

its alkaline solution upon acidification and subsequently recrystallized to constant melting point.

The amount of sulfone formation was considerable (27%) only in the case of benzene. In various runs toluene gave 1-10%, ethylbenzene 1-6% and isopropylbenzene 2-3% but the other hydrocarbons gave no evidence of corresponding products.

**Other Hydrocarbons.**—Occasion having arisen to study this procedure on hydrindene and tetrahydronaphthalene these results are included here.

Hydrindene gave 65-70% yield of indane-5-sulfonamide, flakes from dilute ethanol, m. p. 132.5-133.5° uncor.

1,2,3,4-Tetrahydronaphthalene gave a 75% yield of

5,6,7,8-tetrahydronaphthalenesulfonamide-2, flakes from dilute ethanol, m. p. 134.5-135° uncor. In this case the intermediate sulfonyl chloride separated as a wax-like solid recrystallization of which from ligroin gave flakes, m. p. 58.0-58.5° uncor.

### Summary

1. The use of chlorosulfonic acid as a means of identification has been extended to thirty-seven aromatic hydrocarbons, most of which are alkylated benzenes.

CAMBRIDGE, MASS.

RECEIVED SEPTEMBER 3, 1941

[CONTRIBUTION FROM THE DIVISION OF PLANT BIOLOGY, CARNEGIE INSTITUTION OF WASHINGTON]

## Isomerizations of Polyene Acids and Carotenoids. Preparation of $\beta$ -Eleostearic and $\beta$ -Licanic Acids

BY HAROLD H. STRAIN

As a preliminary step in the interpretation of chemical and biochemical transformations of the polyene pigments,<sup>1</sup> the effects of several catalysts on the isomerization of unsaturated aliphatic acids and carotenoids have been compared. Isomerization of olefinic acids is catalyzed by a variety of substances such as sulfur,<sup>2</sup> selenium,<sup>3</sup> phosphorus,<sup>4</sup> halogens,<sup>5,6</sup> oxides of nitrogen<sup>7,8</sup> and oxides of sulfur.<sup>9</sup> With these catalysts and in the absence of secondary reactions such as polymerization and combination with the catalyst, eleostearic and licanic acids have now been found to undergo isomerization much more rapidly than oleic acid. This greater reactivity of the polyene acids as compared to oleic acid may result, in part, from simultaneous changes about two or more conjugated double bonds, rather than from successive changes about individual double bonds in the molecule.

Under some of the conditions employed in these experiments, high yields of the beta or high-melting *trans* forms of eleostearic and licanic acids were obtained from the natural or alpha isomers. These conditions have been utilized for the rapid preparation of the beta acids.

Carotenoids with ten and eleven conjugated

double bonds were altered rapidly by most of the catalysts listed above. The alteration products varied considerably with different catalysts. Reactions produced by acids<sup>1 (p. 87), 10</sup> resulted in the formation of pigments that were adsorbed below the unchanged carotenoids on Tswett columns of specially prepared magnesia.<sup>1</sup> This alteration was most rapid in the presence of strong acids and at elevated temperatures. It often led to complete decomposition of the original carotenoids. It occurred even when solutions of the carotenoids in non-polar solvents were placed in contact with solid, slightly soluble, dibasic organic acids. It was prevented by addition of organic bases such as pyridine to the solutions.

Carotenoid pigments are known to be converted reversibly into isomeric compounds by the action of either heat<sup>1,11,12</sup> or iodine.<sup>12</sup> Dihydroxyxanthophylls yield isomers that are more strongly adsorbed than the unchanged pigments, whereas monohydroxyxanthophylls and the hydrocarbon carotenes yield isomers that are not so strongly adsorbed as the native polyenes.<sup>11,12</sup> In the experiments described in this paper, the dihydroxyxanthophylls have been found to yield a second group of isomerization products. If the reaction with iodine was permitted to proceed for a long period, or if an excess of iodine was used, weakly

(1) Strain, "Leaf Xanthophylls," Carnegie Inst. of Wash. Publication No. 490 (1938).

(2) Maquenne, *Compt. rend.*, **135**, 696 (1902).

(3) Bertram, *Chem. Weekblad*, **33**, 3 (1936).

(4) Rankoff, *Ber.*, **69**, 1231 (1936).

(5) Morrell and Davis, *J. Chem. Soc.*, 1481 (1936).

(6) Kappelmeier, *Chem. Abst.*, **30**, 887 (1936).

(7) Holde and Rietz, *Ber.*, **57**, 99 (1924).

(8) Griffiths and Hilditch, *J. Chem. Soc.*, 2315 (1932).

(9) Rankoff, *Ber.*, **62**, 2712 (1929).

(10) Kuhn, Winterstein and Lederer, *Z. physiol. Chem.*, **197**, 141 (1931); Quackenbush, Steenbock and Peterson, *THIS JOURNAL*, **60**, 2937 (1938).

(11) Carter and Gillam, *Biochem. J.*, **33**, 1325 (1939).

(12) Kuhn and Lederer, *Ber.*, **65**, 637 (1932); Zechmeister and Tuzson, *ibid.*, **72**, 1340 (1939); Zechmeister, Cholnoky and Polgar, *ibid.*, **72**, 1678, 2039 (1939).

adsorbed pigments were also produced. The formation of these weakly adsorbed compounds was prevented by the presence of organic bases, but formation of the strongly adsorbed compounds was not.

Rapid alteration of the carotenoids was promoted by certain adsorbents such as synthetic activated magnesium silicates.<sup>13</sup> Even though neutral in aqueous suspensions, these adsorbents turned adsorbed carotenoids blue, a color reaction similar to that produced by strong acids and by very strong bases such as potassium amide in liquid ammonia.

The rate of isomerization of the carotenoids and the nature and number of the alteration products have been found to vary with the polyene structure in the molecule and also with the presence of hydroxyl and ester groups.<sup>12</sup> Further experiments have now shown that under the same conditions, lutein was altered more than  $\alpha$ -carotene which has the same arrangement of double bonds but which lacks the two hydroxyl groups. Esters of lutein were more resistant to alteration, and the products were not readily resolvable with adsorption columns. However, after regeneration of the hydroxyl compounds with alkalis, the several isomeric products were separable on columns of magnesia. Esters prepared from isomerized lutein were only partially resolvable on such columns. Because the adsorbability of the esters is primarily due to the double bonds, whereas that of the xanthophylls depends mostly upon the hydroxyl groups,<sup>14</sup> one may suggest that the isomerization probably involves changes in the spatial relations or in the polarity of the hydroxyl groups.

By analogy, the complex alterations of the polyene acids induced by various catalysts indicate that alteration of the carotenoids may follow several courses. Presumably, the reversible isomerization of carotenoids by heat and by iodine may involve simple *cis-trans* changes as already suggested.<sup>12</sup> These reversible reactions as well as the changes produced by acids may also involve more deep-seated rearrangements. Occurrence of the absorption maxima of the alteration products at wave lengths shorter than those of the unaltered carotenoids supports this view.

Alteration of the carotenoids by acids and other

catalysts must be considered by all workers engaged in the detection and preparation of polyene pigments. The presence of numerous carotene isomers in commercial fats, like palm oil, that are rich in free fatty acids may be due to alterations of the pigments normally present in the freshly extracted oil.<sup>15</sup> Extraction of carotenoids from leaves of certain species, many of which are known to contain strong, uncombined, fatty acids,<sup>16</sup> may also be accompanied by isomerization of the pigments. A practical method for the elimination of these acid-induced isomerization reactions during the extraction of carotenoids from plant or animal material consists of the addition of organic bases such as pyridine or dimethylaniline to the solutions.

### Experimental

**Isomerization of Oleic Acid.**—At room temperature and in sealed tubes, sulfur, selenium and phosphorus did not catalyze the formation of detectable quantities of elaidic acid from oleic acid in the course of several weeks. At high temperatures (200°) and in agreement with other workers,<sup>2,3,4</sup> small yields of elaidic acid were obtained only after several hours. With a mixture of sodium nitrite and 30% nitric acid at 20–30° as catalyst,<sup>7</sup> oleic acid was isomerized in a few hours. The solidified acid melted at 44° after recrystallization from methanol. This provides a convenient method for preparation of elaidic acid.

With iodine as catalyst, pure oleic acid was isomerized slowly, and the iodine combined with the unsaturated acid. Iodine in solution in 85% methanol (by volume) combined more slowly with the oleic acid, but appreciable isomerization did not take place even after several weeks at 3 or 20°. Bromine in solution in 85% methanol combined irreversibly with the oleic acid in a few seconds. Triolein was not isomerized or polymerized by antimony trichloride, by aluminum trichloride or by boron trifluoride.

**Isomerization of  $\alpha$ -Eleostearic Acid and its Esters.**—When the glyceride of  $\alpha$ -eleostearic acid in tung or China wood oil is isomerized, the oil solidifies at room temperature.<sup>17</sup> With sulfur as catalyst (0.6–5 mg. per g. of oil) solidification took place after about two days at 20°. With selenium, solidification occurred after about a week. Solid, anhydrous aluminum chloride did not cause isomerization even after several days. When sodium nitrite and 30% nitric acid at 20–30° were used as catalyst, nitric oxides apparently combined irreversibly with the double bonds and failed to effect an isomerization, although there was some indication of polymerization reactions. Addition of crystals of iodine or of iodine dissolved in alcohol to the tung oil at 20° caused isomerization in two to three hours. Light was not essential for the isomerization.

(13) Manufactured by Philadelphia Quartz Company of California at Berkeley.

(14) Strain, "Chromatographic Adsorption Analysis," Interscience Publishers, Inc., New York, N. Y., in press.

(15) Kuhn and Brockmann, *Z. physiol. Chem.*, **200**, 255 (1931); Strain, *J. Biol. Chem.*, **111**, 85 (1935); Hunter and Scott, *Biochem. J.*, **35**, 31 (1941).

(16) Wehmer, Thies and Hadders, in G. Klein's "Handbuch der Pflanzenanalyse," J. Springer, Vienna, 1932, Vol. II, p. 496.

(17) Wan and Chen, *This Journal*, **61**, 2283 (1939); Thomas and Thomson, *ibid.*, **56**, 898 (1934).

Hydrogen peroxide (30%) caused little isomerization. Neither ascaridole nor silver oxide were effective catalysts. Small quantities of adsorbents like magnesium silicate that have been found to cause alteration of the carotenes did not accelerate solidification of the tung oil.

Both the natural liquid tung oil and the solid  $\beta$  isomer were polymerized to clear vibrant gels with antimony trichloride (3 g. of fat in 25 ml. of dichloroethane plus 1 g. of antimony trichloride dissolved in dichloroethane). Extraction of these gels with strong hydrochloric acid removed most of the antimony trichloride without altering the gels themselves. When placed in an excess of methanol, these gels were converted into tough resilient masses that were insoluble in water, acids and alkalis. These solvent-free products did not change upon drying at 110°, and when heated on a platinum foil they decomposed without melting. The yield of dried material was equal to the quantity of tung oil utilized in the experiments.

Treatment of concentrated solutions of tung oil in dichloroethane, chloroform, carbon tetrachloride or chlorobenzene with solutions of antimony trichloride resulted in almost instantaneous formation of hard brittle gels. When these gels were broken up and extracted with boiling water and with hydrochloric acid, an infusible residue was also obtained. Similar products were produced quickly by the action of boron trifluoride and of trichloroacetic acid. They were formed slowly by phosphorus trichloride and by thionyl chloride. Stannic chloride in solution in ether produced analogous polymers.<sup>18</sup> The presence of pyridine equal in quantity to the acid chlorides prevented formation of the gels. Neither benzoyl chloride, dry hydrogen chloride, formic acid (57%) nor anhydrous oxalic acid promoted gel formation.

The action of antimony trichloride on dichloroethane solutions of either  $\alpha$ - or  $\beta$ -eleostearic acid resulted in the formation of black, insoluble polymers. It is interesting in connection with this polymerization that sorbic acid, with two conjugated double bonds adjoining a carboxyl group, and linseed oil, with several double bonds separated by three carbon atoms, are not altered by antimony trichloride or by boron trifluoride.

**Preparation of  $\beta$ -Eleostearic Acid.**—Tung oil and twice its weight of ethanol were warmed on a water-bath. Sodium hydroxide equal to one-fifth the weight of the tung oil was dissolved in 1.25 parts of water and added to the warm oil and alcohol. The oil dissolved and then the entire solution set to a solid soap. After this mixture had been heated under reflux on the water-bath for one hour, it was diluted with a large volume of hot distilled water containing more than enough sulfuric acid to combine with all the alkali. As soon as the soaps were converted into the liquid fatty acids, the lower aqueous layer was siphoned off and the residual fatty acids were washed with four liberal portions of hot distilled water. The washed acids, freed of as much water as possible, were dissolved in a quantity of 85 per cent. methanol equal to four times the weight of the tung oil. The warm solution was treated with about 8 mg. of iodine (dissolved in a little absolute methanol) per g. of tung oil used. It was then cooled with running water, and after three hours it was cooled in an ice-bath for an hour. Crystals that separated were collected on a suction filter

and washed with a little cold 85% methanol. These crystals were recrystallized from 85% methanol (four times the weight of the tung oil) by cooling the solution in an ice-bath for one hour. The second crop of crystals was collected and recrystallized from absolute methanol (2.5 times the weight of tung oil) by cooling the solution in an ice-bath for one hour. Crystals that formed were collected and dried in vacuum over calcium chloride and sodium hydroxide. The yield was about 0.45 times the weight of tung oil and the melting point was 71–72°.

If pure  $\alpha$ -eleostearic acid, obtained by crystallization of the washed acids of tung oil from methanol, was dissolved in 85% methanol and treated with iodine as described in the preceding paragraph, the yield of the  $\beta$ -acid was 90% of the quantity of  $\alpha$ -acid employed. Further purification of the  $\beta$ -acid was not required in order to obtain a melting point slightly over 72°. Lower yields of the  $\beta$ -acid were obtained when the reaction was carried out in absolute methanol. The presence of a little pyridine was without effect on the isomerization of the  $\alpha$ -eleostearic acid by iodine. Isomerization of the acid by iodine took place in the dark as well as in the light.

**Licanic Acids and their Esters.**—The behavior of natural oiticica fat when treated with various isomerization catalysts was like that of tung oil. The solid polymer formed by action of boron trifluoride and of antimony trichloride was similar to the analogous product from tung oil.

For the preparation of pure  $\beta$ -licanic acid,  $\alpha$ -licanic acid was first prepared from untreated oiticica fat according to the saponification procedure employed with tung oil. The crude washed acids were then recrystallized from petroleum ether (five times the weight of the fat)<sup>19</sup> and dried in vacuum. This crude  $\alpha$ -licanic acid was dissolved in four times its weight of 85% methanol and treated with 0.01 g. of iodine per g. of acid. After the solution had stood at 20° for two hours, and at 0° for one hour, the crystals that formed were collected, redissolved in about ten times their weight of absolute methanol and recrystallized by cooling the solution in an ice and salt bath. Crystals obtained in this way were collected on a filter and dried in vacuum. They melted at 101–101.5°. The yield was equal to 70% of the  $\alpha$ -acid employed.

**Action of Acids on Carotenoids.**—Solutions of xanthophylls in dichloroethane and solutions of cryptoxanthin, xanthophyll esters and carotenes in carbon tetrachloride were permitted to stand in contact with acids and were then analyzed by adsorption upon columns of specially prepared magnesium oxide and siliceous earth.<sup>1</sup> Traces of hydrogen chloride or hydrogen iodide caused the rapid formation of blue colors. Either anhydrous or hydrated oxalic acid, fumaric, formic, maleic, malonic or tartaric acids caused slight color changes (brown to brown-green). Acetic and stearic acids did not produce color changes. More rapid changes occurred at 60°. With every acid, each carotenoid was converted into the same series of products. With the stronger acids and at higher temperatures the successive series of changes occurred more rapidly. Pyridine, quinoline and dimethylaniline prevented the reactions.

Lutein was converted into two pigments that formed a red-orange and a yellow band below the unchanged xanthophyll.<sup>10</sup> Pigments eluted from these bands did not

(18) Scheiber, *Chem. Abst.*, **22**, 3541 (1928).

(19) Brown and Farmer, *Biochem. J.*, **29**, 631 (1935).

exhibit sharp absorption maxima (about 442 and 473  $m\mu$  in ethanol). All the lutein and these two pigments were converted into non-adsorbed pigments by prolonged action of the acids.

Lutein acetate and *p*-nitrobenzoate were changed slowly by the acids, and the alteration products were only partially resolvable on the columns. Xanthophylls regenerated from the acid-treated esters by saponification were separable into the same isomers described in the preceding paragraph. Zeaxanthin (more resistant than lutein) yielded a pigment as a contiguous yellow band below the unchanged xanthophyll, below this there appeared a red-orange band and then a yellow weakly adsorbed band. In ethanol these weakly adsorbed pigments exhibited poorly defined absorption maxima at about 447 and 477  $m\mu$ . Eschscholtzanthin,<sup>20</sup> cryptoxanthin and  $\beta$ -carotene were converted slowly into substances that were adsorbed both above and below the native pigments.

**Action of Iodine on Carotenoids.**—Lutein that was chromatographically homogeneous was dissolved in 1,2-dichloroethane (4 mg. per ml.) and treated with about 1% of its weight of iodine. After various periods, portions of the solution which gradually turned brown were passed through columns of adsorptive magnesia. After a few minutes, two pigments that were adsorbed above the lutein were formed. As shown by their absorption maxima and by the mixed chromatogram or three column test,<sup>14</sup> these two pigments were identical with the products formed by heating a solution of lutein,<sup>1</sup> and by the action of iodine on a solution of lutein in benzene.<sup>12</sup> Absorption maxima, uppermost band (ethanol) 441, 470  $m\mu$ , (carbon disulfide) 469, 497  $m\mu$ ; middle band (ethanol) 445, 476  $m\mu$ , (carbon disulfide) 474, 505  $m\mu$ .

After several hours or after shorter periods if larger quantities of iodine were used, the lutein solutions were found to contain two pigments that formed an orange-yellow and a yellow band below the unchanged lutein. Pigments eluted from these bands exhibited indefinite absorption maxima at about 441 and 472  $m\mu$  (ethanol). As indicated by their inseparability on adsorption columns, these pigments were identical with those formed from lutein by action of acids.

Lutein *p*-nitrobenzoate (or acetate) (in dichloroethane, 1 mg. per ml.) heated with 1% of its weight of iodine at 60° for one hour was slightly discolored. After saponification at 0° and adsorption of the pigments on magnesia, the products were found to be mostly lutein and the two isomers adsorbed above it. Only a little of the pigments forming orange-yellow and yellow bands below the lutein had been produced. Under the same conditions of isomerization, unesterified lutein was converted into large quantities of the weakly adsorbed compounds.

Iodine converted zeaxanthin into the poorly defined, weakly adsorbed pigments also formed by acids, in addition to the strongly adsorbed pigments observed by others.<sup>1,12</sup> The action of iodine on solutions of cryptoxanthin and  $\beta$ -carotene was not significantly different from that described by Zechmeister and Tuzson.<sup>12</sup>

If iodine dissolved in dichloroethane was treated with a little thoroughly dried pyridine, quinoline, or dimethylaniline, the purple-red color changed rapidly to an orange-

yellow. When such solutions were added to solutions of lutein or zeaxanthin in dichloroethane, a rapid equilibrium appeared to be established between the xanthophyll and the two alteration products that were adsorbed above it. There was no further change in color even after several days, and pigments adsorbed below the xanthophylls were not formed. Essentially the same results were obtained when the reaction was carried out in pure dimethylaniline.

**Action of Various Substances on Carotenoids.**—Treatment of carotene, cryptoxanthin, lutein, zeaxanthin or eschscholtzanthin in solution in carbon tetrachloride with a little magnesium sesquisilicate or magnesium trisilicate followed by elution of the blue adsorbed compounds with alcohol resulted in the recovery of considerable amounts of the yellow pigments. After the alcohol was removed from the extracts, most of the pigments were found to be more strongly adsorbed than the untreated carotenes and xanthophylls. These pigments could not be crystallized, and they did not exhibit well-defined absorption maxima.

When a mixture of  $\alpha$ - and  $\beta$ -carotene was passed through columns of magnesium silicates and siliceous earth, the  $\beta$ -isomer was converted into strongly adsorbed products more rapidly than the  $\alpha$ -isomer. This resulted in a rapid initial separation of the  $\alpha$ -carotene, but this pigment was also gradually decomposed by the adsorbent.

Boron trifluoride as well as antimony trichloride<sup>21</sup> converted carotenoids into unstable blue pigments. Both reactions were prevented by organic bases. Sulfur and selenium converted the carotenoids into the series of isomers produced by iodine but the reaction was very slow. Potassium amide in liquid ammonia converted the carotenes into deep blue products. Alcohol reconverted these pigments into yellow substances that were strongly adsorbed on columns of magnesia and that did not exhibit definite absorption maxima.<sup>22</sup>

In the course of these investigations, many helpful suggestions were made by Drs. H. A. Spoehr, James H. C. Smith and W. G. Young. Some of the unsaturated acids were generously contributed by Dr. C. R. Noller. It is a pleasure to acknowledge this valuable coöperation.

### Summary

Some polyene acids were altered in a number of different ways by various isomerization catalysts. With some catalysts, such as iodine, the products were usually *cis-trans* isomers. With other catalysts, as boron trifluoride and antimony trichloride, the products were complex polymers. Isomerization of carotenoids by organic acids such as those contained in plant and animal products was prevented by organic bases. Isomerization of the carotenoids by iodine took different courses in the presence and in the absence of or-

(21) Strain, *ibid.*, **111**, 85 (1935).

(22) Strain, *ibid.*, **127**, 191 (1939).

(20) Strain, *J. Biol. Chem.*, **123**, 425 (1938).

ganic bases. Strong alkalis and certain adsorbents also caused alteration of the carotenoid pigments. Esters of the xanthophylls were isomer-

ized more slowly than the free xanthophylls.

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RECEIVED JUNE 30, 1941

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

## Condensation Reactions. II. Alkylidene Cyanoacetic and Malonic Esters

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A method for condensing aliphatic ketones with cyanoacetic ester was reported recently,<sup>1</sup> in which the reactants were heated in the presence of acetamide and acetic acid, the water formed in the condensation being removed continuously by slow distillation of the acetic acid. The method is not convenient for condensing ethyl cyanoacetate with low boiling ketones, which are removed during the distillation and must be used in large excess, or for inert ketones, which condense too slowly. In the previous paper it was pointed out that salts catalyze the condensation, and that the water formed could be removed by distillation with an inert solvent such as benzene. Variations of this general method have now been investigated, and experimental conditions developed under which a number of ketones have been condensed with ethyl cyanoacetate (see Table I).

**Condensations.**—In the preferred procedure, a mixture of the ketone, ethyl cyanoacetate, ammonium acetate, acetic acid and benzene is refluxed in a flask which is attached to a constant water separator (Fig. 1). Ammonium acetate and acetic acid are used in larger amounts for aromatic and hindered aliphatic ketones (Experimental Part, procedure B) than for reactive ketones (procedure A). Under these conditions, methyl ketones which are not branched at the  $\alpha$ -carbon atom, as well as diethyl, dipropyl and diamyl ketones gave 75 to 87% yields of alkylidene esters. Aromatic ketones, such as acetophenone, propiophenone, caprophenone and benzophenone condensed to the extent of 60 to 80%. Sufficient branching of the carbon chain retards or inhibits the condensation. The yield of alkylidene cyanoacetic ester obtained from diisobutyl ketone was 40%, while no condensa-

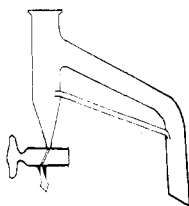


Fig. 1.—Constant water separator (one-third actual size), see ref. 11.

tion occurred with pinacolone or camphor. Anthrone also failed to condense with ethyl cyanoacetate under these conditions.

Piperidine acetate and acetic acid also have been used to condense a number of ketones with ethyl cyanoacetate. The condensations are slower than with ammonium acetate, and the procedure offers no advantage. Ammonium acetate is not a suitable catalyst for the condensation of aldehydes with ethyl malonate, however, while piperidine acetate and acetic acid are useful in certain cases. For example, isobutyraldehyde and isovaleraldehyde were condensed with ethyl malonate very readily by this method in 88 to 92% yield (procedure C). Similar conditions have been employed with other aldehydes (Table I), but the occurrence of side reactions beginning with the aldol condensation of the aldehydes diminished the yields of alkylidene esters to 25 to 59%. Propionaldehyde and butyraldehyde condensed with ethyl malonate most satisfactorily in the presence of acetic anhydride (procedure D).

Several of the alkylidene esters have been used as intermediates in the preparation of substituted vinyl alkylmalonic and cyanoacetic esters.<sup>2</sup>

**Reductions.**—Monoalkylmalonic and cyanoacetic esters have been prepared from a number of the alkylidene esters by hydrogenation in 90 to 97% yield. Palladinized charcoal was used as the catalyst in reducing the alkylidene cyanoacetic esters; platinum also may be used.<sup>3</sup> These catalysts as well as nickel<sup>4</sup> and copper chromite<sup>5</sup> are suitable for use in hydrogenating alkylidene malonic esters.

**Ring Closure.**—When benzyl methyl ketone was condensed with ethyl cyanoacetate in the presence of piperidine acetate in acetic acid solution, a small amount of a solid by-product was

(2) Cope, Hartung, Hancock and Crossley, *ibid.*, **62**, 314 (1940), and preceding papers.

(3) U. S. Patent 2,176,018.

(4) Wojcik and Adkins, *THIS JOURNAL*, **56**, 2424 (1934).

(5) Connor, Folkers and Adkins, *ibid.*, **54**, 1140 (1932).

(1) Cope, *THIS JOURNAL*, **59**, 2327 (1937).