# Ethylene Adduct of Conjugated Octadecadienoic Acids: I. Peracid Oxidation Products[1]

**E. J. DUFEK, L. E. GAST and J. P. FRIEDRICH,**
**Northern Regional Research Laboratory,[2] Peoria, Illinois 61604**

## Abstract

8-(4-*n*-Hexylcyclohex-2-enyl)octanoic acid obtained by the addition of ethylene to *trans,trans*-9,11-octadecadienoic acid was treated with 28% hydrogen peroxide in acetic or formic acid to give the hydroxyacetoxy or -formoxy derivative. Saponification of the hydroxyacetoxy derivative yielded two crystalline glycols. The hydroxyformoxy fatty acid was converted in one step either to the glycol ester, methyl 8-(4-*n*-hexyl-2,3-dihydroxycyclohexyl)octanoate, by reaction with anhydrous hydrochloric acid in methanol or to the acetone derivative of the glycol ester by treatment with dimethoxypropane and anhydrous hydrochloric acid in methanol. Epoxidation of the $C_{20}$ cyclohexene fatty methyl ester gave the oxirane derivative. A ring opening reaction of the diol acid with periodic acid yielded 9,12-diformylstearic acid.

## Introduction

Previous investigations have shown that numerous dienophiles, such as acrolein, acrylonitrile, acrylates, maleates, nitroethylene and β-nitrostyrene, react with conjugated linoleic acid in the *trans,trans* configuration to produce various substituted $C_{20}$ fatty acids containing a cyclohexene moiety (1–4). Friedrich et al. (5) showed that the simplest dienophile, ethylene, will react almost quantitatively with *trans, trans*-9,11-octadecadienoic acid or methyl ester at 260 C and 3400 psig to give 8-(4-*n*-hexylcyclohex-2-enyl)octanoic acid (CHA) (I) or methyl ester (CHA-*me*). Nonconjugated soybean oil was also reacted with ethylene in the presence of excess sodium hydroxide in ethylene glycol to obtain an isomeric mixture of $C_{20}$ cyclohexene fatty acids (ICHA). Under similar conditions propylene and even numbered α-olefins from $C_4$ to $C_{20}$ have been reported to add to linoleic acid to produce 5(6)-alkyl substituted ICHA (6).

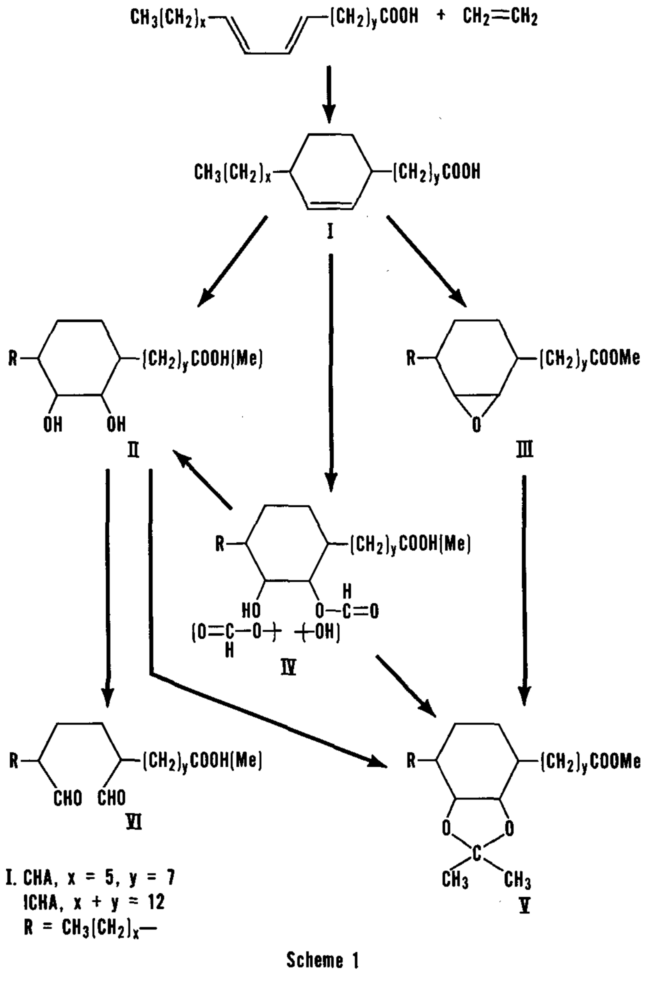
Although experimental results were not given, Kaufmann (7) in his discussion of the Diels-Alder reaction of fats and oils confirms the addition of ethylene, propylene and 1-butene to *trans,trans*-9,11-octadecadienoic acid and to β-elaeostearic acid. Structural proof of these products containing the cyclohexene moiety was obtained by dehydrogenation and oxidation to the corresponding terephthalic and trimellitic acids.

Since ethylene and α-olefin adducts of soybean and linseed fatty acids are readily prepared directly from the corresponding oils, work has been started to prepare new derivatives of these adducts that may prove useful as industrial chemicals. This paper describes some peracid oxidation reactions of the $C_{20}$ cyclohexene fatty acids. Oxidation of the $C_{21}$ cyclohexene fatty acids (propylene adduct) has been started and will be reported later.

## Discussion

Peracid oxidation reactions (Scheme 1) reported in this work were carried out on the pure Diels-Alder adduct (CHA) (I) of ethylene and *trans,trans*-9,11-octadecadienoic acid, the isomeric mixture of acids (ICHA) obtained from a vegetable oil containing 70% linoleate, and the respective methyl esters labeled CHA-*me* and ICHA-*me*. Capillary gas liquid chromatograms of CHA-*me* ($x = 5$; $y = 7$) and the isomeric esters ICHA-*me* ($x + y = 12$) are shown in Figure 1.

Hydroxylation of I with peracetic acid followed by saponification and acidification yielded an oily semicrystalline product containing 81.5% 8-(4-*n*-hexyl-2,3-dihydroxycyclohexyl)octanoic acid (II). Com-



Scheme 1

---

[1] Presented in part at the AOCS-AACC Meeting, Washington, D.C., April 1968.

[2] No. Utiliz. Res. Dev. Div., ARS, USDA.

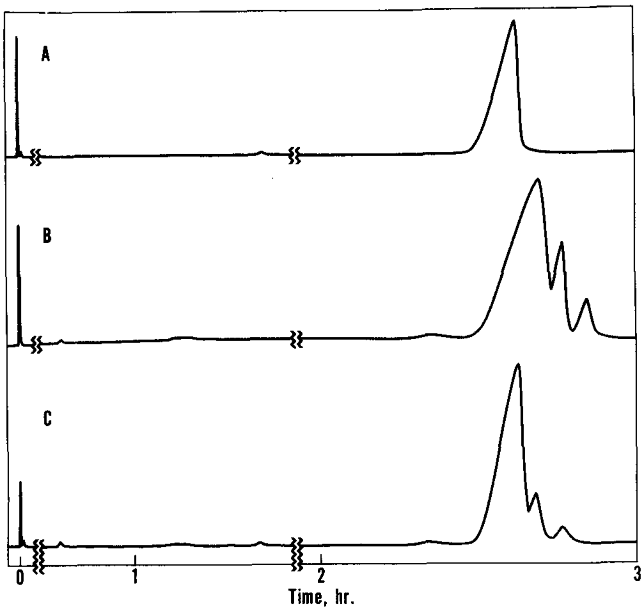
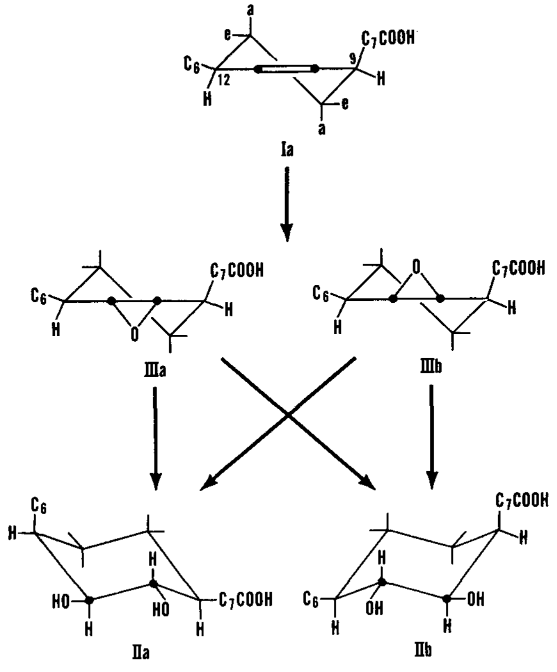


FIG. 1. Gas chromatograms of: (A) Methyl 8-4-*n*-(hexylcyclohex-2-enyl)octanoate (CHA-*me*); (B) Isomeric methyl 8-(4-*n*-hexylcyclohex-2-enyl)octanoate (ICHA-*me*); and (C) 50/50 Mixture of CHA-*me* and ICHA-*me*. Barber Colman chromatograph Model 20, 150 ft × 0.01 in. column packed with polyphenyl ether and programmed at 190 C.

pound II was separated by crystallization into almost equal amounts of two isomeric glycol acids melting at 72–75 C and 107–108 C. The two glycol acids are believed to be conformational isomers which are formed in the following manner (See Scheme 2):



Scheme 2

The addition of a dienophile to a diene is a *cis* addition, which normally preserves the orientation of the substituents in the diene and the resulting cyclohexene that is formed (8–11). Thus the 9(H) and 12(H) in the *trans,trans*-9,11-octadecadienoic acid become bonded predominantly in the pseudoequatorial and pseudoaxial positions of the cyclohexene (Ia). The conformational isomer of Ia with the 9(H) and 12(H) bonded in the pseudoaxial and pseudoequatorial positions cannot be distinquished from Ia because of the low or nonexistent energy barrier between the isomers at room temperature. Hydroxylation of Ia with peracetic acid first produces two isomeric epoxides (IIIa and b) (8,12–14) which then react with acetic acid. After saponification and acidification, the *threo* glycol acids (IIa and b) are formed. The structure of IIa as shown is that of the conformational isomer, believed to be the most stable configuration. Hydroxylation of the conformational isomer of Ia will also produce IIa and b, and the overall reaction will yield equal amounts of IIa and b. Structurally, IIa shows less spatial interaction and is therefore believed to be the higher melting isomer. Further definite structural assignment of the *threo* glycol acids cannot be made without additional experimentation.

Retention times of IIa and b were identical when analyzed by GLC as the methyl esters, trimethylsilyl derivatives, and the acetone addition compounds. GLC analyses were carried out under conditions which separated *erythro* and *threo*-9,10-dihydroxystearates (15,16). Periodic acid oxidation of the high- and low-melting glycol acids gave 9,12-diformylstearic acid (VI). Both dialdehyde products yielded the same bisdinitrophenylhydrazone melting at 157–158 C.

Epoxidation of CHA-*me* with performic acid prepared in situ with 70% hydrogen peroxide and sulfuric acid catalyst yielded methyl 8-(4-*n*-2,3-epoxycyclohexyl)octanoate (III). The GLC analysis of III indicated the presence of two *cis* epoxides, presumably one with the oxygen *trans* to the alkyl chains (IIIa) and the other with the oxygen *cis* to the alkyl chains (IIIb). Although peak heights were the same, the exact amounts of the two epoxides could not be calculated since the peaks overlapped each other. The purity of the epoxide was 94% based on oxirane determination (17). When the free acid was epoxidized under similar conditions, the epoxy acid was obtained in 64% yield. Although a higher yield of oxirane may have been formed during epoxidation, the neutral equivalent of 391 indicates the free acid may have opened the oxirane forming a polyester.

Hydroxyformoxylation of I with 28% hydrogen peroxide in formic acid produced 8-(4-*n*-hexyl-2(3)-hydroxy-3(2)-formoxycyclohexyl)octanoic acid (IV). CHA-*me* when treated similarly with hydrogen peroxide in formic acid gave a product with an acid value of 83. The acidity (residual formic acid or hydrolyzed ester) in the hydroxyformoxylated methyl ester was removed by esterification with diazomethane. The yield was 97.2%.

Reaction of the hydroxyformoxy derivative (IV-*me*) with methanol and anhydrous hydrogen chloride as catalyst removed the formoxy group and yielded the glycol, methyl 8-(4-*n*-hexyl-2,3-dihydroxycyclohexyl)octanoate (II). Both II and IV when treated with dimethoxypropane, methanol and anhydrous hydrogen chloride catalyst gave the acetone addition product, methyl 8-(4-*n*-hexyl-2,3-*O*-isopropylidenecyclohexyl)octanoate (V). Compound V was also obtained by the addition of acetone to the epoxide III with boron trifluoride etherate catalyst (18).

## Experimental Procedures

All melting points were taken on a Kofler hot stage and are uncorrected. Samples (ca. 1 mg) for GLC analysis were treated with diazomethane and run at 225 C or programmed from 180 to 300 C at

4°/min, 30 cc/min on an F&M Model 5750 equipped with a 6 ft × ¼ in., 3% JXR column.

### 8-(4-n-Hexylcyclohex-2-enyl)octanoic acid (CHA) (I)

This compound prepared as previously described (5), had the following properties: bp 172–177 C at 0.07 mm; calculated: IV 82.3; NE 308.5. Found: IV 84.5; NE 307.1.

CHA-*me* prepared by treatment of I with methanol and acidified dimethoxypropane had the following properties: bp 155–157 C at 0.025 mm; IV 82.7. CHA-*me* was also prepared in 92% (GLC) yield by adducting ethylene to methyl *trans,trans*-9,11-octadecadienoate in isooctane at 220 C for 21 hr at 3000 psi.

*Analysis.* Calculated for $C_{21}H_{38}O_2$: C, 78.20; H, 11.88; $CH_3O$, 9.62. Found: C, 77.72; H, 11.81; $CH_3O$, 9.17.

An isomeric mixture of cyclohexene acids (ICHA) was prepared from linoleic acid as previously described (5) (NE 310.2; IV 88.3) and converted to ICHA-*me*. GLC analysis, 97.4% pure.

*Analysis.* Calculated for $C_{21}H_{38}O_2$: C, 78.20; H, 11.88; $CH_3O$, 9.62; IV 79.5. Found: C, 77.77; H, 11.96; $CH_3O$, 9.47; IV 78.5.

### 8-(4-n-Hexyl-2,3-dihydroxycyclohexyl)octanoic Acid (II) and Methyl Ester (II-me)

A solution comprised of I (5 g), glacial acetic acid (50 ml) and hydrogen peroxide (28%, 5 ml) was stirred and the temperature maintained at 75–80 C for 3 hr. Acetic acid (35 ml) was removed in vacuo and the residue poured into ice water. The hydroxyacetate was extracted with ether, washed with water and saponified with ethanolic potassium hydroxide. After removal of the ethanol, the acidified residue was extracted with chloroform, washed with water and dried. The semicrystalline product (IV 5.2; NE 326; glycol anal. 81.5%) was recrystallized slowly at room temperature from hot ethyl acetate (15 ml) to which hexane (30 ml) was added slowly to the cloud point. The crystals were collected and recrystallized twice from ethyl acetate (10 ml). The yield of glycol acid was 1.5 g; mp 107–108 C. Glycol anal.: 100.9%.

*Analysis.* Calculated for $C_{20}H_{38}O_4$: C, 70.13; H, 11.18; NE 342.5. Found: C, 69.83; H, 11.18; NE 340.

Evaporation of the filtrates and three recrystallizations of the residue from ethyl acetate gave 1.6 g of glycol acid; mp 72–75 C.

*Analysis.* Calculated for $C_{20}H_{38}O_4$: C, 70.13; H, 11.18; NE 342.5. Found: C, 69.78; H, 11.23; NE 342. Glycol: 100.2%.

Methyl ester of II was prepared by refluxing a solution of IV-*me* (5 g) in methanol (30 ml) and hydrogen chloride in methanol (5%, 2.5 ml) for 4 hr. The solution was poured into water and extracted with ether. The ether solution was washed carefully with aqueous sodium bicarbonate and dried. The yield was 4.3 g (92.7%).

*Analysis.* Calculated for $C_{21}H_{40}O_4$: C, 70.74; H, 11.31; $CH_3O$, 8.70. Found: C, 70.22; H, 11.12; $CH_3O$, 9.10. IV 3.5. Glycol analysis, 86.4% of theoretical.

The isomeric mixture of II-*me* was prepared in a similar manner from the hydroxyformoxy derivative (60 g) of ICHA-*me* in methanol (300 ml) and hydrogen chloride in methanol (5%, 30 ml), except the washing procedure was omitted. The methanol was removed in vacuo to yield 55.2 g (99.3%) of yellow oil.

*Analysis.* Calculated for $C_{21}H_{40}O_4$: C, 70.74; H, 11.31; $CH_3O$, 8.70. Found: C, 70.27; H, 11.29; $CH_3O$, 8.28. IV 1.3; AV 6.4. Glycol analysis, 90.1% of theoretical.

### Methyl 8-(4-n-Hexyl-2,3-epoxyhexyl)octanoate (III) (Isomeric Mixture)

ICHA-*me* (100 g) and benzene (100 ml) were placed in a three-necked Morton flask equipped with an air condenser, stirrer and thermometer extending below the liquid surface (18). A solution of hydrogen peroxide (70%, 31.3 g, 24.3 ml) and concentrated sulfuric acid (0.207 g, 0.65–0.7% based on weight of peroxide) was added. The solution was heated to 70 C and formic acid (91%, 4.85 g) was added dropwise *cautiously*. The exothermic reaction was controlled by external cooling and the temperature maintained at 72–74 C (about 20 min). The solution was then heated for 1 hr at 72–73 C, cooled, and poured into water. The benzene solution was washed free of acids and peroxides and dried. Evaporation of the solvent in vacuo at room temperature gave 103.8 g (98.1%) of water-white oil.

*Analysis.* Calculated for $C_{21}H_{38}O_3$: C, 74.50; H, 11.31. Found: C, 76.67; H, 11.27. IV 1.8. Oxirane oxygen, 4.45% (94.0% of theoretical).

### 8-(4-n-Hexyl-2(3)-hydroxy-3(2)-formoxycyclohexyl)octanoic Acid (IV) and Methyl Ester (IV-me)

Hydrogen peroxide (28%, 58 g) was added to a solution of ICHA (100 g) in formic acid (90%, 100 g) in a three-necked 1 liter flask equipped with a magnetic stirrer, condenser and thermometer extending below the liquid surface. The reaction was exothermic and became homogeneous at 70–73 C. This temperature was maintained for 3 hr with initial cooling and subsequent heating. After cooling and adding water the product was extracted with ether, washed and dried. Removal of the solvent gave 120.8 g of oil. NE calculated, 370. Found: 383.

ICHA-*me* (100 g) were converted to the hydroxyformoxy derivative in a similar manner. The yield was 116.1 g (97.6%): IV 1.5; AV 51.4; oxirane oxygen, 0%. A sample for analysis was treated with diazomethane to esterify the free acid and then stripped to dryness.

*Analysis.* Calculated for $C_{22}H_{40}O_5$: C, 68.71; H, 10.49; $CH_3O$, 8.07. Found: C, 67.82; H, 10.10; $CH_3O$, 7.84.

CHA-*me* (6 g) was treated with formic acid (30 ml) and hydrogen peroxide (3.5 g) as described above. The AV was 83. The product was treated with diazomethane to esterify the free acid that was present. The yield of IV-*me* was 6.9 g (97.2%).

*Analysis.* Calculated for $C_{22}H_{40}O_5$: C, 68.71; H, 10.49; $CH_3O$, 8.07. Found: C, 67.82; H, 10.15; $CH_3O$, 8.00; IV 1.4.

### Methyl 8-(4-n-Hexyl-2,3-O-isopropylidenecyclohexyl) octanoate (V)

A solution of the hydroxyformoxy acid (IV) (from ICHA, 115 g) dimethoxy propane (350 ml), methanol (200 ml), hydrogen chloride in methanol (5%, 50 ml) and hexane (100 ml) was distilled slowly for 3 hr to remove an azeotropic mixture of hexane-methanol, bp 49–55 C. After the solution was cooled and passed through alumina (125 g), the product was stripped to dryness to give 111 g

(90.3%) of light yellow oil. No hydroxyl was detected by IR. Glycol analysis calculated as the acetone addition product, 76.9%; AV 0.

Rapid distillation of 55 g gave 45.4 g of water-white oil; bp 180–195 C at 0.025 mm. Glycol analysis calculated as acetonate, 82.7% (2 hr analysis). Carbonyl by hydroxylamine, calculated 7.06. Found: 5.92 (83.8% of theoretical).

The isomeric epoxy ester (III) was dissolved in acetone and treated with boron trifluoride etherate (19). After workup and fractional distillation the yield of product V was 53.6%, bp 178–185 C at 0.025 mm. The amount of viscous undistillable residue was 30%.

*Analysis.* Calculated for $C_{24}H_{44}O_4$: C, 72.68; H, 11.18. Found: C, 72.30; H, 11.00. Glycol analysis calculated as the acetonate V: 92.8%. Carbonyl analysis by hydroxylamine was 92.7% of theoretical. No hydroxyl was detected by IR.

### 9,12-Diformylstearic Acid (VI) and Methyl Ester

Periodic acid (9 g) in water (20 ml) and acetic acid (50 ml) were added to a solution of the isomeric diol methyl ester II (12.8 g) in acetic acid (100 ml). The temperature was maintained below 30 C. After stirring for 30 min the solution was poured into water and extracted with ether. The ether solution was washed with saturated sodium bicarbonate, water and dried. The dialdehyde ester was treated with diazomethane to remove a trace amount of acid. The yield was 11.7 g (91.2%).

*Analysis.* Calculated for $C_{21}H_{38}O_4$: C, 71.14; H, 10.80; $CH_3O$, 8.75; carbonyl 15.8%. Found: C, 69.66; H, 10.58; $CH_3O$, 8.92; carbonyl 14.3% (90.5% of theoretical).

The glycol acid (II), mp 72–75 C in ethanol, was treated with periodic acid as above to yield the dialdehyde acid as a viscous oil. NE calculated 340.5. Found: 349. Bisdinitrophenylhydrazone, mp 157–158 C.

*Analysis.* Calculated for $C_{32}H_{44}N_8O_{10}$: C, 54.99; H, 6.31; N, 15.94. Found: C, 55.26; H, 6.66; N, 16.14.

The higher melting glycol acid (II), mp 107–108 C, when treated with periodate as above gave the dialdehyde acid. The bisdinitrophenylhydrazone melted at 157–158 C.

### Analysis of Isopropylidene Stearates—Acetone Adducts of 9,10-Dihydroxystearates

For this analysis authentic samples of methyl *erythro* and *threo*-9,10-*O*-isopropylidene stearates were prepared.

Methyl *erythro*-9,10-*O*-isopropylidene stearate was prepared from *erythro*-9,10-dihydroxystearic acid (10 g) by treatment with dimethoxypropane (50 ml), methanol (20 ml) and hydrogen chloride in methanol (5%, 5 ml). The product was passed through alumina (20 g) and distilled to give 9.4 g (80.3%) of oil, bp 159–160 C at 0.075 mm.

*Analysis.* Calculated for $C_{22}H_{42}O_4$: C, 71.30; H, 11.42. Found: C, 70.99; H, 11.23. Glycol as acetonate 100.2% (1 hr analysis). No hydroxyl was detected by IR. Carbonyl by hydroxylamine, 7.5%.

Methyl *threo*-9,10-*O*-isopropylidene stearate was prepared from *threo*-9,10-dihydroxystearic acid (10 g) in 89.7% yield, bp 153–154 C at 0.06 mm.

*Analysis.* Calculated for $C_{22}H_{42}O_4$: C, 71.30; H, 11.42. Found: C, 71.01; H, 11.18. Glycol as acetonate 100.5% (2 hr analysis). Carbonyl by hydroxylamine, 7.4%.

*Glycol Analysis.* The periodate oxidation procedure described by Handschumaker and Linters (20) was modified. The sample size was decreased to less than 150 mg and the time of reaction was increased from 15 min to 2 hr for complete hydrolysis and oxidation by periodic acid. The following percentages and time of analysis of methyl *threo*-9,10-isopropylidene stearate were: 46.6, 15 min; 79.4, 1 hr; 100.5, 2 hr; and 104.0, 3 hr. The following data were obtained for the *erythro* isomer: 89.9, 15 min; 100.2, 1 hr; 102.1, 2 hr; and 103.8, 3 hr.

## ACKNOWLEDGMENTS

Mrs. Clara McGrew, Mrs. Bonita Heaton and Mrs. Karen Jones performed the microanalyses; George McManis, the infrared analyses; Rex Scholfield, the capillary GLC work; and Robert Beal and Roger Eisenhauer prepared the isomeric cyclohexene methyl esters.

## REFERENCES

1. Danzig, M. J., J. L. O'Donnell, E. W. Bell, J. C. Cowan and H. M. Teeter, JAOCS *34*, 136–138 (1957).
2. Gast, L. E., E. W. Bell and H. M. Teeter, Ibid. *33*, 278–281 (1956).
3. Teeter, H. M., E. W. Bell, J. L. O'Donnell, M. J. Danzig and J. C. Cowan, Ibid. *35*, 238–240 (1958).
4. Teeter, H. M., J. L. O'Donnell, W. J. Schneider, L. E. Gast and M. J. Danzig, J. Org. Chem. *22*, 512–514 (1957).
5. Friedrich, J. P., E. W. Bell and R. E. Beal, JAOCS *39*, 420 (1962).
6. Friedrich, J. P., D. Hejeebu, L. E. Gast and J. C. Cowan, Presented at the 58th AOCS Meeting, New Orleans, La. May, 1967, Abstract No. 126.
7. Kaufmann, H. P., Fette Seifen Anstrichmittel *64*, 1115–1126 (1962).
8. Adams, R., and T. G. Geissmann, J. Am. Chem. Soc. *61*, 2083–2089 (1939).
9. Holmes, H. L., Org. Reactions *4*, 60–173 (1948).
10. Kloetzel, M. C., Ibid. *4*, 1–59 (1948).
11. Martin, J. G., and R. K. Hill, Chem. Rev. *61*, 537–562 (1961).
12. Gould, E. S., "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, 1959, p. 534.
13. Hanack, M., "Conformation Theory," Academic Press, New York, 1965, p. 147.
14. Richborn, B., and S. Y. Luo, J. Org. Chem. *30*, 2212–2216 (1965).
15. Freedman, B., JAOCS *44*, 113–116 (1967).
16. Wood, R. D., P. K. Raju and R. Reiser, Ibid. *42*, 81–85 (1965).
17. Durbetaki, A. J., Anal. Chem. *28*, 2000 (1956).
18. O'Donnell, J. L., L. E. Gast, J. C. Cowan, W. J. DeJarlais and G. E. McManis, JAOCS *44*, 652–655 (1967).
19. Kuester, F. E., U.S. Patent 3,127,418 (1964).
20. Handschumaker, E., and L. Linters, JAOCS *24*, 143–145 (1947).

[Received August 25, 1969]