# Homogeneous Catalytic Conjugation of Polyunsaturated Fats by Chromium Carbonyls[1]

**E. N. FRANKEL, Northern Regional Research Laboratory,[2] Peoria, Illinois 61604**

## Abstract

Various arene-$Cr(CO)_3$ complexes and $Cr(CO)_6$ are effective soluble catalysts for the conjugation of polyunsaturated fats. Methyl benzoate-$Cr(CO)_3$ is one of the most active catalysts. The following conjugation levels were obtained: methyl linoleate, 65%; methyl linolenate, 45%; the polyunsaturates in soybean and safflower oils, 73%; and in linseed oil 48%. Conjugated dienes from linoleate were predominantly *cis,trans* in configuration. Their double bonds were distributed between $C_5$ and $C_{16}$ of the fatty acid chain. Hydrogenation and dehydrogenation are side reactions, which seem to limit the yield of conjugated dienes from methyl linoleate. A conjugation mechanism is proposed that involves allyl-$HCr(CO)_3$ complexes as intermediates undergoing 1,3- and 1,5-hydrogen shifts.

## Introduction

Research at the Northern Laboratory in homogeneous catalysis originally sought selective catalysts for the hydrogenation of soybean oil (1–5). These studies were then extended to other reactions of possible industrial interest (6–8). One previous procedure gave 75–80% yields of conjugation of vegetable oils by treatment with $Fe(CO)_5$ and CO (7). This method required more than stoichiometric amounts of $Fe(CO)_5$ and also special equipment and facilities. More recently arene-$Cr(CO)_3$ complexes have been found to be effective homogeneous catalysts for the hydrogenation of polyunsaturated fats (9,10). These latest studies indicated that conjugation was an intermediate step in the reaction. The chromium carbonyls also proved to be suitable catalysts for the conjugation of polyunsaturated fats. Conjugated polyunsaturated fats were prepared with $Cr(CO)_3$ complexes, as well as with $Cr(CO)_6$. Among the soluble conjugation catalysts examined, methyl benzoate-$Cr(CO)_3$ was particularly effective.

## Experimental Procedures

### Materials and Methods

The vegetable oils used and methods of analyses (GLC, IR, UV) were the same as those described previously (2,3). Methyl linoleate was obtained from The Hormel Institute (Austin, Minn.); methyl linolenate was prepared in this Laboratory (11). Methyl benzoate-$Cr(CO)_3$, cycloheptatriene-$Cr(CO)_3$, benzene-$Cr(CO)_3$ and $Cr(CO)_6$ were purchased (Strem Chemicals, Danvers, Mass.). Conjugated dienes and monoenes from conjugated methyl linoleate were isolated and purified by preparative gas liquid chromatography (GLC) (3,12). Double bond position was determined in these fractions by reductive ozonolysis-GLC (10,13).

### Conjugation

The oils and fatty esters (scale, 10–50 g) were conjugated in a magnetically stirred autoclave by the same procedure as that used for hydrogenations with $Cr(CO)_3$ complexes (9,10) except that either nitrogen or helium was substituted for hydrogen. Removal of air from the autoclave by purging the system repeatedly with inert gas before heating was essential to prevent polymerization and to obtain good yields of conjugated products. An initial pressure of 50 psi ($N_2$ or He) was applied before heating. After heating the autoclave (165–195 C) the pressure in the system reached 70 psi (without solvent) to 140–200 psi (with 50 ml solvent). Conjugation with $Cr(CO)_3$ complexes could be done with or without a solvent, but $Cr(CO)_6$ required a solvent such as cyclohexane or *n*-hexane apparently to remain in solution. After conjugation the triglyceride products were subjected to vacuum stripping to remove unreacted catalyst followed by carbon black treatment to remove decomposed catalyst (9). For analyses a 1 to 2 g sample was transesterified directly with $KOCH_3$ in MeOH without previous treatment. When methyl esters were conjugated, they were treated with $FeCl_3$ to decompose unreacted catalyst (10). Clear conjugated esters were obtained by distillation (135–160 C/0.018 mm) in yields of 85–95%.

## Results

Methyl linoleate was conjugated with various chromium carbonyl catalysts at different temperatures. Reaction times at which conjugation leveled off varied from 2 to 6 hr when determined kinetically. Approximately 45% to 65% diene conjugation resulted with $Cr(CO)_3$ complexes of methyl benzoate, benzene and cycloheptatriene at 165–175 C (Table I). Higher reaction temperatures (185–195 C) were necessary with $Cr(CO)_6$ for comparable results. Analyses of conjugated diene by GLC were in general agreement with UV analyses when an absorptivity of 100 at 232–233 mμ was used. However, formation of nonvolatile material (presumably polymeric) was indicated when GLC values exceeded corresponding UV values by more than 10%. Polymerization is thus indicated when methyl linoleate was heated with methyl benzoate-$Cr(CO)_3$ at 185 C and with cycloheptatriene-$Cr(CO)_3$ at 175–185 C. Analyses by GLC and IR show that the conjugated dienes are predominantly *cis,trans*. The proportion of *trans,trans* isomers increased at higher temperatures, but it was accompanied by the formation of polymeric or nonvolatile material. Formation of monoenes and conjugated trienes provides evidence that hydrogenation and dehydrogenation are side reactions that seem to limit the yields of conjugated diene from methyl linoleate. Isolated *trans* unsaturation varied from 10% to 20% in the product and exceeded the concentration of monoene. Therefore, nonconjugated dienes must also contain *trans* isomers. These isomers may be responsible for the double diene peak observed by GLC.

Further investigations were carried out with methyl benzoate-$Cr(CO)_3$. The rate of catalytic conjugation of methyl linoleate with methyl benzoate-$Cr(CO)_3$ was followed by periodic GLC analyses

---

[1] Presented at the AOCS Meeting, San Francisco, April 1969.

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

TABLE I

Conjugation of Methyl Linoleate With Various Chromium Carbonyl Catalysts[a]

| Analyses[b] | Methyl benzoate-$Cr(CO)_3$ | | | Benzene-$Cr(CO)_3$ | | Cycloheptatriene-$Cr(CO)_3$ | | | $Cr(CO)_6$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 165 C 6 hr | 175 C 5 hr | 185 C 4 hr | 175 C 6 hr | 185 C 6 hr | 165 C 6 hr | 175 C 6 hr | 185 C 5 hr | 175 C 6 hr | 185 C 2 hr | 195 C 2 hr |
| Gas liquid chromatography, % | | | | | | | | | | | |
| Conjugated diene | 63.0 | 65.0 | 64.1 | 60.3 | 63.7 | 52.6 | 63.6 | 78.4 | 25.7 | 65.7 | 66.4 |
| (*cis,trans*) | (49.7) | (39.6) | (38.5) | (48.3) | (46.5) | (42.4) | (51.1) | (57.7) | (21.0) | (33.5) | (27.3) |
| (*cis,cis*) | ( 9.1) | ( 7.8) | ( 6.3) | ( 7.4) | ( 7.1) | ( 2.8) | ( 3.9) | ( 3.8) | ( 2.6) | ( 7.4) | ( 6.7) |
| (*trans,trans*) | ( 4.2) | (17.6) | (19.3) | ( 4.6) | (10.1) | ( 7.4) | ( 8.6) | (16.9) | ( 2.1) | (24.8) | (32.4) |
| Conjugated triene | 7.7 | 5.8 | 5.9 | 5.7 | 5.0 | 1.8 | 3.4 | 2.0 | 1.1 | 10.1 | 7.1 |
| Total conjugation | 70.7 | 70.8 | 70.0 | 66.0 | 68.7 | 54.4 | 67.0 | 80.4 | 26.8 | 75.8 | 73.5 |
| Monoene | 9.8 | 19.6 | 18.9 | 10.6 | 16.9 | 1.7 | 5.6 | 3.0 | 3.2 | 16.4 | 19.1 |
| Unconjugated diene[c] | 19.5 | 9.6 | 11.1 | 23.4 | 14.4 | 43.9 | 27.4 | 16.5 | 70.0 | 7.8 | 7.4 |
| Ultraviolet | | | | | | | | | | | |
| Conjugated diene, [a]232–233 mμ | 56.5 | 65.9 | 50.6 | 51.2 | 54.3 | 45.3 | 52.0 | 65.8 | 22.0 | 59.5 | 60.3 |
| Conjugated triene, [a]267–271 mμ | 13.5 | 5.6 | 4.1 | 12.2 | 12.6 | 6.9 | 5.7 | 5.9 | 3.0 | 16.3 | 14.9 |
| Infrared | | | | | | | | | | | |
| [a]980–985 $cm^{-1}$ | 0.27 | 0.43 | 0.13 | 0.24 | 0.36 | 0.22 | 0.25 | 0.35 | 0.21 | 0.38 | 0.46 |
| [a]948–949 $cm^{-1}$ | 0.18 | 0.18 | 0.33 | 0.16 | 0.15 | 0.14 | 0.16 | 0.19 | 0.07 | 0.12 | 0.09 |
| Isolated *trans*,[d] % | 19.4 | 24.4 | 27.1 | 17.4 | 20.2 | 12.6 | 15.3 | 19.3 | 10.4 | 20.0 | 21.4 |

[a] In *n*-hexane, He and 10 M % catalyst.
[b] On nondistilled esters.
[c] Partially resolved into a double peak.
[d] As methyl elaidate.

(Fig. 1A). Rate curves show that as diene disappears conjugated diene forms as the main product and levels off after 3–4 hr at 65%. Small levels of monoene and conjugated triene are also formed. Analyses by GLC of the conjugated dienes (Fig. 1B) show that *cis,trans* is the main isomer formed initially. The formation of the *cis,cis* and the *trans,trans* isomers follows and corresponds after 2 hr to a decrease of the *cis,trans* isomer. The evidence indicates conversion of some *cis,trans* to *trans,trans* isomers during the reaction.

Conjugation data obtained with methyl benzoate-$Cr(CO)_3$ catalyst are summarized in Table II. With methyl linolenate diene conjugation varied from 26% to 31% and triene conjugation from 14% to 15%. Isolated *trans* unsaturation varied from 15 to 18%. Since only about 0.5% monoene was found in the product, the isolated *trans* unsaturation must be due mainly to the nonconjugated diene and triene components.

TABLE II

Conjugation of Methyl Linolenate and Vegetable Oils With Methyl Benzoate-$Cr(CO)_3$[a]

| Analyses[b] | Methyl linolenate[c] | | Soybean oil,[d] | Safflower oil,[d] | Linseed oil,[d] |
|---|---|---|---|---|---|
| | 175 C | 185 C | 175 C | 175 C | 175 C |
| Gas liquid chromatography, % | | | | | |
| Conjugated diene | ...... | ...... | 39.9 | 51.0 | ...... |
| Conjugated dienetriene[e] | 26.3 | 31.4 | 2.0 | ...... | 23.0 |
| Conjugated triene | 14.8 | 13.6 | 4.3 | 4.4 | 9.5 |
| Total conjugation | 41.1 | 45.0 | 72.9[f] | 73.3[f] | 48.2[f] |
| Palmitate | ...... | ...... | 10.6 | 7.2 | 6.8 |
| Stearate | ...... | ...... | 3.8 | 2.9 | 4.4 |
| Monoene | 0.5 | 0.6 | 30.2 | 24.4 | 25.2 |
| Unconjugated diene[g] | 4.7 | 4.3 | 9.2 | 10.1 | 14.2 |
| Unconjugated triene[h] | 53.7 | 50.1 | ...... | ...... | 16.9 |
| Ultraviolet | | | | | |
| Conjugated diene, [a]233–235 mμ | 23.5 | 25.6 | 35.3 | 43.6 | 23.6 |
| Conjugated triene, [a]267–273 mμ | 26.7 | 23.9 | 7.8 | 7.9 | 16.7 |
| Infrared | | | | | |
| [a]985–990 $cm^{-1}$ | 0.21 | 0.20 | 0.16 | 0.19 | 1.41 |
| [a]945–950 $cm^{-1}$ | 0.06 | 0.06 | 0.09 | 0.11 | 0.06 |
| Isolated *trans*,[i] % | 14.5 | 18.4 | 12.3 | 14.8 | 16.5 |

[a] 10 M % catalyst, 6 hr.
[b] On nondistilled esters.
[c] In cyclohexane solution, He.
[d] No solvent, $N_2$.
[e] Triene with two conjugated double bonds and one isolated.
[f] Based on total linoleate and linolenate in original samples: soybean, 63.4; safflower, 75.6; and linseed, 67.4%.
[g] Partially resolved into two peaks.
[h] Includes *cis,trans*-conjugated diene.
[i] As methyl elaidate.

Methyl benzoate-$Cr(CO)_3$ was also an effective catalyst for the conjugation of vegetable oils (Table II). The polyunsaturates in soybean and safflower oils were 73% conjugated; in linseed oil, 48%. UV analyses for conjugated diene agreed with corresponding GLC analyses and indicated no polymerization. Another approach to determine the formation of any nonvolatile or polymeric material can be made by using palmitate as an internal standard in the GLC analyses. Comparisons of palmitate values before and after conjugation gave increases of 0.3% for soybean oil, of 0.6% for linseed oil, and no change for safflower oil. These results confirm the conclusion reached from the GLC and UV analyses that little or no polymerization occurred in vegetable oils during the catalytic conjugation. Analyses by IR showed the presence of *trans,trans*- and *cis,trans*-conjugation ($a_{985}$ and $a_{950}$ $cm^{-1}$) and isolated *trans* unsaturation (12–17%).

A more detailed study was made of the isomers in conjugated dienes and monoenes from linoleate to elucidate the mechanism of catalytic conjugation by chromium carbonyls. Conjugated linoleate was separated by preparative GLC, and the monoene and conjugated diene fractions were analyzed for double bond position by reductive ozonolysis-GLC. The main diene isomers obtained with methyl benzoate-$Cr(CO)_3$ and $Cr(CO)_6$ are 8–10, 9–11, 10–12 and 11–13 and constitute 67% to 71% of the total (Fig. 2A). The remaining isomers include 5–7, 6–8, 7–9, 12–14, 13–15 and 14–16. The monoene fractions show distribution of the double bond between $C_5$ and $C_{13}$ with the 9-, 10-, 11- and 12-monoenes making up 82% to 88% of the total (Fig. 2B). These monoene isomers are those expected if hydrogenation occurs by 1,4-addition of hydrogen after conjugation of methyl linoleate (10,14).

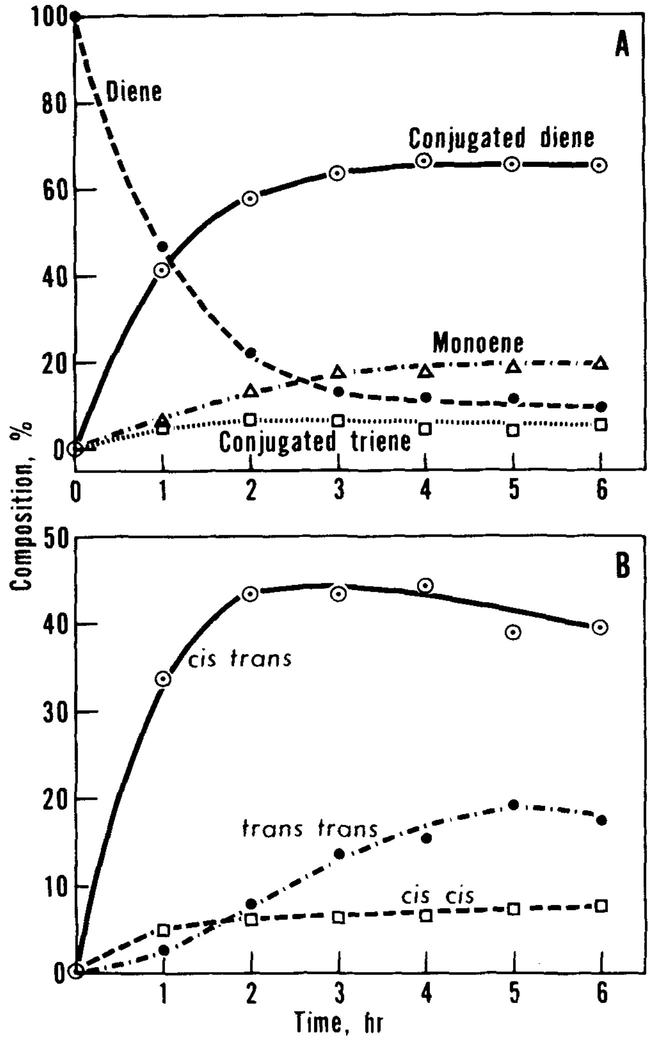


FIG. 1. Rate of conjugation of methyl linoleate with methyl benzoate-Cr(CO)$_3$ (175 C, *n*-hexane solution, He): (A) fatty esters, (B) conjugated diene isomers.

## Discussion

Conjugation is an important intermediate step in hydrogenation of fats by most homogeneous, as well as many heterogeneous catalysts (5). Some of these catalysts would be expected to promote conjugation also. Chromium carbonyl compounds proved to be effective soluble catalysts for the conjugation of polyunsaturated fats, and methyl benzoate-Cr(CO)$_3$ was one of the best.

The *cis,cis*-1,4-pentadiene structure of linoleate is involved in autoxidation, alkali conjugation and catalytic hydrogenation. Allylic intermediates postulated in these reactions (5,15,16) may be invoked also to explain the results of catalytic conjugation with chromium carbonyls. In the following mechanism (Scheme 1) the formation of Cr(CO)$_3$ is postulated as the active catalytic intermediate by dissociation (17). The arene-Cr(CO)$_3$ complexes would be expected to dissociate more easily than Cr(CO)$_6$, and higher temperatures are required with the latter than with the former. The next step in the mechanism involves the formation of allyl H–Cr(CO)$_3$ complexes with either the $\Delta^9$ or $\Delta^{12}$ double bond of linoleate. Conjugation results by a 1,3-hydrogen shift yielding *trans*-10,*cis*-12- and *cis*-9,*trans*-11-dienes as main initial products. To account also for the formation of the 8,10- and 11,13-diene isomers in significant

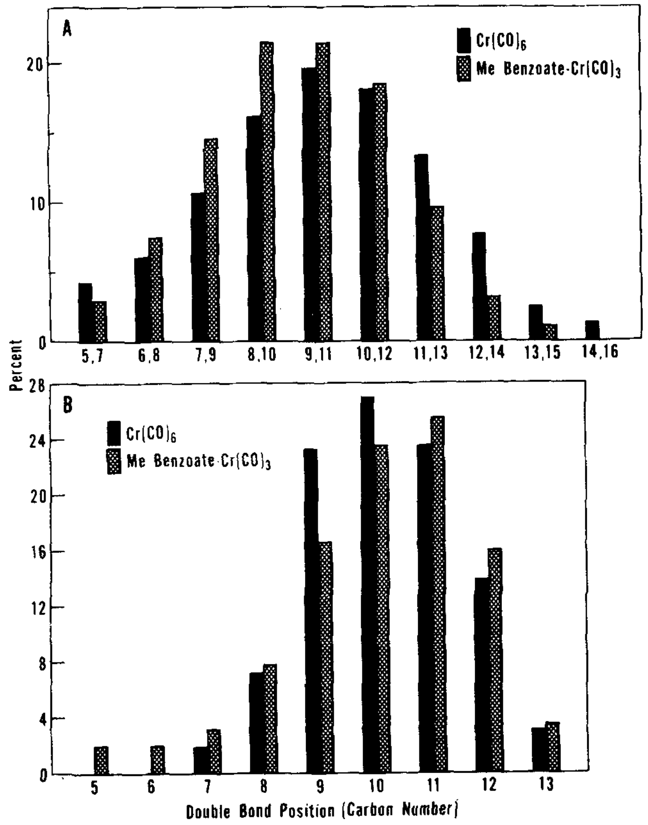
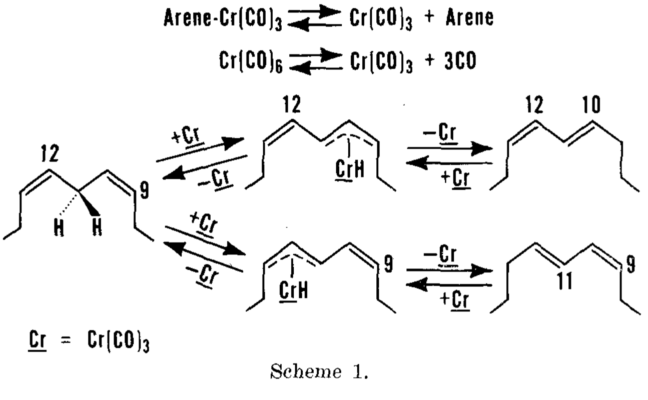
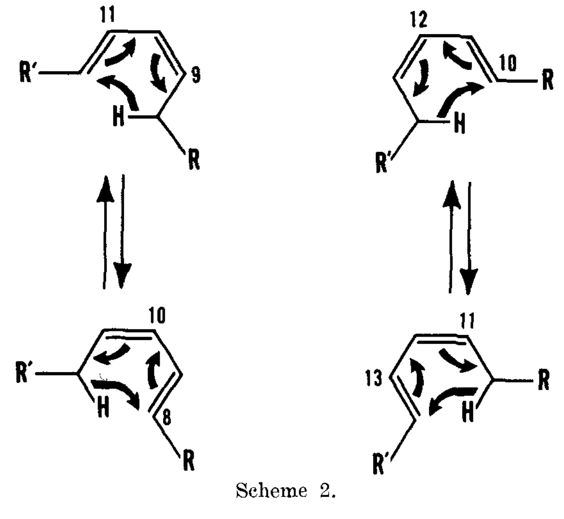


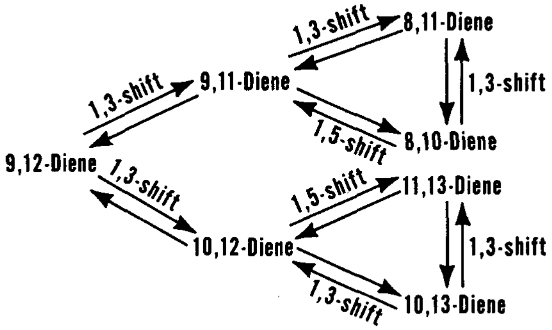
FIG. 2. Double bond distribution in fractions from methyl linoleate conjugated with Cr(CO)$_6$ and methyl benzoate-Cr(CO)$_3$ (185 C, *n*-hexane solution, He): (A) conjugated dienes, (B) monoenes.



Scheme 1.



Scheme 2.



Scheme 3.

amounts, isomerization of the 9,11- and 10,12-dienes is postulated by a 1,5-hydrogen shift (Scheme 2). This type of shift requires a *cis,trans* configuration. Evidence for it has been obtained in our hydrogenation studies (17). To explain the scattering of the conjugated diene isomers through the length of the fatty ester chain, a general scheme is formulated which involves both 1,3- and 1,5-hydrogen shifts (Scheme 3). This mechanism is supported by kinetic results that show *cis,trans*-conjugated dienes are the initial products of conjugation. Analyses by IR also provide evidence of the formation of both *cis,trans*-conjugated and nonconjugated dienes with isolated *trans* unsaturation. Scheme 3 may also be advanced for the isomerization of double bonds during catalytic hydrogenation of diene fatty esters (5).

Hydrogenation and dehydrogenation are side reactions that would limit the yield of conjugated dienes from linoleate. Analyses of the monoene components indicated that the positional isomers are derived from conjugated dienes by 1,4-reduction. The corresponding conjugated trienes have not been examined. However, dehydrogenation involving the methylenes alpha to the conjugated diene systems may be postulated as a reaction occurring concurrently with hydrogenation.

Methyl benzoate-$Cr(CO_3)$ and $Cr(CO)_6$ are effective conjugation catalysts for polyunsaturated fats. Better yields of conjugation were obtained with methyl linoleate (up to 65%) than with methyl linolenate (up to 45%). The polyunsaturates of vegetable oils were conjugated to the extent of 60% to 70%. The conjugated products would be suitable for investigation as drying oils or as chemical intermediates.

## ACKNOWLEDGMENT

Experimental assistance by F. L. Little; preparation of methyl linolenate by J. M. Snyder.

## REFERENCES

1. Mabrouk, A. F., H. J. Dutton and J. C. Cowan, JAOCS *41*, 153–158 (1964).
2. Frankel, E. N., H. M. Peters, E. P. Jones and H. J. Dutton, Ibid. *41*, 186–191 (1964).
3. Frankel, E. N., E. A. Emken, H. M. Peters, V. L. Davison and R. O. Butterfield, J. Org. Chem. *29*, 3292–3297 (1964).
4. Frankel, E. N., T. L. Mounts, R. O. Butterfield and H. J. Dutton, Advan. Chem. Ser. *70*, 177–194 (1968).
5. Frankel, E. N., and H. J. Dutton, in press.
6. Frankel, E. N., E. A. Emken and V. L. Davison, JAOCS *43*, 307–311 (1966).
7. Frankel, E. N., and S. Metlin, Ibid. *44*, 37–39 (1967).
8. Frankel, E. N., S. Metlin, W. K. Rohwedder and I. Wender, Ibid. *46*, 133–138 (1969).
9. Frankel, E. N., JAOCS *47*, 11–14 (1970).
10. Frankel, E. N., and F. L. Little, Ibid. *46*, 256–261 (1969).
11. Butterfield, R. O., H. J. Dutton and C. R. Scholfield, Anal. Chem. *38*, 86–88 (1966).
12. Emken, E. A., C. R. Scholfield, V. L. Davison and E. N. Frankel, JAOCS *44*, 373–375 (1967).
13. Stein, R. A., and N. Nicolaides, J. Lipid Res. *3*, 476–478 (1962).
14. Frankel, E. N., E. Selke and C. A. Glass, J. Am. Chem. Soc. *90*, 2446–2448 (1968).
15. Frankel, E. N., C. D. Evans, D. G. McConnell, E. Selke and H. J. Dutton, J. Org. Chem. *26*, 4663–4669 (1961).
16. Nichols, P. L., Jr., S. F. Herb and R. W. Riemenschneider, J. Am. Chem. Soc. *73*, 247–252 (1951).
17. Frankel, E. N., and R. O. Butterfield, J. Org. Chem. *34*, 3930–3936 (1969); Frankel, E. N., E. Selke and C. A. Glass, Ibid. *34*, 3936–3942 (1969).

[Received September 16, 1969]