The Journal of the American Oil Chemists' Society

Volume 33 JULY, 1956 No. 7

Isomerization During Hydrogenation.
II. Methyl cis-10, cis-12-Octadecadienoate

R. R. ALLEN,[1] Research Division, Armour and Company, Chicago, Illinois

THE PROCESS OF HYDROGENATION of unsaturated fatty acids, even monoenes, has been shown to result in the production of isomeric acids (5). As the number of double bonds per molecule increases, the number of possible isomers that could be produced becomes greater. For example, the addition of one mole of hydrogen to linoleic acid, *cis*-9, *cis*-12-octadecadienoic acid, results in the production of *cis* and *trans*-9-, 10-, 11- and 12-octadecenoic acids. This process will be more fully described in the next paper of this series. In order to make more complete the study of the hydrogenation of linoleic acid, it was felt that the hydrogenation of a conjugated diene system should be included. The *cis, cis* conjugated isomer of linoleic acid had not been reported, but since this structure would simplify the geometrical isomerization study, *cis*-10, *cis*-12-octadecadienoic acid was selected for this work and its synthesis was undertaken.

Experimental

Preparation of 10, 12-Octadecadiynoic Acid. 10,12-Octadecadiynoic acid was prepared by the oxidative coupling of 10-undecynoic acid and 1-heptyne as described by Black and Weedon (3). 10-Undecynoic acid, m.p. 43°, was prepared in 40–50% yield by the bromination-dehydrobromination procedure from 10-undecyclenic acid as reported by Jeffry and Vogel (7). The acids obtained from the dehydrobromination were composed of about 10% of 10,11-undecadienoic and 90% 10-undecynoic acid. However crystallization of the acetylenic acid from Skellysolve F removed the isomeric acid.

Eighty-six grams of 10-undecynoic acid and 50 g. 1-heptyne were dissolved in 1,320 ml. of ethanol and added to a solution of 102 g. of cuprous chloride and 310 g. of ammonium chloride dissolved in 1,300 ml. of 0.08N HCl. The flask containing the dark blue solution was attached to an oxygen supply and shaken until adsorption of oxygen was complete (about 10 l. of O_2 was absorbed in 12 hrs. at room temperature). The light green suspension was treated with 2 liters of 3N HCl and extracted with ether. The ether extract was washed once with water and then extracted with 2N KOH solution to remove the free acids. The ether solution was washed, dried, and evaporated to give 16 g. of crude 6,8-tetradecadiyne. The KOH extract was acidified with HCl and extracted with ether; the extracts were washed and dried, and the ether was removed under vacuum. The residue was poured into 2 liters of Skellysolve F and cooled to 5°. Fifty-four grams of 10,12-docosadiyndioic acid (m.p., 114°) were obtained. The filtrate was cooled to —20° and yielded 38 g. (30% yield) of 10,12-octadecadiynoic acid, m.p. 43° neut. equiv. 276.5; added 3.95 moles H_2 to give stearic acid, m.p. and mixed m.p. 69.5°. Oxidative cleavage with ozone, followed by partition chromatographic separation of the acids (1), showed that only sebacic and caproic acids were present. The infrared spectrum, as shown in Figure 1, does not show any bands due to the acetylenic system. This is probably because of its position near the center of a long hydrocarbon chain.

Methyl 10,12-Octadecadienoate. 10,12-Octadecadiynoic acid was esterified with methanol, using HCl as a catalyst in the usual manner. Isolation of the ester gave methyl 10,12-octadecadiynoate, m.p. 14°, n_D^{25} 1.4827. Semi-hydrogenation of the ester was carried out at room temperature and pressure in ethyl acetate solution (10 ml./g.) in the presence of quinoline, using a lead-poisoned palladium on calcium

---

[1] Present address: Anderson, Clayton and Company, Foods Division, Sherman, Tex.

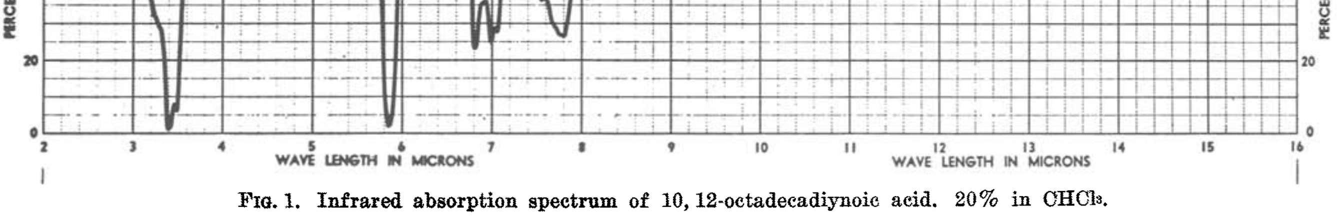

FIG. 1. Infrared absorption spectrum of 10, 12-octadecadiynoic acid. 20% in $CHCl_3$.

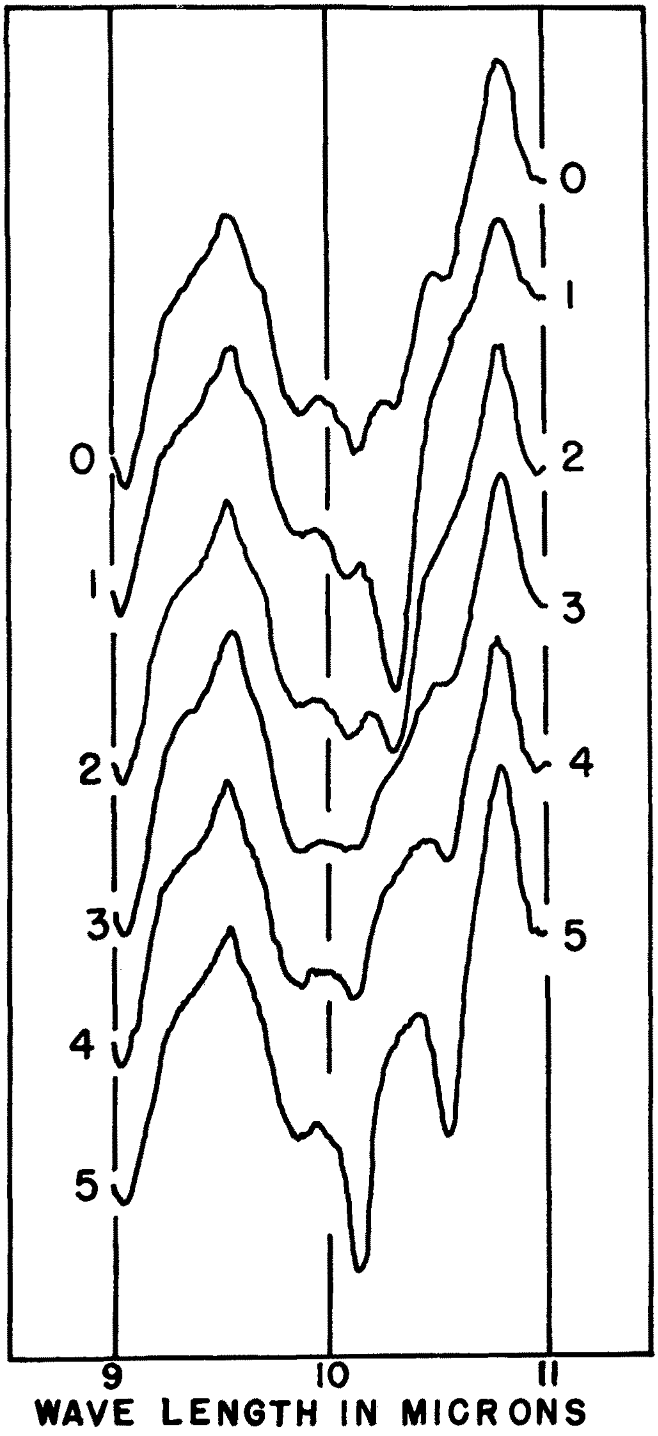

FIG. 2. Infrared absorption spectra of fractions of methyl 10,12-octadecadienoate. 20% in $CHCl_3$. Numbers refer to fractions in Table I.

carbonate catalyst, as described by Lindlar (8). The hydrogenation did not show any appreciable reduction in rate when 2 moles of hydrogen/mole of ester had been absorbed so the reaction was stopped when 2.1 moles of hydrogen were absorbed. The catalyst was removed by filtration, and the product was dissolved in ether and washed with 2N H_2SO_4 to remove the quinoline, then with water; the solution was dried and the ether removed to give crude methyl 10,12-octadecadienoate. Infrared examination revealed that several geometric isomers were present (Figure 2, curve 0), as evidenced by the peaks at 10.1, 10.3, and 10.5 μ.

The fractionation of the ester was carried out by the use of urea complexes. Thirty-eight grams of the crude ester were dissolved in 400 ml. of methanol, 40 g. of urea were added, and the mixture was heated until the urea dissolved. The solution was held at room temperature until the complex had crystallized; the crystalline complex was removed by filtration. The filtrate was treated with 30 g. of urea to remove another fraction of the ester. This procedure was repeated until all of the ester had been recovered. The ester was isolated from the complex by dissolving the crystals in 0.1 N HCl and extracting with petroleum ether. The extract was washed and dried, and the solvent was removed.

Results of the fractionation are shown in Table I. The infrared spectra of the fractions are shown in Figure 2.

TABLE I
Fractionation of Methyl 10,12-Octadecadienoate as Urea Complex

Fraction	Per Cent	Hydrogen Iodine Value
1	21.0	125
2	14.5	147
3	27.7	158
4	15.8	151
5	21.0	190

As judged by the infrared spectra, sample 3 shows the least amount of material containing *trans* double bonds. Further purification of this material was carried out by low temperature crystallization from acetone solution (20 ml./gm.). The solution was cooled to —35° and filtered; the filtrate was cooled to —50°, and the crystals were removed by filtration. This material was recrystallized twice from acetone at —50° and dried under vacuum. This final product was shown to be methyl *cis*-10, *cis*-12-octadecadienoate of about 90% purity, m.p. 1.0°, n_D^{25} 1.4690, hydrogen iodine value 163 (theory 172.1). Oxidative cleavage with ozone followed by chromatographic separation of the dibasic acids showed 92% sebacic with the remainder distributed among the 9-, 11- and 12-carbon acids. The infrared and ultraviolet spectra of the material are shown in Figures 3 and 4.

Hydrogenation Procedure. The hydrogenation of the *cis,cis*-diene were carried out in an apparatus described previously (2) in which the amount of hydrogen taken up could be measured. Five hundred-mg. samples of ester were dissolved in 5 ml. of ethyl acetate, which contained about 10 mg. of Raney nickel catalyst. All hydrogenations were carried out at room temperature and pressure. After the calculated amount of hydrogen had been absorbed, the reaction was stopped, the catalyst was removed by filtration, and the ethyl acetate was removed under vacuum. The hydrogen iodine value, quantitative *trans* determination, and ultraviolet absorption were carried out on the ester. The determination of the double bond positions was made after saponification to the free acid as described prviously (1).

Results and Discussion

The use of acetylenic intermediates followed by stereospecific reductions to the double bond has given much impetus to the synthesis of unsaturated fatty acids. However the stereospecific reduction of a triple bond to a *cis* double bond even with the use of the Lindlar (8) catalyst presents some difficulty. This catalyst does not seem to give selective reduction, nor is the reaction entirely stereospecific as shown by various fractions described in Table 1 and Figure 2. How-

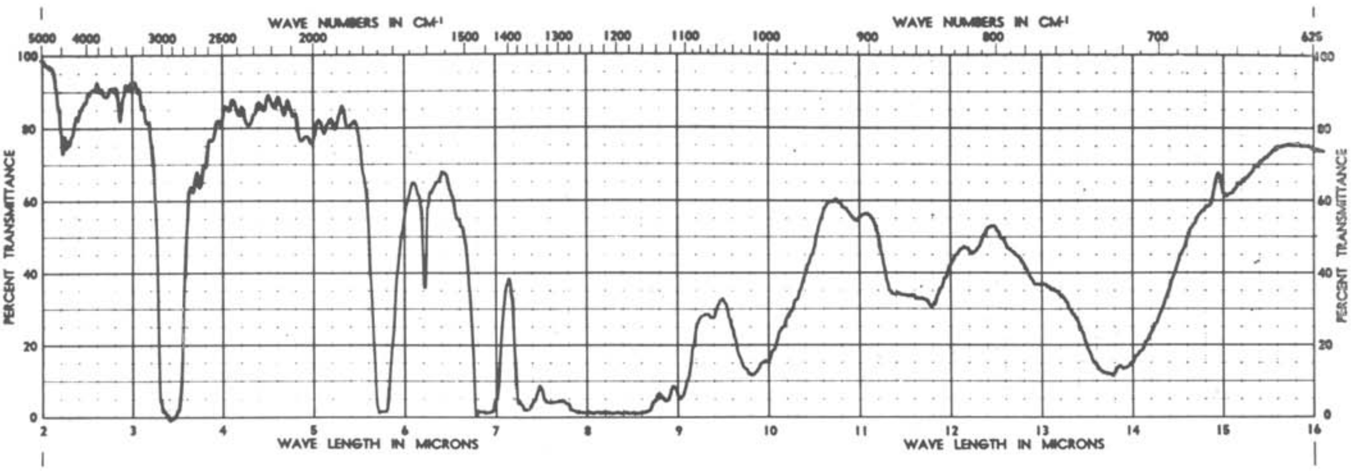

FIG. 3. Infrared absorption spectrum of methyl *cis*-10, *cis*-12-octadecadienoate. 100% conc.

ever this catalyst offers the best available route to *cis* double bonds if it is recognized that the reduction is neither wholly stereospecific nor selective.

The use of the urea complex technique offers a means to separate the isomers that are produced by the catalytic reduction. Examination of the spectra shown in Figure 2 reveals that the ease of formation of urea complexes proceeds in the order: isolated *trans* > *cis,cis* conjugated > *cis,trans* conjugated. This order can be explained by the linearity of the various molecules. The *trans* would be the most linear with the *cis,cis* conjugated more linear than the *cis, trans*. The linearity is also reflected in the melting points of the methyl esters containing a conjugated diene, *trans, trans*, m.p. 24° (6), *cis,cis*, m.p. 1°, and the *cis,trans* m.p. —56° to —49° (9). Evidently the more linear structure allows closer packing of the chains in the crystal, and it conseqiently has a higher melting point (4).

The spectral properties of methyl *cis*-10,*cis*-12-octadecadienoate are consistent with the assigned structure. The absorption peak at 235 mμ, $a = 95.0$ would be expected since it has been shown that the *cis,trans* and *trans,trans* conjugated systems absorb at shorter wavelengths (9). The value of 95 for the sp. a agree with the linear character of the chromophore as shown in Figure 5. Since the intensity of the absorption is proportional to the square of the distance between the ends of the chromophore (11), the *cis,cis* structure should not be too different from the *trans,trans*.

The infrared absorption of the ester (Figure 3) shows no peaks between 10 and 11 μ. This indicates that the hydrogens attached to the double bonds are in the *cis* configuration and lends support to the view that the *cis* 2, *cis*,4-decadienoate reported by Crombie (4) contained some *cis,trans* as an impurity. The region of C=C stretching shows only a single peak at 6.3 μ. An isolated double bond shows a peak at 6.02 μ, but if conjugated with a second double bond, vibrational interaction occurs; and it is possible for two bands to appear at ν 6.0 and 6.3 μ unless one is forbidden by molecular symmetry (10). In the *cis,cis* structure the diene is buried in a long chain and therefore would be expected to show symmetrical properties which would account for the appearance of only one band at 6.3 μ.

The results of the hydrogenation of methyl *cis*-10, *cis*-12-octadecadienoate are shown in Figures 6 and 7. As the hydrogenation proceeds, the hydrogenation is very "selective" in that the drop in iodine value is proportional to the decrease in diene content as measured by ultraviolet absorption. Figure 7 shows the positional and geometrical isomers that are formed during the hydrogenation. As hydrogenation takes place, there is a decrease in the amount of 10 double bonds but a proportional increase in the amount of 11 and 12. Since the analysis for positional isomers was carried out by the determination of the dibasic acids produced on oxidative scission, determination of the 10 carbon dibasic acid would include both the 10-octadecenoate and the unreacted 10,12-octadeca-

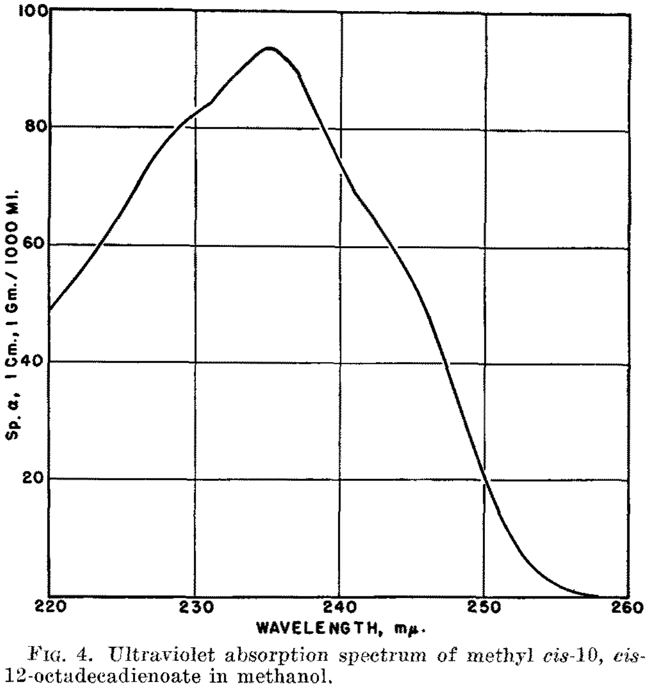

FIG. 4. Ultraviolet absorption spectrum of methyl *cis*-10, *cis*-12-octadecadienoate in methanol.

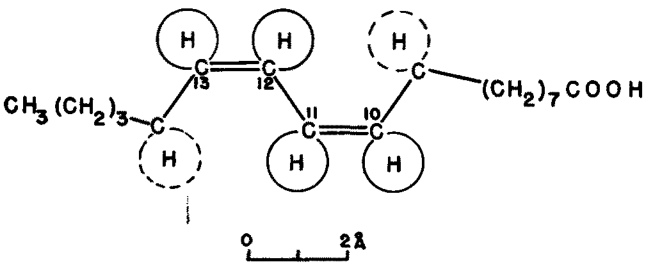

FIG. 5. Structure of *cis*-10, *cis*-12-octadecadienoic acid.

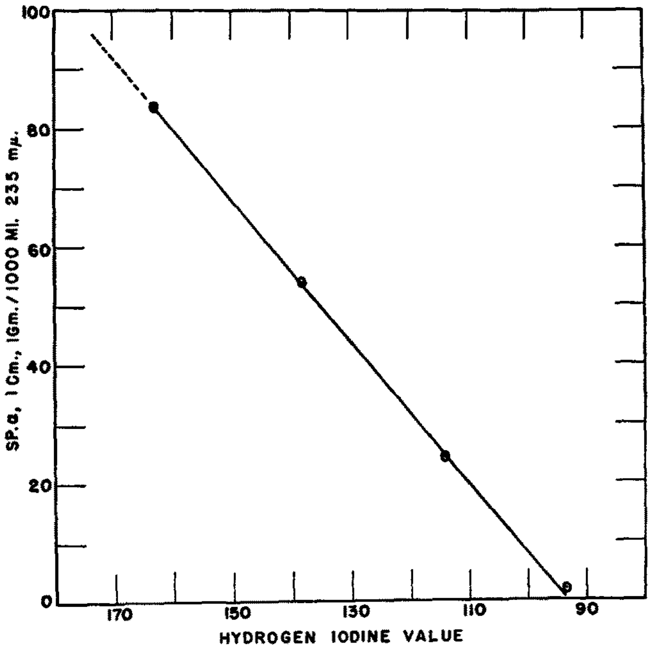

FIG. 6. Hydrogenation of methyl *cis*-10, cis-12-octadecadienoate. 10% sol. in ethyl acetate, Raney nickel catalyst, 25°, atmospheric pressure.

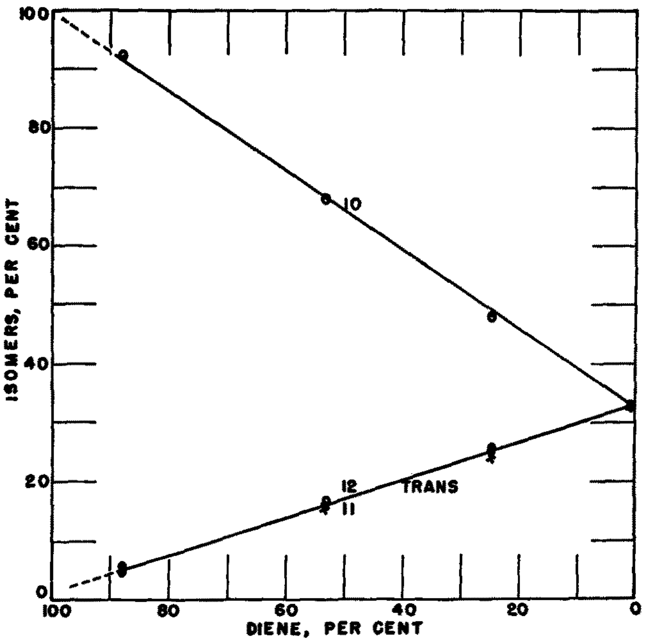

FIG. 7. Isomers produced during the hydrogenation of methyl *cis*-10, *cis*-12-octadecadienoate. The numbers refer to the positions of the double bond.

dienoate. However the analysis for the 11- and 12-carbon dibasic acids would indicate only the 11 and 12 monoenes. The analysis shows that, when one mole of hydrogen has been added to the diene, the resulting monoenes consist of an equal mixture of 10-, 11- and 12-octadecenoates. This indicates that the hydrogen has added with equal ease to the 1,2, 1,4, and 3,4 positions of the diene system. There was no shift of the double bond away from the conjugated system, but all the reaction was confined to this 4-carbon group. This is also true in the hydrogenation of eleostearic acid which contains the conjugated triene; the hydrogenation reaction is confined to the 6-carbon system of the triene. This work will be reported in detail in a subsequent publication.

The amount of *trans*-monoene that was produced increased as the extent of hydrogenation increased, and when one mole of hydrogen was added, it was found that ⅓ mole of *trans* octadecenoate had been produced. To determine the position of the *trans* bond, a small amount of the diene was hydrogenated to the monoene and saponified to the free acid; the *trans* acids were isolated and partially purified by crystallization from acetone. The material isolated melted at 40° (pure *trans*, 11-octadecenoic acid, m.p. 43°), and was found by oxidation and chromatography to consist of over 80% *trans*, 11-octadecenoic acid. It is believed that *all* of the *trans* that is formed during the hydrogenation is in the 11 position. This may be explained by an examination of the structure of the *cis,cis* diene as shown in Figure 5. This shows that the hydrogens attached to the 11 and 12 carbons are *trans* to each other since it is sterically impossible for these hydrogens to be *cis*. During the hydrogenation, if a hydrogen atom is attached to the 10 (or 13) position of the diene, the double bond character of the 11 bond increases by resonance and thus resists stereomutation. The second hydrogen may then add to the 11 or 13 position (12 or 10 if the first hydrogen added to the 13). If it adds to the 11 position, the remaining double bond at the 12 position retains the *cis* configuration; but if it adds to the 13, the new bond that is formed will have the *trans* configuration. Thus all of the 11-octadecenoate that is produced would be *trans*, and the 10- and 12-octadecenoates would be *cis*. The data fit the explanation quite well. Therefore it is believed that the hydrogenation of a conjugated diene proceeds in a stepwise reaction with no stereomutation of the original bonds but that the new bond which is formed by 1–4 addition may be *cis* or *trans*, depending on the initial configuration of the hydrogens attached to the two carbons of the new bond.

Summary

Methyl *cis*-10, *cis*-12-octadecadienoate was prepared and found to have an ultraviolet absorption peak at 235 mμ, $a = 95$. The infrared spectrum revealed no diagnostic peaks for the *cis,cis* conjugated system.

The hydrogenation of the ester showed that when one mole of hydrogen was added, 1–2, 1–4, and 3–4 addition took place with equal ease to produce an equimolar mixture of *cis*-10-, *trans*-11-, and *cis*-12-octadecenoates. An explanation of the reaction is offered on the basis of the structure of the diene system.

Acknowledgment

The author wishes to thank C. W. Hoerr for the extensive infrared work during this study and D. H. Wheeler of General Mills Inc. for checking and confirming the infrared ond ultraviolet spectra of the methyl *cis*-10, *cis*-12-octadecadienoate.

REFERENCES

1. Allen, R. R., and Kiess, A. A., J. Am. Oil Chemists' Soc., *32*, 400 (1955).
2. Allen, R. R., J. Am. Oil Chemists' Soc., *32*, 671 (1955).
3. Black, H. K., and Weedon, B. C. L., J. Chem. Soc., *1953*, 1785.
4. Crombie, L., J. Chem. Soc., *1955*, 1007.
5. Hilditch, T. P., Vidyarthi, N. L., Proc. Ray. Soc. (London), *A122*, 552-570 (1929).
6. Jackson, J. E., Paschke, R. F., Tolberg, Wesley, Boyd, H. M., and Wheeler, D. H., J. Am. Oil Chemists' Soc., *29*, 229 (1952).
7. Jeffry, G. H., and Vogel, A. I., J. Chem. Soc., *1948*, 674.
8. Lindlar, H., Helv. Chim. Acta, *35*, 446 (1952).
9. Nichols, P. L. Jr., Herb, S. F., and Riemenschneider, R. W., J. Am. Chem. Soc., *73*, 247 (1951).
10. Sheppard, N., and Simpson, D. M., Quart. Rev. (London), *6*, 1 (1952).
11. Zechmeister, L., Le Rosen, A. L., Schroeder, W. A., Polgar, A., and Pauling, L., J. Am. Chem. Soc., *65*, 1940 (1943).

[Received January 10, 1956]