could make the detection and isolation of a possible allenic intermediate difficult or impossible. Therefore, methyl crepenynate (**1**) was isomerized with potassium *t*-butoxide in *t*-butyl alcohol at or below room temperature in an effort to determine whether this rearrangement is mediated by an allenic intermediate. The infrared spectrum of the recovered product (**7**, Figure 1D) shows allenic absorption[24] at 1935 cm.$^{-1}$, but no conjugated triene absorption in the 930–1000-cm.$^{-1}$ region. The band at 874 cm.$^{-1}$ is attributed to the effect of the double bond in conjugation with the allene grouping. The ultraviolet spectrum of **7** (Figure 2B) is similar to the spectra obtained for various compounds containing an allenic group conjugated with a triple bond.[25] Therefore, **7** is probably a conjugated *cis*-enallene.

This enallene was rearranged to conjugated triene by heating under nitrogen on a steam bath. Periodic infrared analyses showed a continuous decrease in the intensities of the 1935- and 874-cm.$^{-1}$ bands. Simultaneously, bands at 978, 960, and 938 cm.$^{-1}$ appeared and their intensities gradually increased. The spectrum obtained for the product after 1 hr. and 50 min. of heating was identical with that of **2a**–**3** (Figure 1A). However, the conjugated triene isomers actually formed were not determined.

After compound **7** was esterified with diazomethane, the infrared spectrum of the esters showed the allenic group was still intact. Analysis of the esters by g.l.c. gave results comparable to those obtained by analysis of the conjugated triene methyl esters **2b** and **3**. These results support the conclusion that the rearrangement of methyl crepenynate proceeds through an allenic intermediate.

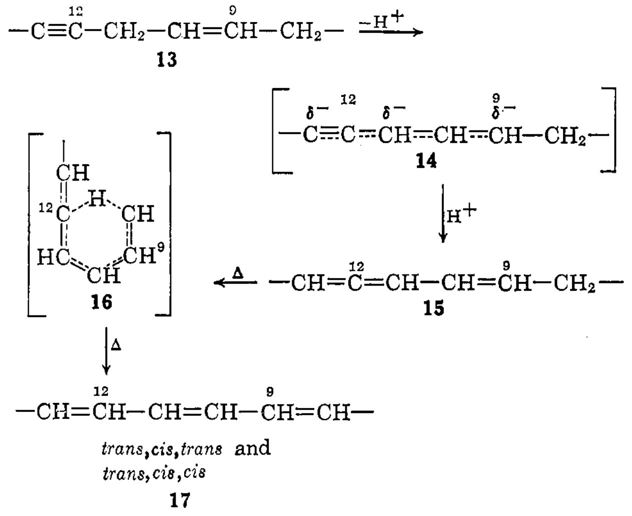
Discussion

Rearrangement Mechanism.—Conjugated trienoic acids having a *cis* center double bond have been reported in the literature. One of these reports concerned the synthesis of *cis,cis,trans*-9,11,13-octadecatrienoic acid.[26] Another report states that conjugated trienoic acids containing a *cis* center double bond are formed during heat treatment of fatty acids from Japanese cuttlefish oil.[27] However, the data given indicate that the yield of these conjugated trienes was quite low. Cartoni, Liberti, and Ruggieri[28] have reported that 68% of the acids obtained by alkaline isomerization of linolenic (*cis,cis,cis*-9,12,15-octadecatrienoic) acid is *trans,cis,trans*-10,12,14-octadecatrienoic acid. Their conclusion is based on theoretical considerations of the isomerization process and not actual chemical characterization of the acid. A gas–liquid chromatogram of isomerized linolenic acid appearing in their report shows a large peak supposedly due to the *trans,cis,trans* conjugated triene. In the light of our findings, we believe this g.l.c. peak is more probably a cyclic ester similar to our compound **4**.

Exclusive *cis* configuration of the Δ^{10} double bond in the 8,10,12-octadecatrienoic acid cannot readily be explained by mechanisms which have been applied to alkali isomerization of acids containing methylene-interrupted double bonds.

The probable mechanism for the rearrangements described is shown in Scheme II. The enyne compound **13** first loses a proton to give the hybrid carbanion **14**, which is then protonated to give the conjugated enallene **15**. This step of the rearrangement (from enyne to enallene) is base catalyzed, since methyl crepenynate did not rearrange when heated without base.[4] The conversion of the enallene to conjugated triene **17** is thermal and probably goes through the cyclic transition state **16**, which is possible only when the double bond of the enallene **15** has the *cis* configuration. The geometry of this intramolecular 1,5-proton transfer mechanism requires that the newly

SCHEME II



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formed Δ^{10} double bond have the *cis* configuration. The Δ^{8} and the Δ^{12} double bonds could be either *cis* or *trans* depending primarily on the amount of steric interaction between the cyclic portion of the transition state and the remainder of the molecule.

The *trans,cis,trans* conjugated triene appears to be the dominating factor in the infrared spectrum of this mixture of isomers (Figure 1A). The contribution of the *trans,cis,cis* isomer is not known, although data have been reported for a *cis,cis,trans* conjugated triene.[26] The appearance of only one strong band (960 cm.$^{-1}$) is surprising. Punicic (*cis,trans,cis*-9,11,13-octadecatrienoic) acid is an isomer with a symmetrical system of double bonds and its infrared spectrum has two strong bands at 989 and 938 cm.$^{-1}$.[17]

A similar thermal rearrangement (at 115°) of a conjugated enallene to a conjugated triene with a *cis* center double bond was reported recently by Crowley.[29] He also observed that, if the temperature is somewhat higher (270°), a cyclohexadiene results.

The apparent differences between our results and those of Oroshnik[9] and Bertrand[10] can be readily explained if it is assumed that their enallenes had *trans* double bonds.

Cyclization Mechanism.—Facile cyclization of **2b** in the absence of base supports the contention of others[16,30–32] that the cyclization reaction is not base catalyzed. If a precursor having the double bonds in positions and configurations that are conducive to cyclization is available, the cyclization will proceed thermally in good yield.

Friedrich and co-workers[33,34] have suggested a base-catalyzed cyclization mechanism which involves a hydroxylated intermediate. A reason given for this type of mechanism is that hydroxylated materials have been detected in the products; however, we found no evidence of hydroxyl-containing materials in any of our products.

In a recent communication, Marvell and co-workers[32] reported that thermal cyclization of a *trans,cis,trans* conjugated triene produced mainly the cyclohexadiene having *cis* substituents. We have no direct evidence concerning the configuration of the ring substituents on **4**, but have no reason to believe our results would differ from Marvell's in this respect.

Experimental[35]

Alkali Isomerization of Methyl Crepenynate (1).—Methyl crepenynate was obtained by c.c.d. of the methyl esters of *Crepis foetida* L. seed oil as described previously.[3] A preliminary report[4] discusses the procedure for carrying out the alkaline isomerization reaction and for recovery of the products. The infrared spectrum (Figure 1A) of the free acids **2a–3** has a strong band at 960 cm.$^{-1}$ and weaker bands at 938 and 978 cm.$^{-1}$. No stability problems were encountered during handling or storage of the isomerization products as free acids, but the methyl esters prepared by acid catalysis were very unstable.

Maleic Anhydride Adduct.—A 0.019-g. sample of **2a–3** in 5 ml. of benzene was refluxed under nitrogen with 0.017 g. of maleic anhydride for 3 hr.[18] Infrared analysis of the recovered product (yield 0.017 g.) showed that only a small amount of adduction had occurred.

Preparation of Cyclohexadiene Ester 4.—The conjugated trienoic acids **2a–3** were treated with diazomethane and the methyl esters **2b–3** were recovered. The infrared spectrum of the esters showed that diazomethane did not cause geometric isomerization of the double bonds. The methyl esters were injected into an LAC-2-R 446 g.l.c. column and the component with an equivalent chain length of 19.9[4] was trapped by bubbling the emerging carrier gas through ethanol at about 0°. The conditions were as follows: injection port, 260°; column bath, 196°; detector bath (thermal conductivity), 249°; fraction collector, 252°; helium flow rate, 102 cc./min. The yield of collected material (**4**) was 0.210 g. (of 95% purity by g.l.c.) from the 0.680 g. of esters that were injected. This represents a recovery of 65% since the conversion of conjugated triene to cyclic ester was about 45% in this column.

The infrared spectrum of the collected material (Figure 1B) showed a strong band at 704 cm.$^{-1}$ with a shoulder at 707 cm.$^{-1}$ and a weak band at 1013 cm.$^{-1}$. The ultraviolet spectrum (Figure 2A) of **4** showed $\lambda_{\max}^{\text{isooctane}}$ 264 mμ (ϵ 5300).

A 0.063-g. sample of **2a–3** was also cyclized by heating under nitrogen in a small, air condenser equipped flask at 235–240° for 45 min. During the heating period the sample darkened and became quite viscous. The infrared spectrum of the recovered material (yield 0.061 g.) showed that the original 960-cm.$^{-1}$ band had almost disappeared and a new band at 704 cm.$^{-1}$ was present.

Quantitative Hydrogenation of 4.—A 0.0164-g. portion of **4** dissolved in 95% ethanol was hydrogenated with platinum oxide catalyst, and the cyclic ester consumed 1.94 moles of hydrogen/mole of ester. Analysis of the recovered product by g.l.c. and infrared indicated that none of the original cyclohexadiene **4** remained.

Aromatization of 4.—A 0.188-g. portion of **4** and 0.050 g. of 10% palladium on charcoal were placed in a round-bottom flask fitted with an air condenser. The flask and contents (under nitrogen) were heated at 240–250° for 3 hr. The cooled product was dissolved in petroleum ether (b.p. 30–60°), and the solution was filtered to remove the catalyst. The solvent was removed *in vacuo*, and 0.111 g. of product (**5**) was obtained. Aerosol formation occurred during the heating period and the nitrogen flow forced some of this mist out the condenser.

The infrared spectrum of **5** (Figure 1C) had a strong, sharp band at 750 cm.$^{-1}$ and a weak band at 1013 cm.$^{-1}$. The ultraviolet spectrum had a weak maximum at 271 mμ (ϵ 430) and inflection points at 261, 256, 250, 246, and 238 mμ.

The mass spectrum showed the following bands corresponding to aromatic fragments (with relative intensities indicated): 77 (6%), 91 (34%), 105 (most intense, 100%), 147 (12%), 161 (7%), 175 (4%), M − 71 (3%), M − 57 (3%), and a parent peak at 290 (30%). Other carboxyl fragments of diagnostic interest were M − 147 (6%), M − 161 (7%), and M − 175 (7%).

Oxidative Degradation of Aromatic Ester 5.—The aromatic ester (0.035 g.) was refluxed for 26 hr. with 5 ml. of water containing 0.100 g. of sodium hydroxide. Small samples of potassium permanganate were added periodically until a total of 0.525 g. had been added. The mixture was cooled, acidified with dilute hydrochloric acid, and reduced with sodium metabisulfite. This solution was saturated with sodium chloride and extracted thoroughly with ethyl ether. The extract was dried over anhydrous sodium sulfate and filtered. An inhomogeneous white solid (0.021 g.) remained after the ether had been removed with a stream of nitrogen.

The solid product was sublimed to give 0.014 g. of white needles (**6**), m.p. 129–132°. Resublimation gave 0.009 g., m.p. 130–132°. An admixture with pure phthalic anhydride (m.p. 131.5–132.5°) melted at 131–133°. The ultraviolet analysis of this

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[35] Infrared spectra were obtained with a Perkin-Elmer Model 137-0001 spectrophotometer, ultraviolet spectra with a Beckman DU spectrophotometer, and g.l.c. analyses with a Burrell Kromo-Tog K-5 chromatograph equipped with both Apiezon L and LAC-2-R 446 columns. All identifications by g.l.c. are based on retention characteristics of the material in polar or nonpolar columns or both compared with the retention characteristics of similar known compounds (see ref. 5). Compositions obtained by g.l.c. are expressed as area percentages. The percentage of conjugated trienes obtained by g.l.c. should be interpreted with the findings of Morris, *et al.*,[22] in mind. Melting points were determined on a Fisher-Johns block and are corrected.

product compared with that of pure phthalic anhydride showed it to be 91% pure.[36]

Potassium *t*-Butoxide Isomerization of Methyl Crepenynate (1).—Redistilled *t*-butyl alcohol was partially dried over anhydrous sodium sulfate and decanted. An excess of metallic sodium was added cautiously over a 4-hr. period. The mixture was refluxed for 1 hr. and the *t*-butyl alcohol was distilled. Potassium (1.3 g.) was added slowly to 30 ml. of the dry alcohol, and the mixture was allowed to stand at room temperature overnight. Precautions were taken to exclude moisture throughout this procedure.

The potassium *t*-butoxide in *t*-butyl alcohol reagent (9.0 ml.) was added to a 0.050-g. sample of methyl crepenynate (**1**) and the solution was stored at 1° overnight. The solidified reaction mixture was warmed to room temperature and allowed to stand 4 hr. This solution was diluted with water, acidified with dilute hydrochloric acid, and extracted with ethyl ether. The recovered product (**7**, 0.046 g.) showed strong allenic absorption in the infrared (Figure 1D). Ultraviolet analysis (Figure 2B) gave $\lambda_{\max}^{\mathrm{EtOH}}$ 222 mμ (ϵ 18,900) and also 268 mμ (ϵ 3800).

Infrared analysis of the methyl esters of **7** prepared with diazomethane showed that the allenic absorption at 1935 and 874 cm.$^{-1}$ remained unchanged. Analyses of these esters by g.l.c. gave 42% cyclic ester **4** and 49% conjugated trienes on the LAC-2-R 446 column (196°), and 69% cyclic ester and 20% conjugated trienes on the Apiezon L column (250°).

Rearrangement of Enallene 7 by Heat.—The enallenic acid **7** was heated in a nitrogen atmosphere on a steam bath and infrared spectra of the products were determined periodically. The bands at 1935 and 874 cm.$^{-1}$ had completely disappeared after the sample had been heated for 1 hr. and 50 min. and the spectrum of the final material was identical with that of the conjugated trienes **2a–3** from potassium hydroxide isomerization of methyl crepenynate.

Hydrazine Reduction of Rearrangement Products 2a–3.—The partial hydrazine reduction of the conjugated trienes and c.c.d. of the esterified reduction products were done as previously described.[21] Analysis of the esterified reduction mixture by g.l.c. gave the following composition (all components are C_{18}): saturated, 12%; monoenes, 24%; isolated diene, less than 1%; *cis,trans* (*trans,cis*) conjugated diene, 25%; *cis,cis* conjugated diene, 6%; *trans,trans* conjugated diene, 4%; cyclic, 12%; and conjugated triene, 15%.

Quantitative infrared analysis of the monoene fraction (97% monoene by g.l.c.) from c.c.d. showed absorption at 963 cm.$^{-1}$ equivalent to 19.6% of isolated *trans* double bonds calculated as methyl elaidate.[23] The conjugated diene fraction was shown by g.l.c. to contain 69% *cis,trans* (*trans,cis*), 16% *cis,cis*, and 11% *trans,trans* dienes.

Separation of Monoenes 9.—The monoene fraction was separated into a *cis* (**11**) and *trans* (**12**) fraction by preparative t.l.c. on silver nitrate impregnated silica gel G plates as described previously for the hydrazine reduction of α-eleostearic acid.[21] The *trans* fraction contained 15% of *cis* isomers, and the *cis* fraction contained no *trans* isomers. Total recovery from the t.l.c. plates was 91%.

Permanganate–Periodate Oxidation of 11 and 12.—Both the *cis*- and *trans*-monoene fractions were cleaved by permanganate–periodate oxidation in 60% *t*-butyl alcohol as described by von Rudloff.[37] The products were recovered as usual, and the free acids were subjected to analysis by g.l.c. only for identification of the monobasic fragments. Hexanoic, heptanoic, octanoic, nonanoic, and decanoic acids were produced from the *cis*-monoene fraction. The *trans*-monoene fraction yielded all the straight-chain monobasic acids from pentanoic through undecanoic acid. The remaining oxidation products were esterified by refluxing with 1% sulfuric acid in methanol, and the esters were analyzed by g.l.c. for identification and percentages of the various dibasic cleavage fragments. The percentages were converted into the original composition of the monoene fractions (Table I).

Permanganate–Periodate Oxidation of 10.—The conjugated diene fraction **10** was cleaved like the monene fractions, and the products were recovered and analyzed as free acids by g.l.c. This analysis showed that all the straight-chain monobasic acids from butanoic through decanoic were present and that hexanoic and octanoic acids were the major components. The remainder of the cleavage products was esterified by sulfuric acid in methanol, and the esters were analyzed by g.l.c. The percentages of dibasic acid methyl esters were hexanedioate, 1%; heptanedioate, 1%; octanedioate, 34%; nonanedioate, 10%; decanedioate, 42%; undecandieoate, 10%; and dodecanedioate, 2%.

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Base-Induced Cyclization Reactions of Propargyloxyethanol and the 2-Haloallyloxyethanols[1a]

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Cyclization reactions of propargyloxyethanol (**7**) and the 2-haloallyloxyethanols **5** and **6** induced by sodium hydroxide or potassium hydroxide were found to be markedly dependent on solvent. In water, 3,6-dioxacycloheptene (**11**) and 2-methylene-1,4-dioxane (**9**) are the main products; 2-vinyl-1,3-dioxolane (**8**) is also formed. In decalin, dimethyl sulfoxide, and triglyme, **8** and 2-methyl-1,4-dioxene (**10**) are the major products, and only small amounts of **9** and **11** are formed. The mechanisms of formation of **8–11** are discussed.

Treatment of a 2-haloallyl compound with base can bring about one or more of a large number of transformations. Dehydrohalogenation across either the double bond or the single bond of a 2-haloallyl group (a) can occur to give a propargyl group (b) or an allenyl group (c), respectively; the 2-haloallyl group can also undergo prototropic rearrangement to a *cis*- or *trans*-2-halopropenyl group (d). Reactions of the initially formed products can also occur; thus, dehydrohalogenation of d can lead to c or a 1-propynyl group (e), and prototropic rearrangement of the propargyl group (b) can lead to an allenyl group (c), which in turn can undergo protropic rearrangement to e. Further, each unsaturated carbon in a–e is susceptible to attack by a nucleophile. Therefore, a 2-haloallyl compound or a propargyl compound that contains a nucleophilic atom can undergo conceivably a number of base-induced cyclization reactions. From these considerations, we concluded that detailed study of the fate of such 2-haloallyl or propargyl compounds, on treatment with base,

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