**3,3'-Di(cyclohexa-1,3-dienyl)biphenyl.**—A mixture of 4.4 g. of the above crude dihydroxyl compound and 0.026 mole of crystalline boric acid[10] was placed in a test tube and heated in a Wood's metal bath at 280–300° for 5 min. The mixture was stirred with a stirring rod while being heated. After cooling, the material in the test tube became a yellow glass. This material was dissolved in hot benzene by portionwise extraction. The benzene solution was filtered, washed with water, sodium hydrogen carbonate solution, and finally with water. The yellow organic layer was dried and after removal of the drying agent, the solution was evaporated to 15 ml. This was chromatographed on alumina (80–200 mesh) with benzene as an eluent. After complete removal of the solvent from the eluate, 2.0 g. of a yellow gum was obtained. This material could not be induced to crystallize.

*m*-**Quaterphenyl** (**VII**).—A solution of the prior crude diene (3.5 g.) in 10 ml. of *p*-cymene was heated under reflux with 5% palladium–charcoal (0.35 g.) to effect aromatization. The solvent was slowly and almost completely removed by distillation and at a temperature of 300–310° rapid evolution of hydrogen was observed. This temperature was maintained until no further gas evolution was seen (2 hr.). The resulting black glassy material was dissolved in hot benzene and filtered through a 20-cm. alumina column. Evaporation of the benzene from the eluate left a pale yellow glass. This material was distilled and a colorless distillate was collected at 240–250° at 1-mm. pressure. A solution of the distillate in absolute ethanol deposited white plate-like crystals after standing for 2 days which were recrystallized from ethanol. The over-all yield of *m*-quaterphenyl based on the starting diketone (IV) was 30% (1.2 g.); m.p. 83–84° (lit. m.p. 85–86°).[11]

*Anal.* Calcd. for $C_{24}H_{18}$: C, 94.12; H, 4.88. Found: C, 93.33; H, 5.60.

*m*-**Sexaphenyl** (**VIII**).—A Soxhlet extractor was employed for the addition of diketone (IV) (0.01 mole) to an ethereal solution (150 ml.) of phenylmagnesium bromide which had been prepared in the usual manner from 0.12 mole of bromobenzene. The addition required approximately 4 days. The Grignard complex was decomposed with dilute sulfuric acid. The yellow ethereal layer was separated and the water layer was extracted again with benzene. The combined organic extracts were submitted to steam distillation from dilute phosphoric acid. The residue in the steam pot was extracted with benzene, and the resulting benzene solution was washed with water, saturated sodium hydrogen carbonate solution, and finally with water. The benzene volume was reduced to approximately 10 ml. by distillation, and this solution was passed through a small alumina column with the aid of a further 25 ml. of benzene. By evaporation of the solvent, 3 g. of glassy material was obtained which could not be induced to crystallized.

Direct aromatization of this material was effected with palladium–charcoal in the manner described earlier. The product was treated also as described before. *m*-Sexaphenyl (2.1 g., 44%) was obtained upon recrystallization from ethanol; m.p. 144–145° (lit.[8] m.p. 147–147.5°).

*Anal.* Calcd. for $C_{36}H_{26}$: C, 94.32; H, 5.68. Found: C, 94.41; H, 5.55.

*m*-**Octaphenyl** (**IX**).—In the manner described in the preceding preparation and employing the Soxhlet apparatus, 0.01 mole of diketone (IV) was added to the Grignard reagent prepared from 0.082 mole of 3-xenyl bromide in ether. The addition was effected in 4 days. The Grignard reaction mixture was then hydrolyzed and worked up as described before for the analogous reaction mixture. The amount of yellow glass obtained after the final evaporation of solvent was 4.4 g. This material could not be crystallized.

The prior crude tetraene (4.4 g.) in 10 ml. of *p*-cymene was aromatized with palladium–charcoal as described for *m*-sexaphenyl. The flask was cooled and the material dissolved in ether. The solution was filtered through a 10-cm. alumina column. The eluate was evaporated to dryness and the residue was crystallized from ether–petroleum ether (b.p. 30–60°) and recrystallized from ether to yield *m*-octaphenyl (1.4 g., 23%); m.p. 127–129° (lit.[8] m.p. 127–129°).

*Anal.* Calcd. for $C_{48}H_{34}$: C, 94.42; H, 5.38. Found: C, 94.22; H, 5.85.

**3,3'''''-Dibromo-*m*-sexaphenyl** (**X**).—3-Bromophenylmagnesium bromide was prepared from magnesium (0.98 g., 0.04 g.-atom) and 1,3-dibromobenzene (9.4 g., 0.04 mole) in 60 ml. of ether. Most of the magnesium had reacted when the diketone IV (0.013 mole), dissolved in 150 ml. of benzene, was added slowly. The mixture was stirred under reflux for 40 hr., cooled, hydrolyzed by cold dilute sulfuric acid, and extracted with benzene. The benzene layer was submitted to steam distillation from a dilute sulfuric acid medium, and the steam pot residue was extracted with hot benzene. The benzene layer was washed with water, dilute base, and water and finally dried. Evaporation of the solvent left behind a viscous yellow-orange glass. This residue was dissolved in chloroform and aromatized by the previously described bromine method. The resulting solution, after expulsion of hydrogen bromide, was passed through a small alumina (80–200 mesh) column. Petroleum ether (b.p. 60–80°)–benzene (4:1) was employed as the eluent. An orange viscous material was isolated after evaporation of the first 200 ml. of solvent and recrystallized from acetone (six times). It was finally recrystallized from a mixture of carbon tetrachloride and ethanol to provide X in small yield; m.p. 143–145°.

*Anal.* Calcd. for $C_{36}H_{24}Br$: C, 70.15; H, 3.93; mol. wt., 616. Found: C, 70.43; H, 4.21; mol. wt., 620.

**Acknowledgment.**—The author wishes to thank Dr. Franz Kasler for the microanalyses and Mr. Donald Glover of the Naval Ordnance Laboratory for the molecular weight determinations.

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[11] G. F. Woods and F. T. Reed, *J. Am. Chem. Soc.*, **71**, 1348 (1949).

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# Preparation of Linear *m*-Polyphenyls from Mono- and Dichalcones[1]

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A new method has been developed for the synthesis of linear *m*-polyphenyls. This procedure involves the following steps: (1) chalcone formation, (2) Michael condensation and ring closure, (3) decarbethoxylation, (4) reduction, (5) dehydration, and (6) aromatization. The preparation of *m*-terphenyls, *m*-quinquephenyls, certain intermediates, and the possible preparation of *m*-sexaphenyls will be discussed.

Heretofore, the only useful general method for the preparation of linear *m*-polyphenyls has been the one which employs the reaction of 3-ethoxy-2-cyclohexenone[4,5] with organolithium or Grignard reagents. The resulting ketone is treated with another organolithium or Grignard reagent and, after dehydration and aromatization steps, the desired polyphenyl is obtained.

Another general method for the synthesis of *m*-polyphenyls which is reported herein has been desired for two reasons. The first was that an alternate syn-

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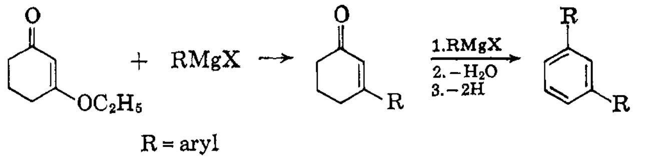
[1] This work was supported in part by the U. S. Air Force contract AF 33(616)-5063.

[2] Du Pont Teaching Fellow, 1960–1961.

[3] Gillette-Harris Research Fellow, 1961–1962.

[4] G. F. Woods, F. T. Reed, T. E. Arthur, and H. J. Ezekiel, *J. Am. Chem. Soc.*, **73**, 3854 (1951).

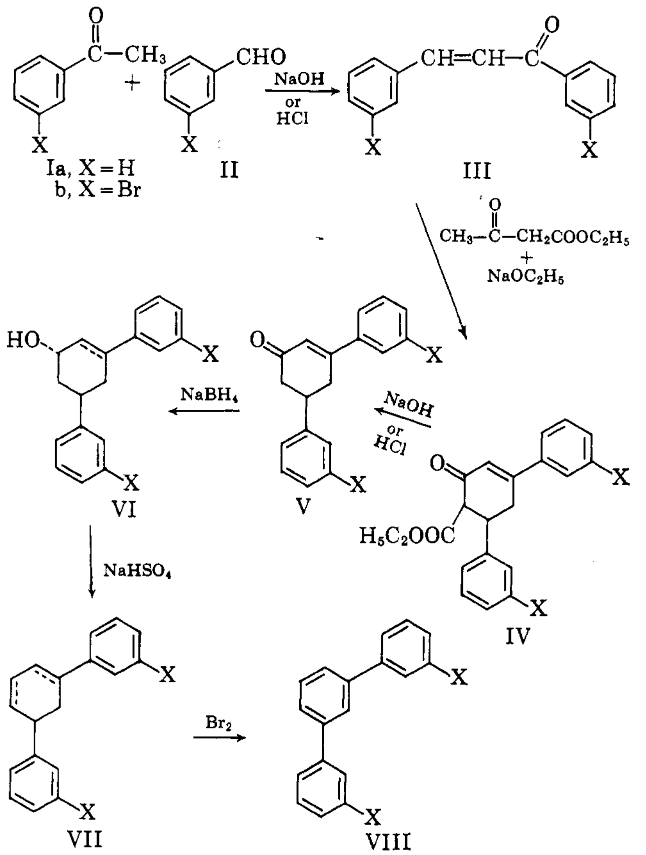
[5] G. F. Woods, D. D. Centola, H. E. Ruskie, and C. D. Miller, *ibid.*, **82**, 5227 (1960).



thesis of these *m*-polyphenyls applied to a particular substance would lend credence to the structure assigned particularly since there is as yet no proof of structure for these compounds. Secondly, a better or superior method to the previous "enol ether" synthesis was desired.

This new procedure is shown for the preparation of *m*-terphenyl (VIIIa) and 3,3''-dibromo-*m*-terphenyl (VIIIb).

CHART I



3-Bromoacetophenone (Ib) and 2-bromobenzaldehyde (IIb) were prepared by the use of the "swamping" catalyst procedure.[6] The initial condensation reaction which involved chalcone formation of (IIIb) is both acid- and base-catalyzed. Acid catalysis (gaseous hydrogen chloride[7]) consistently gave better results. The Michael condensation of acetoacetic ester with the chalcone IIIa or IIIb and subsequent cyclization were usually effected in 20–50% yield. Decarbethoxylation was observed under either basic or acidic conditions, but the latter procedure gave superior results. Acid decarbethoxylation was accomplished by heating the ester with an acid solution in a sealed tube,[8] and reduction of the resulting substituted cyclohexenone compound (Va or Vb) was done with sodium borohydride. A heterogeneous dehydration system (sodium hydrogen sulfate in benzene[9]) was employed to effect dehydration of the cyclohexenol compound (VIa or VIb). Aromatization was achieved by the use of bromine.[5] Compound VIIIb could not be obtained as a solid at room temperature. This compound had been synthesized earlier by another method and the same results were found.[10]

The prior procedure was adapted for the preparation of *m*-quinquephenyl (XVIIa) and 3,3''''-dibromo-*m*-quinquephenyl (XVIIb) which themselves may be considered as substituted *m*-terphenyls.

The methyl groups of *m*-xylene (IX) were brominated in the presence of infrared radiation to give a good yield of $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*m*-xylene (X). The tetrabromide was hydrolyzed by an alcoholic–aqueous solution of potassium oxalate[11] from which isophthalaldehyde (XI) was obtained. The ensuing reactions were carried out as before in the *m*-terphenyl series, and *m*-quinquephenyl (XVIIa) and 3,3''''-dibromo-*m*-quinquephenyl (XVIIb) were isolated. Both XVIIa and XVIIb had been prepared earlier in our laboratory by the employment of the "enol ether" method.[10] Physical data were in good agreement for the two *m*-quinquephenyls, XVIIa and XVIIb, with the previously prepared *m*-quinquephenyls.

Similarly, the preparation of 3,3'''''-dibromo-*m*-sexaphenyl (XXVII) might be prepared *via* the chalcone route.

3,3'-Dimethylbenzidine (XVIII) was tetraazotized and dideaminated by the use of hypophosphorus acid.[12] The resulting 3,3'-dimethylbiphenyl (XIX) was brominated while being irradiated by an infrared lamp and $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-3,3'-dimethylbiphenyl (XX) was isolated. Hydrolysis of the tetrabromo compound (XX) afforded 3,3'-diformylbiphenyl (XXI). This dialdehyde treated with two moles of 3-bromoacetophenone produced the dichalcone (XXII) which subsequently reacted as in the *m*-terphenyl and *m*-quinquephenyl systems. The diketone (XXIV) was obtained after decarbethoxylation in an acid medium but in poor over-all yield. The utilization of this diketone (XXIV) for the preparation of XXVII was not explored further because of the poor yield. Further, the chalcone method in general does not appear to be as satisfactory as the "enol ether" method.

## Experimental

All melting points and boiling points are uncorrected. Ultraviolet spectra were obtained with a Beckman spectrophotometer Model DK-1 using spectrograde isooctane or 95% ethanol as the solvent. All infrared absorption spectra were obtained with a Beckman IR-5 recording spectrophotometer using melts on sodium chloride plates.

Absolute ethanol used in the reactions with sodium was distilled from calcium hydride. Ethyl acetoacetate used in the Michael condensation reactions was purified according to Vogel.[13]

**3,3'-Dibromobenzalacetophenone (IIIb).**—A mixture of Ib[6] (0.05) mole and IIb[6] (0.05 mole) was dissolved in 100 ml. of

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[6] D. E. Pearson, H. W. Pope, W. W. Hargrove, and W. E. Stamper, *J. Org. Chem.*, **23**, 1412 (1958).

[7] A. Leon, A. Robertson, R. Robinson, and T. Seshadri, *J. Chem. Soc.*, 2665 (1931).

[8] S. M. Nadkarni, A. M. Warriar, and T. S. Wheeler, *ibid.*, 1798 (1937).

[9] R. L. Huang, *ibid.*, 3655 (1954).

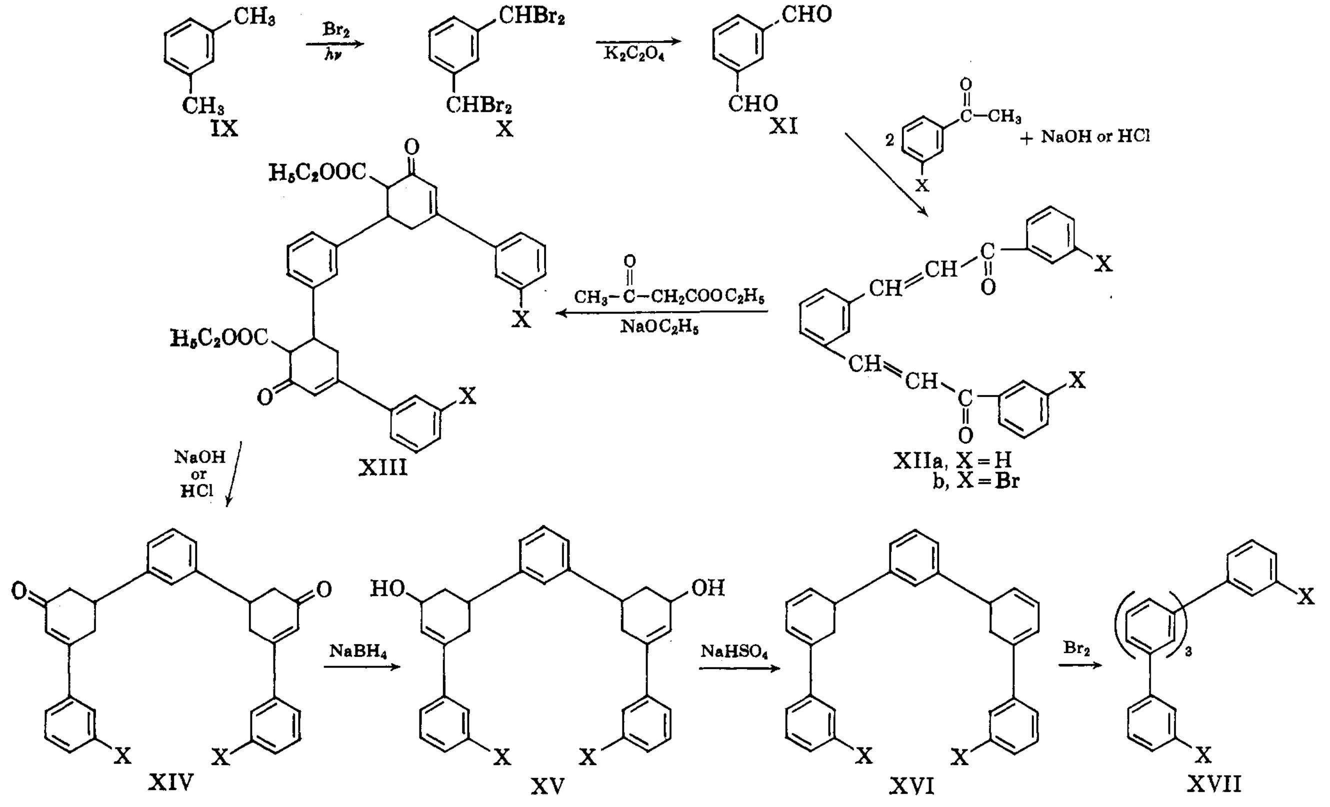
[10] G. Forrest Woods and Norman B. Sunshine, *J. Org. Chem.*, **28**, 2514 (1963).

[11] J. Thiele and O. Gunther, *Ann.*, **347**, 109 (1906).

[12] A. I. Vogel, "A Textbook of Practical Organic Chemistry Including Qualitative Organic Analysis," 3rd Ed., Longmans Green and Co., Inc., New York, N. Y., 1956, p. 616.

[13] Ref. 12, p. 487.

CHART II



methyl alcohol. To this solution was added dropwise 3 ml. of a saturated solution of sodium hydroxide in methyl alcohol. This mixture was stirred for 24 hr. at room temperature during which time a yellow solid precipitated. The solid was isolated by filtration and recrystallized from absolute ethanol; m.p. 80–81°; yield, 15.2 g. (83%); $\lambda_{max}^{isooctane}$ 291 mμ (ε 15,700), 252 (12,200), $\lambda_{max}^{EtOH}$ 303 mμ (ε 31,400), 231 (16,900); infrared spectrum showed C=O, 1665 cm.$^{-1}$.

*Anal.* Calcd. for $C_{15}H_{10}Br_2O$: C, 49.22; H, 2.75. Found: C, 49.00; H, 2.78.

The 2,4-dinitrophenylhydrazone derivative was prepared by the usual procedure and was recrystallized from ethanol, m.p. 222–224°.

*Anal.* Calcd. for $C_{21}H_{14}N_4O_4Br_2$: C, 46.18; H, 2.58. Found: C, 46.47; H, 2.83.

**2-Carbethoxy-3,5-di(3-bromophenyl)-5-cyclohexenone (IVb).**—Ethyl acetoacetate (0.055 mole) was added to an alcoholic solution of sodium ethoxide that had been prepared from sodium (0.013 g.-atom) and 140 ml. of absolute ethanol. After stirring the reaction mixture for 1 hr. IIIb (0.012 mole) was added and the resulting solution was refluxed for 3 hr. The solution while still hot was added to cold dilute hydrochloric acid. A yellow precipitate was isolated by suction filtration and recrystallized from 95% ethanol to give a white solid; m.p. 103–104°, yield, 2.3 g. (40%). Absorption bands at 1740 cm.$^{-1}$ (ester carbonyl) and at 1665 cm.$^{-1}$ (C=O) were observed in the infrared spectrum.

*Anal.* Calcd. for $C_{21}H_{18}Br_2O_3$: C, 52.73; H, 3.79. Found: C, 52.67; H, 3.97.

**3,5-Di(3-bromophenyl)-2-cyclohexenone (Vb).**—The keto ester (IVb) (0.006 mole) was added to a solution containing sodium hydroxide (0.05 mole) dissolved in a mixture of 50 ml. of ethanol and 30 ml. of water. This mixture was refluxed for 3 hr., cooled, and extracted with benzene. The benzene layer was washed with water and dried over magnesium sulfate. The benzene was evaporated and a yellow oil was isolated which crystallized from ethanol to give a white solid; m.p. 98–99°; yield, 2.35 g. (92%); $\lambda_{max}^{isooctane}$ 270 mμ (ε 19,700), 230 (inflection), 225 mμ (inflection). The infrared spectrum showed carbonyl absorption at 1665 cm.$^{-1}$. A mixture melting point was taken with the starting material and the range observed was 83–93°. The infrared spectrum showed the absence of the ester group.

*Anal.* Calcd. for $C_{18}H_{14}Br_2O$: C, 53.23; H, 3.47. Found: C, 53.28; H, 3.60.

The 2,4-dinitrophenylhydrazone derivative was prepared by the usual procedure and was recrystallized from ethyl acetate, m.p. 245–247°.

*Anal.* Calcd. for $C_{24}H_{18}N_4O_4Br_2$: C, 49.17; H, 3.09. Found: C, 49.17; H, 3.37.

**3,5-Di(3-bromophenyl)-2-cyclohexenol (VIb).**—The keto compound Vb (0.0016 mole) was dissolved in 25 ml. of Ethyl Cellosolve. A solution composed of sodium borohydride (0.2 g.) dissolved in 5 ml. of water containing 1 ml. of 10% sodium hydroxide solution was added to effect reduction of the keto group. This reaction mixture was allowed to stand for 24 hr. at room temperature. The resulting solution was added to cold dilute sulfuric acid and a yellow viscous oil separated from the solution. This oil could not be induced to crystallize. The infrared spectrum showed a complete absence of the carbonyl band and an emergence of a strong hydroxyl band. The yield was 0.57 g. (86%).

*Anal.* Calcd. for $C_{18}H_{16}Br_2O$: C, 52.97; H, 3.95. Found: C, 53.13; H, 4.13.

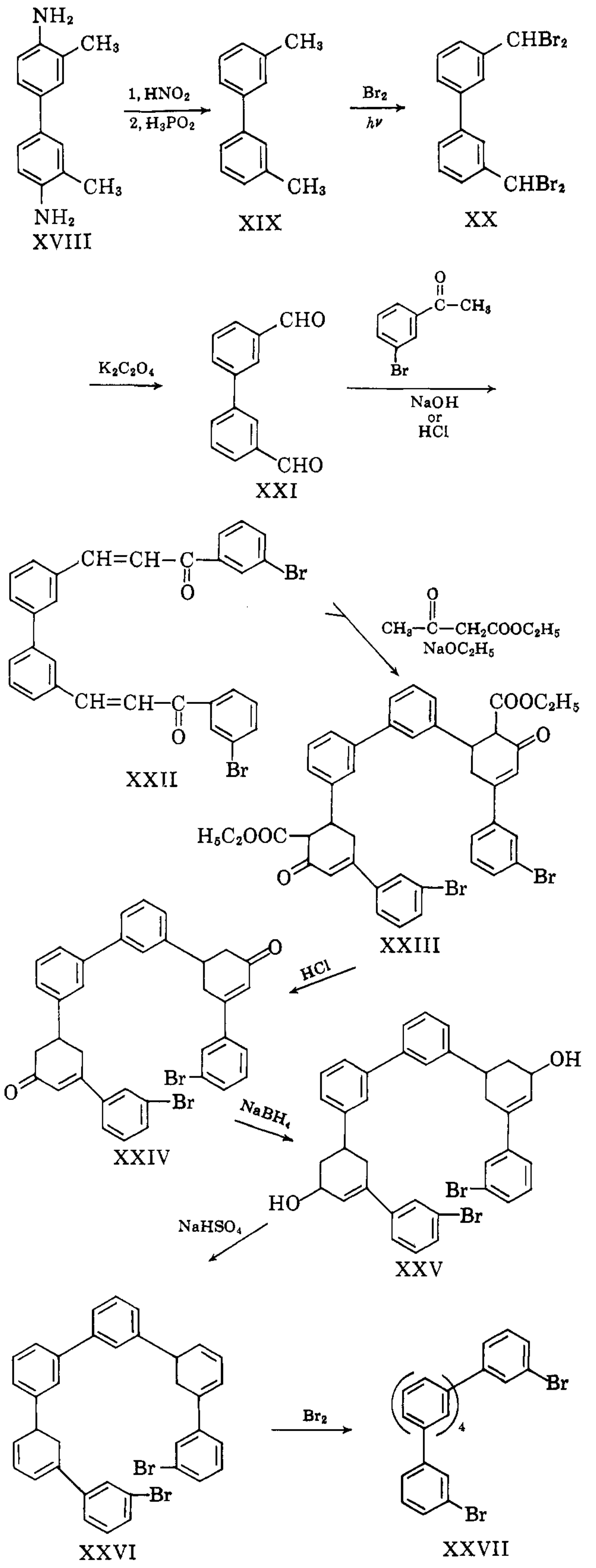
**3,3′′-Dibromo-*m*-terphenyl (VIIIb).**—A mixture of VIb (0.006 mole) and fused sodium hydrogen sulfate (1.5 g.) was refluxed for 24 hr. in benzene to effect dehydration. The reaction mixture was cooled and passed through an alumina chromatographic column (80–200 mesh) using benzene as the eluent. The benzene was evaporated and a yellow oil remained. This oil was dissolved in chloroform and cooled. A solution of bromine in chloroform was added slowly until a pink color persisted. The solution was warmed on the steam bath to expel hydrogen bromide and to evaporate most of the solvent. The residue, which was a dark viscous glass, was dissolved in a mixture of 50% benzene and petroleum ether (b.p. 60–80°). This solution was passed through an alumina chromatographic column, using petroleum ether (b.p. 30–69°) as the eluent. The solvent was evaporated and a colorless oil was obtained which could not be made to crystallize; $\lambda_{max}^{isooctane}$ 247 mμ (44,700).

*Anal.* Calcd. for $C_{18}H_{12}Br_2$: C, 55.68; H, 3.11. Found: C, 55.50; H, 3.40.

An earlier synthesis of 3,3′′-dibromo-*m*-terphenyl by another method parallels this work in that a solid substance could not be obtained.[10]

**2-Carbethoxy-3,5-diphenyl-5-cyclohexenone (IVa).**—Ethyl acetoacetate (0.6 mole) was added to a solution of sodium ethoxide in ethyl alcohol that had been prepared from sodium (0.2 g.-atom) and 350 ml. of absolute ethyl alcohol. Benzalacetophenone (0.2 mole) was added in one batch and the resulting solution was refluxed for 4 hr. While still hot, the reaction mixture was added to a cold solution of dilute hydrochloric acid. A yellow precipitate was isolated by filtration and recrystallized from alcohol; m.p. 109–110° (lit.[14] m.p. 111–112°); yield, 40 g. (62%).

CHART III



**3,5-Diphenyl-2-cyclohexenone (Va).**—The keto ester (IVa) (0.016 mole) was heated for 4 hr. at 150° with 25 ml. of 10% hydrochloric acid in a sealed tube. The tube was opened and the contents were extracted with benzene. Washing and drying of the benzene layer were carried out as described earlier. Removal of the drying agent by filtration, followed by evaporation of most of the benzene yielded a yellow oil. This oil was dissolved in alcohol and crystallized from alcohol–water; m.p. 80–81° (lit.[15] m.p. 82–83°); yield, 3.22 g. (85%).

The oxime was prepared and recrystallization from alcohol-water produced a white precipitate; m.p. 160–162° (lit.[16] m.p. 163°).

**3,5-Diphenyl-2-cyclohexenol (VIa).**—Va (0.006 mole) was dissolved in 35 ml. of methyl alcohol. Reduction of the ketone was accomplished by the addition of a solution composed of sodium borohydride (0.003 mole) in 4 ml. of water containing 1 ml. of 10% sodium hydroxide solution. The temperature was kept near 20° for 5 hr. Most of the alcohol was evaporated by warming the reaction mixture on a steam bath and after the addition of water, the solution was extracted with benzene. The benzene layer was dried over magnesium sulfate and a yellow glass was isolated after removal of the drying agent by filtration and evaporation of most of the solvent. This glass was dissolved in a minimum amount of petroleum ether (b.p. 60–80°)-benzene and passed through an alumina column (80–200 mesh) using petroleum ether (b.p. 60–80°) as the eluent. Yellow-colored material was adsorbed on the column, and a colorless oil was obtained upon evaporation of the solvent. This oil could not be induced to crystallize but gave a satisfactory carbon and hydrogen analysis. The infrared spectrum showed the presence of an hydroxyl band and an absence of the carbonyl band. The yield was 1.25 g. (80%).

*Anal.* Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.24. Found: C, 86.08; H, 7.04.

**1,5-Diphenylcyclohexa-1,3-diene (VIIa).**—The alcohol (VIa) (approximately 4.2 g.) was placed in a 100-ml. flask with 50 ml. of benzene and (2.5 g.) of sodium hydrogen sulfate. This dehydration reaction mixture was refluxed for 24 hr. with vigorous stirring, cooled, and passed through an alumina column (80–200 mesh). Benzene was used as the eluent. The benzene was evaporated and a yellow solid was obtained which was dissolved in petroleum ether (b.p. 60–80°) and again passed through an alumina column using petroleum ether (b.p. 60–80°) as the eluent. The yellow impurity remained on the column and after evaporation of the solvent, a white glass was isolated. This white viscous material was crystallized from alcohol; m.p. 55–60°. The infrared spectrum indicated the absence of the hydroxyl group and the ultraviolet spectrum showed the possibility of a structure which might include a phenylcyclohexa-1,3-diene system.

*Anal.* Calcd. for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.86; H, 7.20.

***m*-Terphenyl (VIIIa).**—The diene (VIIa) was dissolved in carbon tetrachloride and aromatized by the bromine method. Warming on the steam bath expelled hydrogen bromide and evaporated most of the solvent. This solution was passed through an alumina column (80–200 mesh) and eluted with petroleum ether (b.p. 60–80°). The solvent was evaporated and the glassy residue was crystallized from alcohol, then recrystallized three times from petroleum ether (b.p. 60–80°), m.p. 85–86° (lit.[17] m.p. 86–87°); there was no depression on admixture with an authentic sample. Also, the infrared spectrum matched perfectly with infrared spectrum of an authentic sample of *m*-terphenyl. The yield of the last two reactions was 0.69 g. (17%).

**1,3-Di[3-keto-3-(3-bromophenyl)-1-propenyl]benzene (XIIb).**—A mixture of isophthalaldehyde (0.016 mole) and Ib (0.036 mole) was dissolved in 100 ml. of methyl alcohol. One milliliter of a saturated solution of sodium hydroxide in methyl alcohol was added, and the reaction mixture was allowed to stand for 24 hr. at room temperature. The resulting yellow-white precipitate was isolated by filtration and recrystallized from alcohol-benzene; m.p. 151–153°, yield, 80% (7.14 g.); $\lambda_{\max}^{\text{EtOH}}$ 308 mμ (ε 48,100), 262 (14,700). The infrared spectrum showed carbonyl absorption at 1665 cm.$^{-1}$.

*Anal.* Calcd. for $C_{24}H_{16}O_2Br_2$: C, 58.07; H, 3.25. Found: C, 58.26; H, 3.50.

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[14] E. Knoevenagel, *et al.*, *Ann.*, **281**, 68 (1894).

[15] G. R. Ames and W. Davey, *J. Chem. Soc.*, 3480 (1957).

[16] E. P. Kohler, *Am. Chem. J.*, **37**, 386 (1907).

[17] N. A. Lange, "Handbook of Chemistry," 8th Ed., Handbook Publishers, Inc., Sandusky, Ohio, 1952, p. 508.

The 2,4-dinitrophenylhydrazone derivative was prepared by using a Soxhlet technique and was recrystallized from dioxane, m.p. 267–269°.

*Anal.* Calcd. for $C_{36}H_{24}N_8O_8Br_2$: C, 50.48; H, 2.82. Found: C, 50.51; H, 3.03.

**1,3-Di[2-carbethoxy-5-(3-bromophenyl)-3-keto-4-cyclohexenyl]benzene (XIIIb).**—A solution of sodium ethoxide in ethanol was prepared from sodium (0.0017 g.-atom) and 100 ml. of ethanol. Ethyl acetoacetate (0.009 mole) was added to this solution and 1 hr. later the dichalcone (XIIb) (0.0015 mole) was dropped in quickly. The reaction mixture was refluxed for 3 hr. While still hot, the resulting solution was added to cold dilute hydrochloric acid. A yellow solid formed which was isolated by filtration and washed with cold ethanol. The yellow precipitate was recrystallized from ethanol–benzene and melted over a range of 86–92°. It would be tempting to assume that this melting point range is a consequence of stereoisomerism; however, the fact is that the substance was impure and could not be obtained in a state of purity satisfactory for analysis. The infrared spectrum however indicated the presence of an ester group. It is this impure substance that was employed in the next step which involved (a) hydrolysis of the ester group and (b) decarboxylation of the acid group.

**1,3-Di[3-keto-5-(3-bromophenyl)-4-cyclohexenyl]benzene (XIVb).**—The preceding impure Michael addition product (XIIIb) (0.34 g.) was refluxed for 3 hr. in a solution containing 0.1 g. of potassium hydroxide dissolved in 37 ml. of 20% aqueous ethanol. This reaction mixture was cooled, acidified with dilute hydrochloric acid, and the resulting solution was extracted with benzene. The benzene layer was washed with water and dried over magnesium sulfate. A yellow gum was obtained after evaporation of most of the benzene and was crystallized from ethanol; m.p. 140–141°; $\lambda_{max}^{EtOH}$ 275 m$\mu$ ($\epsilon$ 46,300), 230 (inflection), 223 (inflection). The infrared spectrum showed carbonyl absorption at 1665 cm.$^{-1}$.

*Anal.* Calcd. for $C_{30}H_{24}Br_2O_2$: C, 62.50; H, 4.19. Found: C, 62.25; H, 4.45.

**1,3-Di[3-hydroxy-5-(3-bromophenyl)-4-cyclohexenyl]benzene (XVb).**—The diketone (XIVb) (0.0007) mole) was dissolved in 20 ml. of Ethyl Cellosolve and reduced with a solution composed of sodium borohydride (0.003 mole) in 5 ml. of water containing 1 ml. of a 10% sodium hydroxide solution. This reaction mixture was allowed to stand for 24 hr. at room temperature and then was acidified with cold dilute hydrochloric acid. A white precipitate was isolated by suction filtration and recrystallized from ethanol–benzene. A melting point range of 80–97° was observed. Since a satisfactory carbon and hydrogen analysis was obtained and the hydroxyl band appeared in the infrared spectrum while the carbonyl band was shown to be absent, the melting point range might be a result of stereoisomerism. The yield was 89% (0.36 g.).

*Anal.* Calcd. for $C_{30}H_{26}Br_2O_2$: C, 62.28; H, 4.53. Found: C, 62.40; H, 4.54.

**3,3''''-Dibromo-*m*-quinquephenyl (XVIIb).**—The diol (XVb) (0.007 mole) was dissolved in 50 ml. of benzene and this solution was refluxed for a period of 24 hr. in the presence of sodium hydrogen sulfate (3 g.). The mixture was cooled and passed through an alumina column (80–200 mesh) using benzene as the eluent. A yellow oil was isolated after evaporation of the benzene. No hydroxyl band was observed for this substance in the infrared region. This oil was dissolved in chloroform, cooled, and aromatized by the bromine method. The resulting solution was heated to evolve hydrogen bromide and to remove most of the solvent. Finally it was passed through an alumina (80–200 mesh) column using petroleum ether (b.p. 30–60°)–benzene (10:1) as the eluent. A white glass was obtained which was crystallized from ethanol; m.p. 105–107°[10]; yield of these two reactions was 8%; $\lambda_{max}^{isooctane}$ 247 m$\mu$ (87–300).

*Anal.* Calcd. for $C_{30}H_{20}Br_2$: C, 66.68; H, 3.74; Br, 29.58. Found: C, 66.90; H, 3.77; Br, 29.32.

**1,3-Di(3-keto-3-phenyl-1-propenyl)benzene (XIIa).**—A mixture of acetophenone (0.1 mole) and isophthalaldehyde (0.05 mole) was dissolved in 100 ml. of methyl alcohol. The solution turned yellow immediately upon the addition of 80 drops of a saturated solution of sodium hydroxide in methyl alcohol. This reaction mixture was allowed to stand for 24 hr. at room temperature. A yellow precipitate was obtained which was isolated by filtration and recrystallized from ethanol–benzene; m.p. 140–142° (lit.[18] m.p. 143–144°); yield, 14.9 g. (87%).

**1,3-Di(2-carbethoxy-3-keto-4-cyclohexenyl-5-phenyl)benzene (XIIIa).**—Ethyl acetoacetate (0.144 mole) was added to a solution of sodium ethoxide in ethanol which had been prepared from sodium (0.024 g.-atom) and 250 ml. of ethanol. With continued stirring, the dichalcone (XIIa) (0.024 mole) was added and the resulting mixture was refluxed for 4 hr. The solution was added while still hot to cold dilute hydrochloric acid. A yellow precipitate was isolated and recrystallized from ethanol–benzene. This substance could not be obtained in a state pure enough for an adequate analysis. It was used in this impure form in the next step. The infrared spectrum indicated a strong similarity to XIIIb.

**1,3-Di(3-keto-4-cyclohexenyl-5-phenyl)benzene (XIVa).**—The Michael addition product (XIIIa) (4 g.) was heated in a sealed tube which contained 15 ml. of acetic acid and 12 ml. of 20% hydrochloric acid. This mixture was shaken for 4 hr. at 150°. The tube was opened and the contents were extracted with benzene. Washing of the benzene layer was done as described previously. The benzene solution was dried over magnesium sulfate and after removal of the drying agent, the solution was evaporated to a volume of approximately 50 ml. Alcohol was added and upon cooling a yellow precipitate was formed. This solid was isolated by filtration and recrystallized from absolute ethanol; m.p. 143–145°; yield, 2.56 g.

**1,3-Di(3-hydroxy-4-cyclohexenyl-5-phenyl)benzene (XVa).**—The preceding diketone (XIVa) (0.0096 mole) was dissolved in 170 ml. of Ethyl Cellosolve. Reduction of the diketone was carried out by the addition of a solution composed of sodium borohydride (0.04 mole) in 12 ml. of water containing 2 ml. of 10% sodium hydroxide solution. This reduction mixture remained at room temperature for 24 hr. and then was poured slowly into a cold dilute sulfuric acid solution. A yellow-white solid was isolated, dissolved in benzene, and washed with water. After drying over magnesium sulfate, the benzene was evaporated and a yellow viscous liquid was left behind. No attempt was made to purify this substance any further. The infrared spectrum showed the disappearance of the carbonyl band and the appearance of the hydroxyl band.

***m*-Quinquephenyl (XVIIa).**—Approximately (3 g.) of the diol (XVa) was dissolved in 50 ml. of benzene and this solution refluxed for 24 hr. in the presence of sodium hydrogen sulfate (8 g.). The reaction mixture was cooled and passed through an alumina column (80–200 mesh) using benzene as the eluent. The benzene was evaporated and the yellow viscous liquid that remained was dissolved in chloroform and cooled. A solution of bromine in chloroform was used to aromatize the tetraene. The addition of the bromine solution was arrested when a pink color persisted. Hydrogen bromide was evolved upon warming the solution on the steam bath, and after evaporation of most of the solvent, the solution was passed through an alumina column (80–200 mesh). Petroleum ether (b.p. 60–80°)–benzene (90:10) was used as the eluent. Evaporation of the solvent from the first two fractions collected (200 ml. each) left behind a yellow oil. Both of these fractions were extracted with petroleum ether (b.p. 60–80°) and a tan-white precipitate was obtained upon cooling. Recrystallization (five times) from absolute ethanol yielded a white precipitate; m.p. 114–115° (lit.[19] m.p. 117–118°).

Ultraviolet and infrared spectra were consistent with the *m*-quinquephenyl that had been prepared earlier by Alexander.[19]

*Anal.* Calcd. for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 93.82; H, 6.00.

**$\alpha,\alpha,\alpha',\alpha'$-Tetrabromo-3,3'dimethylbiphenyl (XX).**—3,3'-Dimethylbiphenyl (0.15 mole) was placed in a three-neck flask which was equipped with a stirrer, a condenser containing a gas trap, and a dropping funnel. Irradiation from a 250-w. infrared lamp was employed and bromine (105 g.; 0.65 mole) was added slowly. The bromine addition was completed in 3 hr., and the resulting mixture was dissolved in hot chloroform and cooled. A white solid was isolated, filtered, and recrystallized from chloroform; m.p. 120–122°; yield, 45 g. (60%).

*Anal.* Calcd. for $C_{14}H_{10}Br_4$: C, 33.77; H, 2.02. Found: C, 34.00; H, 2.30.

**3,3'-Diformylbiphenyl (XXI).**—$\alpha,\alpha,\alpha',\alpha'$-Tetrabromo-3,3'-dimethylbiphenyl (XX) (0.02 mole) was heated under reflux for 40 hr. with a solution containing (20 g.) of potassium oxalate monohydrate in 200 ml. of 50% (by weight) aqueous ethanol.

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[18] Personal communication, D. H. Maass.

[19] R. L. Alexander, Jr., *J. Org. Chem.*, **21**, 1464 (1956).

The reaction mixture was added to 400 ml. of water and upon cooling a white precipitate appeared. This white solid was isolated by filtration and recrystallized from petroleum ether (b.p. 60–80°). The yield was essentially quantitative. An analytical sample was prepared by sublimation; m.p. 92–94°.

*Anal.* Calcd. for $C_{14}H_{10}O_2$: C, 79.98; H, 4.79. Found: C, 79.98; H, 5.04.

3,3′-Diphenic acid was prepared by permanganate oxidation and was recrystallized from ethanol; m.p. 353–356° (lit. m.p. 330–332°,[20] 356–357°[17]).

**3,3′-Di(3-keto-3-(3-bromophenyl)-1-propenylbiphenyl (XXII).**—A mixture of XXI (0.02 mole) and IIb (0.04 mole) was dissolved in 60 ml. of ethyl acetate. This solution was saturated with hydrogen chloride gas and was allowed to stand for 3 days at room temperature. A tan-brown precipitate was isolated, washed with cold alcohol, and recrystallized from benzene; m.p. 180–182°. The filtrate was evaporated and more of the dichalcone product was isolated and combined with the initial crop of crystals. The over-all yield was 9.8 g. (94%). The infrared spectrum showed carbonyl absorption at 1665 cm.$^{-1}$.

*Anal.* Calcd. for $C_{30}H_{20}Br_2O_2$: C, 62.93; H, 3.52. Found: C, 62.90; H, 3.80.

The 2,4-dinitrophenylhydrazone derivative was prepared by a Soxhlet technique and was recrystallized from dioxane; m.p. 266–268°.

*Anal.* Calcd. for $C_{42}H_{28}N_8O_8Br_2$: C, 54.08; H, 3.03. Found: C, 53.83; H, 3.30.

**3,3′-Di[2-carbethoxy-5-(3-bromophenyl)-3-keto-4-cyclohexenyl]biphenyl (XXIII).**—A solution of sodium ethoxide in ethanol was prepared from sodium (0.002 g.-atom) and 100 ml. of ethanol. Ethyl acetoacetate (0.014 mole) was added to this solution, and 1 hr. later the dichalcone XXII (0.0034 mole) was added. The reaction mixture was refluxed for 3 hr. and while still hot was added to a cold solution of dilute hydrochloric acid. A yellow precipitate was isolated by filtration, washed with cold ethanol, and recrystallized from ethanol–benzene; m.p. 90–97°; yield, 1.8 g. (64%).

*Anal.* Calcd. for $C_{42}H_{36}O_6Br_2$: C, 63.32; H, 4.54. Found: C, 63.15; H, 4.33.

**3,3′-Di[3-keto-5-(3-bromophenyl)-4-cyclohexenyl]biphenyl (XXIV).**—The Michael addition product (XXIII) 0.00085 mole) was heated in a sealed tube with 22 ml. of acetic acid and 11 ml. of 20% hydrochloric acid. This tube was shaken for 4 hr. at 150°, cooled, opened, and the contents were extracted with benzene. The benzene layer was washed successively with water, 10% sodium hydrogen carbonate solution, and water. Drying of the benzene layer was done by magnesium sulfate and, after filtration of the drying agent, the solution was evaporated to approximately 20 ml. Ethanol was added and upon cooling a yellow-white solid appeared. This solid was isolated and recrystallized from ethanol–benzene; m.p. 95–98°; yield, 0.24 g. (43%); $\lambda_{\max}^{\mathrm{EtOH}}$ 270 mμ (ε 49,200), 228 (39,900). The infrared spectrum showed carbonyl absorption at 1665 cm.$^{-1}$.

*Anal.* Calcd. for $C_{36}H_{26}Br_2O_2$: C, 66.26; H, 4.32. Found: C, 65.98; H, 4.44.

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# The Structure of a Cyclic $C_{18}$ Acid from Heated Linseed Oil

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One of the cyclic fatty acids formed by heating linseed oil in the absence of air was isolated in pure form and was shown to be ethyl 11-(2-methylcyclohex-2-en-1-yl)undec-*trans*-9-enoate. A combination of chemical degradation, synthesis, and physical measurements was used to determine the structure.

Crampton and co-workers showed that heating of linseed oil at 275° under carbon dioxide produced substances which were toxic when fed to rats.[1–3] They found that the toxic materials were formed from linolenate esters and could be concentrated greatly by conversion to ethyl esters, distillation, and treatment with urea. The portion which formed an adduct with urea was harmless. Wells and Common suggested that the nonurea-adductable materials contained a nonterminal ring structure.[4] Others have obtained indirect evidence for a cyclic structure.[5]

Later, MacDonald obtained direct evidence that cyclic compounds were formed during the heating of linseed oil in the absence of oxygen.[6] He isolated phthalic anhydride after aromatization and oxidation of the distillable, nonurea-adductable fraction. He established that the distillable, nonurea-adductable fraction contained esters of $C_{18}$-monocarboxylic acids averaging two double bonds per molecule. More recently, MacDonald, *et al.*, have postulated specific structures for two compounds from heated linseed oil.[7] None of this structure work, however, was carried out with pure compounds.

In the current investigation, one of the compounds in the distillable, nonurea-adductable material (DNUA) from anaerobically heated linseed oil was isolated in pure form and its structure was elucidated. The biological studies on this and similar materials from the DNUA of heated linseed oil is the subject of another study in these laboratories.

Although gas chromatography showed the DNUA from heated linseed oil to contain at least five unknown compounds, information for only one is presented. The compound discussed is called α 1.38. The α value is the ratio of the gas chromatography (g.c.) retention time of this material to the g.c. retention time of ethyl linoleate on a polyester column.

The α 1.38 was concentrated by distillation of the DNUA mixture on a spinning band column, and was isolated in pure form from the distillation fractions most concentrated in α 1.38 by preparative gas chromatography (Fig. 1). The resulting ester was proved to have the structure I. The analytical data were consistent with the empirical formula for I, $C_{17}H_{29}CO_2C_2H_5$.

The behavior of α 1.38 during isolation suggested that it was a monomeric cyclic compound. It distilled

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(5) Matsuo, N., *J. Chem. Soc. Japan, Pure Chem. Sec.*, **81**, 469 (1960).

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(7) A. McInnes, F. Cooper, and J. MacDonald, *Can. J. Chem.*, **39**, 1906 (1961).