

Oxidation of Methyl Formylstearate with Molecular Oxygen¹

J.P. FRIEDRICH, Northern Regional Research Laboratory, ARS, USDA, Peoria, Illinois 61604

ABSTRACT

Methyl formylstearate, containing soluble rhodium complex from rhodium-catalyzed hydroformylation of methyl oleate, is oxidized in an emulsion to methyl carboxystearate. The reaction is carried out in a closed system at 20-25 C in the presence of either air or oxygen (1-3 atm). Conversion to methyl carboxystearate is 87-89% in 2-3 hr; when catalytic amounts of calcium acetate are present, 93-95% is converted. The principal byproduct of oxidation is methyl formyloxystearate, formation of which is suppressed by calcium acetate. Distillation of crude methyl carboxystearate yields a residue containing soluble rhodium (and calcium acetate if used), which after calcining in the presence of a refractory support produces an effective hydroformylation catalyst. Recovery and regeneration of this catalyst provide an economically feasible batch process for methyl carboxystearate.

INTRODUCTION

The reaction of synthesis gas (equimolar proportions of hydrogen and carbon monoxide) with methyl oleate produces methyl formylstearate (1), and its oxidation produces methyl carboxystearate (2). Carboxystearates have potential commercial value in lubricants (3), but commercial feasibility of the reactions involved need to be demonstrated, particularly because the catalyst for the hydroformylation is a high cost group VIII metal (rhodium). Feasibility has been reported for recovery and recycling of the catalyst in methyl formylstearate (MFS) (4), but not in methyl carboxystearate (MCS) preparations. For the oxidation step, Schwab, et al., (2) described an autoxidation procedure with metal naphthenate catalysts. The disadvantages of that system include a high concentration of catalyst, up to 24-hr reaction time, and two distillations.

An emulsion-type oxidation of MFS to MCS has been developed that employs the soluble rhodium complex hydroformylation catalyst, already present in crude MFS, as the oxidation catalyst. Data are presented that incorporate this oxidative procedure in extending the previous MFS process studies (4) to MCS.

EXPERIMENTAL PROCEDURES

Materials

Methyl oleate (MO) was prepared from Hercules Pamolyn 100, a commercial grade oleic acid, by direct esterification with methanol and sulfuric acid. The washed reaction product was vacuum distilled to give 98% pure MO. Activated rhodium catalyst (ARC) was prepared by heating commercial 5% rhodium on alumina (Englehard, Murray Hill, NJ) to 600 C in the presence of air for 3 hr. Other reagents were used as supplied: synthesis gas (Matheson Gas Products, New York, NY), triphenylphosphite (TPP) (Aldrich Chemical Co., Milwaukee, WI), calcium naphthenate (5% Ca) (Tenneco Chemicals, Inc., Elizabeth, NJ), copper oleate (Witco Chemical Co., New York, NY), cobalt resinate (Harshaw Chemical Co., Cleveland, OH), calcium acetate hydrate (Fisher Scientific Co., Fairlawn, NJ), and lithium chloride (Baker Chemical Co., Philipsburg, NJ).

Equipment

Small scale oxidations were carried out in a Parr low pressure glass shaker apparatus with a standard 450-ml reaction bottle, while hydroformylation reactions and oxidations for recycling studies were conducted in either a 300-ml or 2-liter electrically heated, 316 SS Magne-Drive autoclave manufactured by Autoclave Engineers (Erie, PA).

Large scale molecular distillation was done in a centrifugal molecular still manufactured by Consolidated Electrodynamics Corp. (Rochester, NJ). This still had a capacity of 1500 ml and a distillation rate of 0.3-10 ml per min. Large scale pot distillations were carried out in a 2-liter round bottomed flask containing a thermowell and fitted with a 4-in. jacketed Vigreux column, air cooled condenser, and receiver. Large scale semicontinuous distillations were conducted in a 200-ml 3-necked round bottomed flask fitted with thermowell, addition funnel, and 4-in. jacketed Vigreux with condenser and receiver. The apparatus used to reactivate the catalyst in the distillation residues has been described previously (4).

Hydroformylation

The substrate, principle products, and byproducts of hydroformylation and oxidation are:

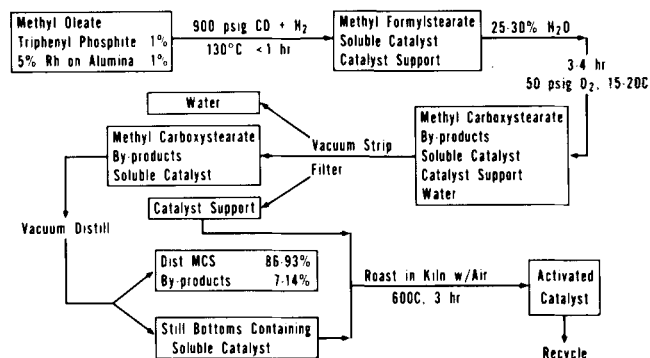
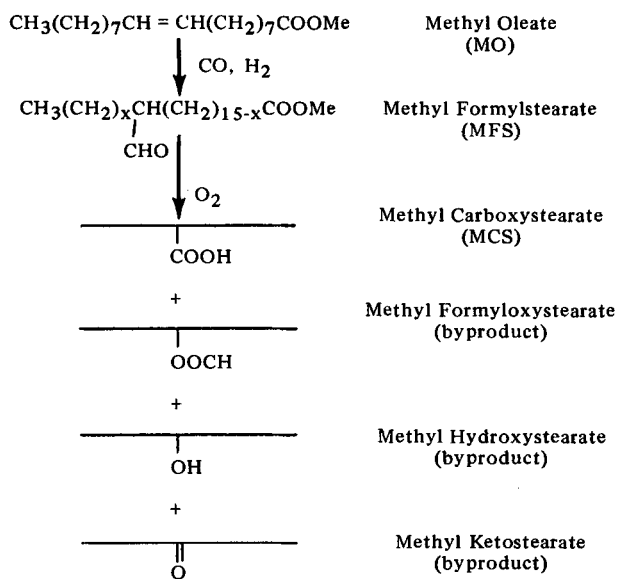


FIG. 1. Flow sheet for the preparation of methyl carboxystearate from methyl oleate.

¹ Presented at AOCS spring meeting, Dallas, April, 1975.

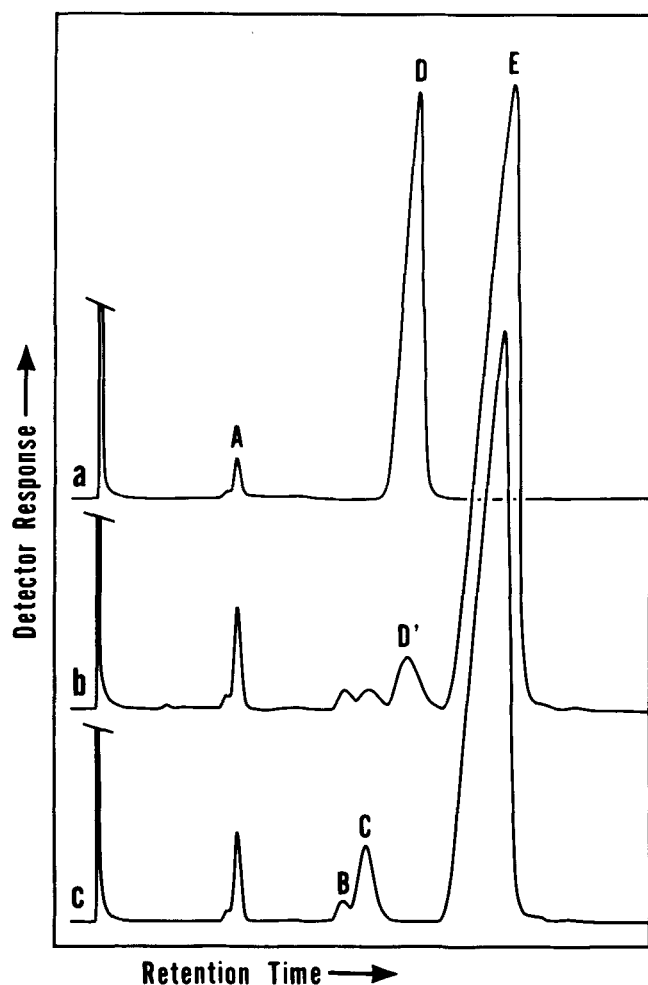


FIG. 2. Gas chromatograms of (a) methyl formylstearate, (b) oxidized methyl formylstearate, and (c) saponification product of (b). Peaks: (A) methyl stearate, (B) methyl ketostearate, (C) methyl hydroxystearate, (D) methyl formylstearate, (D') methyl formyloxystearate, and (E) methyl carboxystearate. Oxidized and saponified samples were methylated before injection into a 1/8 in. X 6 ft column filled with 3% JXR on Gas-Chrom Q and programmed between 200 and 250 C and 2 C/min.

Preliminary hydroformylation was done on 75-g batches of MO, whereas, the final runs were done on 750 g. As described, the various steps of the process (Fig. 1) are based on the 750-g runs.

MO (750 g), TPP (7.5 g), and ARC (7.5 g) were placed in a 2-liter Magne-Drive autoclave, which was flushed and pressurized to 500 psig with a 1:1 mixture of carbon monoxide and hydrogen and heated to 130 C with agitation. Reaction began at about 100 C as shown by a drop in the pressure, and pressure then was increased to 950 psi and cycled manually between 900 and 950 psig. The exothermic reaction was controlled by a small internal heat exchanger circulating cooling water. In ca. 40 min after reaching the desired temperature, the reaction was complete as indicated by no further drop in pressure and as verified by the disappearance of MO on gas liquid chromatography (GLC).

Oxidation

The reactor was cooled and the dissolved synthesis gas removed from the reaction product (ca. 825 g) under vacuum with stirring. Distilled water (300 ml) and calcium acetate monohydrate (15.5 g) were added to the reactor. After the reactor was cooled to 18 C, closed, and flushed with oxygen, the pressure was raised to 50 psig with agitation. Reaction in the emulsion was immediate and rapid;

the temperature rose sharply to 22 C and was maintained at ca. 20 C by cooling water and by limiting the supply of oxygen. After 1.5 hr, when the reaction was nearly complete, the temperature was raised to 60 C under 50 psig of oxygen for 1 hr. The reactor was vented and the opened fill port fitted with a distillation head, condenser, and receiver. With the agitator running at ca. 600 rpm, a vacuum was applied and the water stripped off. As the distillation slowed, the temperature was raised to 100 C to remove the last traces of water.

Filtration

The contents of the reactor were cooled to ca. 40 C and removed by siphoning. The warm crude product was filtered through qualitative filter paper in a heated Buchner funnel. The solid, spent catalyst, and filter paper were transferred to a kiln (4) for the oxidative regeneration step.

Distillation

The crude filtered product (92.8% MCS by GLC) was vacuum distilled in a semicontinuous system described previously. Distillation began at a pot temperature of 185 C and 0.1 mm pressure. The bulk of the distillation was carried out at 205-210 C at a rate of 3-6 ml/min. The pot was allowed to reach a final temperature of 240 C before cooling. A total of 800 g of distillate was collected and 63 g of dark, viscous still bottoms remained. GLC analysis of the distillate indicated 92.5% MCS, 1.25% methyl stearate, <0.5% methyl ketostearate, 1.1% methyl hydroxystearate, and 4.8% methyl formyloxystearate. The pot residue was transferred to the kiln and the catalyst regenerated as described previously (4).

RESULTS AND DISCUSSION

Oxidation

Autoxidation of MFS yielded, in addition to MCS, three principal by-products in various proportions depending upon the catalyst and conditions employed. Two of these, methyl keto and hydroxystearate, were identified by previous investigators (2). The third, methyl formyloxystearate, may not have been recognized as a byproduct, because it has the same GLC retention time (3% JXR on Gas Chrom Q) as MFS and might have been mistaken for unreacted starting material. GLC curves for (a) MFS, (b) oxidized MFS, and (c) the saponification product of (b) are shown in Figure 2. It is obvious that peak D', which corresponded in retention time to MFS, was alkali-sensitive, and appeared to be converted to hydroxystearic acid. The unknown D' was isolated by low temperature crystallization and liquid-liquid chromatography. The unknown was completely resistant to oxidation by either permanganate or oxygen under normal conditions for MFS oxidation. Carbon-hydrogen analysis of D' (97.5%) versus theoretical values for methyl formyloxystearate gave 69.67% C (70.13) and 11.3% H (11.18). Methoxy analysis gave 8.87% CH₃O (9.06). The NMR spectrum of D' confirmed the absence of aldehyde and was identical to an authentic sample of methyl formyloxystearate prepared by esterification of 9(10)-hydroxystearic acid with formic acid followed by methylation with diazomethane. Mass spectral analysis of the authentic sample indicated significant peaks

at 155 and 169 corresponding to the fragments $\begin{matrix} \text{H} \\ | \\ -\text{C}(\text{CH}_2)_7\text{C}- \\ | \quad | \\ \text{O} \quad \text{O} \end{matrix}$ and $\begin{matrix} \text{H} \\ | \\ -\text{C}(\text{CH}_2)_8\text{C}- \\ | \quad | \\ \text{O} \quad \text{O} \end{matrix}$ which would be expected from cleavage of

the 9 and 10 formyloxy isomers. The unknown D' showed the same fragments plus peaks at 141 and 183 corresponding to the 8 and 11 isomers. This fragmentation is consistent, because under the conditions reported here, hydro-

TABLE I
Oxidation of Methyl Formylstearate^a

Run	Substrate ^b	Time (hr)	Temperature ^c (C)	Reaction medium, ^d (emulsion [E], neat [N])	Gas liquid chromatographic analysis (%)			
					Methyl stearate	Methyl keto and hydroxystearate	Substrate plus methyl formyloxystearate	Methyl carboxystearate
1	Distilled	1.0	25	E	---	---	55.5	27
2	Distilled	1.0	25	N	3.6	1.4	44.5	51.6
3	Distilled	1.0	25	E	3.5	nil	36.7	59.8
4	Crude	1.0	25	N	3.6	2.3	35.6	58.5
5	Crude	1.0	25	E	2.7	2.5	12.7	82.1
6 (control)	Crude	1.5 ^e	25	E	2.2	<1	12.3	85.5
7	Crude ^f	1.5 ^e	35	E	3.8	1	4.3	91
8	Crude ^g	1.75 ^e	35	E	3.3	2.4	4.3	90

^aOxidant for run no. 1 was air; oxygen was used for succeeding runs.

^bCrude substrate is the filtered hydroformylated reaction product containing soluble rhodium complex. The distilled substrate is free of catalyst.

^cOxidations were carried out in a Parr glass shaker; temperatures listed are starting temperatures. An exothermic increase of about 10 C during the course of the reaction was not uncommon.

^dEmulsion consisted of 25 g MFS and 10 g distilled water.

^eOxidation run to completion (no substrate remaining).

^f0.5% (% by wt of substrate) Ca as calcium naphthenate added.

^g0.5% (% by wt of substrate) Ca as calcium acetate monohydrate added.

TABLE II
Effects of Recycled Catalyst on Oxidation of Methyl Formylstearate^a

Run	Catalyst ^b	Gas liquid chromatographic analysis (%)			
		Time to completion (hr)	Methyl keto and hydroxystearates (%)	Methyl formyloxystearate (%)	MCS ^c (%)
1	7.5 g Calcium naphthenate (5% Ca)	3.5	3.1	3.3	90.5
2	0.525 g Calcium oxide ^d	5.0	6.0	7.3	82.5
3	0.525 g CaO ^d + 2 ml HAC	3.5	> 0.5	8.5	88.0
4	0.525 g CaO ^d + 5 ml HAC	2.5	3.0	8.6	85.3
5	0.525 g CaO ^d + 2 ml HCOOH	2.5	15.56	16.3	54.8

^aThe emulsion (75 g methyl formylstearate [MFS] and 30 g distilled water) was oxidized in a 300-ml Magne Drive autoclave at 50 psig oxygen and 20 C until uptake ceased and then 60 C to completion.

^bMFS contains the rhodium catalyst in addition to materials listed.

^cMCS = methyl carboxystearate.

^dCalcium assumed to be CaO after regeneration of combined catalysts at 600 C in the presence of air.

formylation of methyl oleate produced considerable isomerization.

Oxidation of MFS to MCS is influenced by several factors. In the first 5 runs (Table I) at 25 C for 1 hr, reactivity increased under the following conditions. If oxygen replaced air (1 vs 3), an emulsion system was used (2 vs 3 and 4 vs 5), and crude MFS contained the soluble rhodium catalyst as opposed to distilled MFS (2 vs 4 and 3 vs 5). Reactions 6, 7, and 8 ran to completion as indicated by failure to absorb additional oxygen, and show greatly reduced overall reaction time of < 2 hr as compared to 24 hr previously reported (2). Aqueous oxidation systems are quite common and several theories exist on the role of water in such systems (5). The increased reaction rate of the system discussed here may well be a surface phenomenon with increased contact between aldehyde, catalyst, and oxygen. More vigorous agitation, which would be expected to increase the contact area, also was observed to increase the reaction rate. The effectiveness of either calcium acetate or calcium naphthenate in reducing formation of byproduct, methyl formyloxystearate (6 vs 7 and 8), is clearly indicated. Several other metal salts, including calcium chloride, lithium chloride, copper resinate, copper oleate, and cobalt stearate also were tried at the same molar level of active metal with crude MFS in an emulsion.

Because none of these salts showed any improvement over the control, they were not included in Table I.

Recycling Catalyst (Small Scale)

It was not known if the presence of calcium salts would adversely affect the hydroformylation of methyl oleate or not, so a study was conducted to see if the combined rhodium catalyst containing calcium salts could be recycled as described previously (4), and if the proposed process for MFS could be extended to one for MCS.

The first series of reactions was conducted on 75-g batches of methyl oleate. After initial hydroformylation (Table II), 7.5 g of calcium naphthenate (0.375 g Ca) and 30 ml of distilled water were added to the autoclave, and the mixture was oxidized as described previously. The GLC of 90.5% MCS was essentially equivalent to runs 7 and 8 in Table I. After filtration and vacuum distillation of the crude product, the residue that contained the calcium naphthenate and soluble rhodium was recombined with the spent rhodium-on-alumina catalyst and regenerated in a kiln at 600 C in the presence of air. The regenerated catalyst was assumed to be a mixture of calcium and rhodium oxides on alumina.

This catalyst was recycled with fresh methyl oleate. The temperature range normally used for this hydroformyla-

TABLE III
Effects of Recycled Catalyst on Formation and Oxidation of Methyl Formylstearate (MFS)^a

Run	Hydroformylation ^b Time to completion (hr)	Oxidation catalyst ^d	Time to completion (hr)	Gas liquid chromatographic analysis (%)				Distilled product	
				Methyl keto and hydroxystearate	Methyl formoxystearate	MCS	Type of distillation	Recovered (g)	GLC (%)
A	1.0 ^e	3.5 g Calcium as Ca(Ac) ₂	2.5	1.0	4.1	92.8	Semicontinuous	800	92.5
A1	10.5	3.5 g Ca as oxide ^f + 10 ml HAC	6.0	2.8	6.4	88.1	Semicontinuous	796	88.0
A2	5.5	3.5 g Ca as oxide ^f + 10 ml HAC	4.0	2.5	7.8	88.0	Semicontinuous	807	88.4
A3	5.5	3.5 g Ca as oxide ^f + 10 ml HAC	4.0	1.6	7.4	88.0	Semicontinuous	789	86.9
B	2/3	None	3.5	2.3	10.4	85.9	Semicontinuous	801	85.6
B1	2/3	None	3.25	3.4	7.9	86.2	Molecular	834	86.5
B2	2/3	None	3.25	3.4	8.0	86.1	Molecular	835	86.2
C	1.0 ^e	3.5 g Calcium as Ca(Ac) ₂	3.0	1.6	4.7	91.1	Pot	828	86.4

^aReactions were carried out in a 2-liter Magne-Drive autoclave on 750-g batches of methyl oleate (MO) containing ca. 2% stearate.

^bHydroformylations were carried out at 130 C and 900-950 psig of synthesis gas.

^cOxidations were carried out on the crude MFS, after addition of 300 ml water, at 50 psig oxygen and 15-20 C until uptake ceased, and then 60 C to completion.

^dThe MFS substrate contained the rhodium catalyst in addition to materials listed.

^eNo calcium salts present during the hydroformylation, but added for the oxidation step.

^fCalcium assumed to be CaO after regeneration of rhodium catalyst at 600 C in the presence of air.

tion, 100-120 C, was not sufficient to bring about a reaction; however, increasing the temperature to 130 C did allow complete conversion to MFS. Oxidation was slower than in the first run (Table II) and conversion to MCS (82.5%) much poorer with a marked increase in by-products. The catalyst was recovered and regenerated again. This time hydroformylation also required a 130 C reaction temperature. Because calcium acetate appeared to be equivalent to calcium naphthenate (Table I, runs 7 and 8), 2 ml of glacial acetic acid was added along with the water before oxidation to see if calcium acetate could be produced in situ and improve the yield of MCS. Oxidation was more rapid and the conversion to MCS was 88% (Table II, run 3). There was a striking decrease in the formation of keto and hydroxy byproduct. Increasing the amount of acetic acid to 5 ml decreased the yield of MCS (Table II, run 4).

Formic acid (2 ml) was used for run 5 (Table II) instead of acetic acid. Large increases in all byproducts, including methylstearate, were observed, and the yield of MCS was reduced to 54.8%. Hassall (6), ascribes the presence of formyloxy byproducts when aliphatic aldehydes are oxidized to carboxylic acids to a type of Baeyer-Villiger (ionic) mechanism. Aliphatic aldehydes react with hydrogen peroxide in neutral media to produce hydroxyhydroperoxides that, in turn, rearrange to give a mixture of carboxylic acid and the formate ester of the next lower alcohol. He further points out that in acid media, hydrocarbons also may be formed through a radical mechanism. This observation could account for the increase in methyl stearate when oxidation was conducted in the presence of strongly acidic formic acid.

Recycling Catalyst (Large Scale)

Adding HAc to the regenerated catalyst (Table II, run 3) before oxidation improved the yield of MCS over both the control (Table I, run 6) and calcium oxide (Table II, run 2), although it did not bring the yield up to that obtained with either fresh calcium acetate or calcium naphthenate (Table I runs 7 and 8; Table II, run 1). Adding fresh calcium salts for each oxidation in the proposed recycling process would cause an undesirably rapid buildup of calcium oxide in the mixed catalyst.

Final scale-up studies (Table III) were conducted on 750-g batches of methyl oleate in a 2-liter Magne-Drive autoclave. The first oxidation (A) was run at two-thirds of the calcium concentration (15 g calcium acetate) that was used in the 75-g batches. Yields (92.8% MCS) were the best obtained under any conditions. Recycling the regenerated catalyst from run A led to an extremely slow hydroformylation of 10.5 hr on the following run (A1). After addition of 10 ml of acetic acid and 300 ml of water to the crude MFS, oxidation also was comparatively slow; however, the yield of MCS was comparable to that obtained on the

smaller scale (Table II, run 3) under similar conditions. The next two recycles (Table III, runs A2 and A3) in which acetic acid was added before oxidation were also slow to hydroformylate as compared to calcium-free catalyst (run A) but were much faster than A1. The yields of MCS in the crude were almost identical for the three runs with regenerated catalyst.

A second series (Table III, run B) was conducted without any calcium salts, and results were similar to those for the control (Table I, run 6). There were two notable differences between this series and that conducted in the presence of calcium salts. The yields of MCS in the crude were 2% less, but the reaction time for hydroformylation was much shorter.

Three different types of distillation (pot, semicontinuous, and molecular) were used. A typical pot distillation (Table III, run C) while giving a good total recovery showed a marked decrease in MCS content from crude to distilled. Some decomposition was experienced previously in the pot distillation of MFS (4). The distilled product from run C contained ca. 7.3% oleate. By comparison, there was no decrease in purity when semicontinuous distillation was used. Molecular distillation likewise gave no decrease in purity, but did improve overall recovery more than 4%. The molecular still available did not lend itself readily to distillation of MCS containing calcium salts, because the salts precipitated on the moving parts causing mechanical problems as well as making cleanup difficult.

The process as described requires mechanical handling of precious metal catalyst and could result in significant losses. Although suitable equipment was not available to us, conceivably an autoclave could be designed so that the entire process could be carried out in one vessel, i.e., hydroformylation, oxidation, distillation, and regeneration of the catalyst. Such a vessel would eliminate handling losses as well as reduce space requirements and labor.

ACKNOWLEDGMENTS

Pressure reactions were run by R.L. Reichert; mass spectra by W.K. Rohwedder; NMR by C.A. Glass; and elemental analysis by B.R. Heaton and C.E. McGrew.

REFERENCES

1. Frankel, E.N., *JAOCS* 48:248 (1971).
2. Schwab, A.W., E.N. Frankel, E.J. Dufek, and J.C. Cowan, *Ibid.* 49:75 (1972).
3. Dufek, E.J., W.E. Parker, and R.E. Koos, *Ibid.* 51:351 (1974).
4. Friedrich, J.P., G.R. List, and V.E. Sohns, *Ibid.* 50:455 (1973).
5. Taylor, J.E., and J.C. Weygandt, *Can. J. Chem.* 52:1925 (1974).
6. Hassall, C.H., *Org. React.* 9:84 (1957).

[Received July 3, 1975]