

*panula rapunculoides*. The present data are in general agreement with previous work with some variations in oil content observed. Earle and Jones (1) have reported 11.2% HBr absorbing acids in *Coreopsis drummondii*, whereas the present work found only 3.9% polar acids, but such variations in oxygenated fatty acid content has been reported previously for *Chrysanthemum coronarium* (17).

The compositions of the oils examined are in general quite similar to existing commercial oils, suggesting that any utilization of the species reported here will depend on more favorable crop characteristics which these may possess. *Artemisia biennis* appears to represent an easily accessible source of polyene I.

*Atriplex hortensis* may represent a useful source of protein, since the yield of seed per plant appears to be high. However, Salgues (18) has reported that the seed of this species may contain toxic materials.

#### ACKNOWLEDGMENT

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Council, selected most of the species to be investigated, and also helped in the collection and identification of samples. M. Vetter provided assistance in the analysis of the oils.

#### REFERENCES

1. Earle, F. R., and Q. Jones, *Econ. Bot.* **16** (4), 221 (1962).
2. Earle, F. R., C. A. Glass, G. C. Geisinger, I. A. Wolff and Q. Jones, *JAOCS* **37**, 440 (1960).
3. Moldenhawer, K., *Przemysl Rolny i Spozyczezy*, **7** (2), 58 (1953).
4. Craig, B. M., and M. K. Bhatti, *JAOCS* **41**, 209 (1964).
5. Kleiman, R., F. R. Earle, I. A. Wolff and Q. Jones, *JAOCS* **41**, 459 (1964).
6. Bohlmann, F., P. Herbst, C. Arndt, H. Schonowsky and H. Gleinig, *Chem. Ber.* **94**, 3193 (1961).
7. ASTM designation D 271-48.
8. American Oil Chemists Society "Official and Tentative Methods of Analysis," Chicago, 1957.
9. Morris, L. J., and R. T. Holman, *J. Lipid Res.* **2**, 77 (1961).
10. Van Etten, C. H., *Anal. Chem.* **23**, 1697 (1951).
11. Craig, B. M., and N. L. Murty, *JAOCS* **36**, 549 (1959).
12. Tulloch, A. F., *Can. J. Chem.* **43**, 415 (1965).
13. Diamond, M. J., R. E. Knowles, R. G. Binder and L. A. Goldblatt, *JAOCS* **41**, 430 (1964).
14. Miwa, K., *Anal. Chem.* **32**, 1739 (1960).
15. Earle, F. R., E. H. Melvin, L. H. Mason, C. H. Van Etten and I. A. Wolff, *JAOCS* **36**, 304 (1959).
16. Chisholm, M. J., and C. Y. Hopkins, *Can. J. Chem.* **34**, 459 (1956).
17. Smith, C. R., M. O. Bagby, R. L. Lohmar, C. A. Glass and I. A. Wolff, *J. Org. Chem.* **25**, 218 (1960).
18. Salgues, R., *Qual. Plan. Mat. Veg.* **9**, (2), 71 (1962).
19. Earle, F. R., personal communication to the author.

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## A Comparison of Participating Solvents During Ozonization<sup>1</sup>

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#### Abstract

Sixteen different participating solvents and certain combinations thereof were evaluated for their effects on the conversion of methyl oleate to carbonyl compounds by ozonolysis. Depending upon the alcohol or carboxylic acid used as a single solvent, chemical reduction with zinc and acetic acid gave yields of 70–100%; catalytic hydrogenation with 10% Pd/C, 62–84%. When equimolar mixtures of an acid and a primary, unhindered alcohol were used, catalytic hydrogenation gave yields of 94–98%. In preparative scale experiments, catalytic hydrogenation gave 98% yields of methyl azelaaldehyde in the representative solvent combinations of 2-methoxyethanol/acetic acid and 1-butanol/propionic acid. When anhydrous calcium sulfate was used as a drying agent for aldehyde/alcohol solutions significant acetal was formed in the absence of other catalysts.

#### Introduction

NUMEROUS COMPOUNDS with varying degrees of polarity and functionality have been used as solvents for the ozonization of unsaturated fatty materials (1–13). Best results have been achieved from solvents described as reactive and participating. Of this type, methanol (10,11) reportedly gives the best yields of carbonyl compounds; however, methanol has certain disadvantages as an ozonization medium for other than small-scale or exploratory investigations. It has high volatility and poor solubilizing properties; furthermore, the by-product methyl acetals and methyl esters complicate purification by distillation. Consequently, we sought a more suitable solvent system for preparative-scale ozonizations. We investigated various solvents that could be classified as

reactive and participating. Criteria for such solvents were boiling points, solubilizing properties, and predicted reactivity. Four properties were measured for each solvent system: miscibility with methyl oleate, volatility, ozone absorption, and carbonyl yield.

#### Ozonization and Reduction

Ozonization procedures used have been previously reported (10). All alcohols were commercial grade, dried and distilled from potassium hydroxide. Acids were also commercial grade and used without further purification. The methyl oleate (Applied Science Laboratory) contained approximately 91% of its monounsaturations in the C<sub>9</sub> position as shown by oxidative cleavage (5).

#### Chemical Reduction

*Ozonization in 2-Methoxyethanol.* Methyl oleate (15.41 g 0.052 mole) and 2-methoxyethanol (242.0 g) were cooled to 10°C in a reaction flask. Oxygen, containing 2–3% ozone, was bubbled through the mixture until a rapid increase in ozone concentration in the exit gases, as determined by a Welsbach Model C ozone meter, was noted. The ozone consumption was 108% of theory, and loss of volatile solvent was less than 0.5%/hr.

After 10 g of glacial acetic acid was added to the reaction mixture, 5 g of zinc dust was added slowly with stirring, and the reaction flask was immersed in a water bath to maintain the temperature at 20–25°C. An aliquot of the reaction mixture then gave a negative peroxide test with potassium iodide in glacial acetic acid and was filtered through diatomaceous earth to remove excess zinc and zinc salts. Both reaction flask and filter cake were washed with 500 ml of methylene chloride, and the combined filtrate was washed with water until neutral to acid-alkali test paper. After drying, the solvent was removed on a rotary evaporator at <25°C and reduced pressure. Carbonyl yield was 97% as determined by GLC procedure outlined below.

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**Other Solvents.** Methyl oleate was ozonized in various other solvents. Values indicated in the following order, (bp °C, % ozone consumed, % solvent loss/hr, % carbonyl yield), were: methanol (65, 120, —, 93); ethanol (79, —, 3.44, ~100); 1-propanol (98, —, 0.85, ~100); 2-propanol (83, —, 1.0, 95); 1-butanol (117, —, 0.45, ~100); 2-butanol (100, —, <1, 91); 2-methyl-1-propanol (108, —, <1, 92); 2-methyl-2-propanol (83, —, 17/10C, 69); benzyl alcohol (205, 110, 0, 93); cyclohexanol (161, —, 0, 98); 2-methoxyethanol (124, 108, 0.3, 97); 2-(2-methoxyethoxy) ethanol (193, 114, 0, 80); ethylene glycol (197, 118, 0, 93); diethylene glycol (245, 117, 0, 88); 2-chloroethanol (129, 110, 0.8, 90); acetic acid (118, 110, 16/10C, 83); propionic acid (141, 118, <<1, 90) and 2-hydroxyethyl acetate (186, 102, 0, 78). Methyl oleate was insoluble in ethylene glycol, diethylene glycol and 2-hydroxyethyl acetate resulting in two phase systems.

#### Catalytic Reduction

**Ozonization in 2-Methoxyethanol.** A. 10% Pd/C: Methyl oleate was ozonized in 2-methoxyethanol as in the previous example. Reduction was accomplished by adding 0.1 g 10% Pd/C and bubbling hydrogen through at 15–20°C and atmospheric pressure. Reduction was complete when an aliquot gave negative peroxide test with potassium iodide in acetic acid. The reduced material was filtered through diatomaceous earth, and the filter cake and reaction flask were washed with two 250 ml portions of methylene chloride. The combined filtrates were washed with water to remove 2-methoxyethanol and after drying, the solvent was removed on a rotary evaporator under reduced pressure at <25°C. Carbonyl yield was 75%.

B. Lindlar Catalyst: Reduction of an ozonized solution of methyl oleate in 2-methoxyethanol was accomplished by using 1.5 g of Lindlar (6) catalyst (10 weight percent of original methyl oleate) and bubbling hydrogen through at 10–15°C and atmospheric pressure. When the peroxide test was negative, the reaction mixture was filtered through diatomaceous earth and the filter cake and reaction flask were washed with 500 ml of methylene chloride. The combined filtrates were washed with two 100-ml portions of 10% HCl to remove CaCO<sub>3</sub> dissolved from the catalyst. Acid washes were followed by water washes to remove excess HCl before drying. The solvent was removed in a rotary evaporator and carbonyl yield was 76%, with 15% of the double bonds being converted to free acid.

**Ozonization in 2-Methoxyethanol with Other Solvents Added and 10% Pd/C Reduction.** A. With 10% Pyridine Added: Methyl oleate (15.0 g, 0.051 mole) was ozonized in 2-methoxyethanol (242.0 g) and pyridine (28.0 g). Ozone uptake was 121% of theory. Reduction was carried out over 0.1 g 10% Pd/C while bubbling hydrogen through reaction mixture at ambient temperature and atmospheric pressure until a neutral peroxide test was obtained. The reaction mixture was treated as in the preceding examples, and the carbonyl yield was 68%. The double bond also underwent a 23% conversion to free acid.

B. With Acetic Acid Added: Methyl oleate (30.0 g, 0.102 mole) was ozonized in 2-methoxyethanol (250.0 g) and acetic acid (250.0 g) as in first example. By using 0.6 g 10% Pd/C and a hydrogen flow of ~300 liters/hr at 15°C, reduction was completed in less than 1 hr as shown when an aliquot gave a negative peroxide test. After filtration through diatomaceous earth to remove any catalyst, the product was dissolved in

500 ml of methylene chloride and 500 ml of water were added. Sodium bicarbonate (350 g) was slowly added to this mixture to neutralize the acetic acid. The methylene chloride layer was then washed with water until neutral to acid-alkali test paper. After drying, solvent was removed in a rotary evaporator, and the product was distilled. The carbonyl yield was 98%, and overall recovery of methyl azelaaldehyde (16.66 g) was 97.0% of theory.

The procedures outlined were applied to each of the other alcohols investigated, and results are summarized in Table I.

### Analysis

#### Gas-Liquid Chromatographic Analysis

The gas-liquid chromatographic (GLC) analysis was carried out on an F & M Model 500 gas-liquid chromatograph equipped with a ¼ x 48-in. looped copper column packed with 20% SF-96 on 60–80 Chromosorb W. Column oven was programmed from 100–285°C at 7.9°C/min with a carrier gas flow of 60 cc/min. The injection port temperature was 220°C; block temperature, 335°C; and bridge current, 150 ma.

#### Determination of Free Acid

A 0.6049 g aliquot of the isolated aldehydic material (19.9 g) from an ozonization of methyl oleate in 2-methoxyethanol/pyridine system was titrated to pH 7 with 0.1N sodium hydroxide using a Beckman Zeromatic pH meter. The aliquot contained 0.526 meq of acid, corresponding to an 18.3% conversion of double bond to free acid in the original sample.

Another sample (25.0 g) of isolated aldehydic material from an ozonization of methyl oleate in 2-methoxyethanol-pyridine was dissolved in methylene chloride. The methylene chloride solution was extracted with saturated NaHCO<sub>3</sub> to remove the free acids. The pH of water layer was then adjusted to the methyl orange end point with concentrated HCl and the free acids were extracted with diethyl ether. After removing the ether, a GLC analysis of the residue was compared to a mixture of known free acids. Pelargonic acid and methyl hydrogen azelate were the main components found.

#### By-Product Ratio

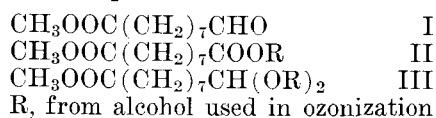
To the isolated aldehyde mixture obtained from ozonization of 15.0 g of methyl oleate was added 0.2825 g of GLC pure dimethyl azelate (DMA) to function as an internal standard for analysis. Peak areas for methyl azelaaldehyde (I), the mixed ester (II), and acetal (III) were converted to moles by means of

TABLE I  
Percent Carbonyl Yields in Various Solvent Systems

Solvent	Chemical reduction	Carbonyl yields		
		Solvent alone	Alcohol + 10% pyridine	Alcohol + propionic acid 1:1 molar
Methanol	93	84	91	94 <sup>a</sup>
Ethanol	100	80	91	97 <sup>a</sup>
1-Propanol	100	85	93	97 <sup>a</sup>
2-Propanol	95	75	—	83
1-Butanol	100	84	92	97 <sup>a</sup> , 97
2-Butanol	91	79	—	87
2-Methyl-1-propanol	92	84	—	82
2-Methyl-2-propanol	69	66	—	79
Benzyl alcohol	93	79	—	97 <sup>a</sup> , 98
Cyclohexanol	98	81	—	89
2-Methoxyethanol	97	74	70	97 <sup>a</sup>
Acetic acid	83	62	—	—
Propionic acid	90	83	—	—

<sup>a</sup> Acetic acid substituted for propionic.

proper correction factors for recovery and known amount of DMA present.



Compounds II and III were the principal by-products encountered.

Correction factors, arbitrarily based upon assumed complete recovery of DMA, were calculated for I, II, III and methyl oleate by running standards of these compounds mixed with DMA in known weight ratios. By dividing known weight percent by GLC area percent, correction factors were obtained. Table II contains representative correction factors for one system and one set of conditions. Any peak area A (any GLC peak) is converted to moles A by Equation 1:

$$\frac{\text{Area} \times \text{correction factor}}{\text{x wt DMA}} = \text{Mole A} \quad (1)$$

Molecular wt A x area DMA

The by-product ratio is then calculated by Equation 2:

$$\frac{\sum \text{Moles of by-product}}{\sum \text{Moles of aldehyde material}} = \text{By-product ratio} \quad (2)$$

The carbonyl conversion is obtained from the by-product ratio by means of Equation 3:

$$100/(1 + \text{By-product ratio}) = \text{Carbonyl conversion} \quad (3)$$

#### Corrected Carbonyl Yields

Carbonyl yields were determined by the hydroxylamine hydrochloride method, after correction for unreacted C<sub>18</sub> methyl ester (Equation 4).

$$\frac{\text{ml NaOH} \times N \times \text{grams aldehyde material} \times 148}{\text{Grams sample} \times \text{grams methyl oleate reacted}} = \text{Corrected carbonyl yield} \quad (4)$$

Weight of C<sub>18</sub> methyl ester reacted was determined by using GLC and Equation 1. GLC analyses for methyl azelaaldehyde conversion and wet analyses for total carbonyl conversion agreed within an experimental error of  $\pm 1\%$ .

#### Discussion

Criegee (1) has postulated the existence of a zwitterion,  $\text{>CH}^{\oplus}\text{OO}^{\ominus}$ , and a carbonyl,  $\text{>C=O}$ , as inter-

mediates in the ozonization of an olefin. The zwitterion can undergo several different and competitive reactions. With a nonparticipating solvent, such as pentane-hexane, ozonides and either dimeric or polymeric peroxides may form. In participating solvents, such as methanol, alkoxy hydroperoxides are formed; in one such as acetic acid, acyloxy hydroperoxides may be formed as well as ozonides or polymeric peroxides. This Laboratory (10-12) has reported that the reactive participating solvent, methanol, gave the highest yields of aldehydes from the ozonization of methyl oleate. Aliphatic primary alcohols higher than methanol, secondary alcohols, acetic acid and propionic acid gave lower yields. Presumably, the lower yields result from formation of other than alkoxy or acyloxy hydroperoxides. The reaction of the zwitterion

with methanol apparently occurs at a much greater rate than with the other species present. In other participating solvents, the reaction rates of all species are more nearly equal.

In an effort to find a participating solvent that does not have the disadvantages of methanol but is as reactive, several hydroxy compounds were selected for evaluation. Bases of selection were either ionization constants comparable to that of methanol or predicted structural effect of substituents on the ionization constant of the alcohol. Other compounds were chosen to complete a series (i.e., aliphatic alcohols).

In the solvents investigated ozone consumption was always below the limit of 120% established as allowable for a good solvent. Solvents with boiling points lower than 100C generally showed solvent losses of greater than 1%/hr under the conditions of ozonization. Solvent losses in excess of 1%/hr are considered too large for an ideal solvent; however, a solvent was not dropped from the investigation because of high volatility alone.

Some solvents failed to dissolve sufficient methyl oleate, and in the resulting two-phase systems too large an amount of ozone passed through the reactor without being consumed. Although the ozonolysis products were somewhat soluble in these solvents, the chemical reduction in ethylene glycol and diethylene glycol was very slow at reduction temperatures of 20-25C. Reduction proceeded smoothly at 40C, but acetal formation occurred as a major side reaction. Lower yields in diethylene glycol, 2-hydroxyethyl acetate and 2-(2-methoxyethoxy)ethanol are thought also to result from structural configuration of the alkoxy hydroperoxide (see discussion and Equation 6 below). For these various reasons, ethylene glycol, diethylene glycol, 2-hydroxyethyl acetate and 2-(2-methoxyethoxy)ethanol were discarded in favor of more suitable solvent systems.

For chemical reduction, no overall trend was detected for a correlation of yield with structure or predicted reactivity of the solvents. Carbonyl yields ranged from 91-100% for all alcohols investigated, except 2-methyl-2-propanol, which gave carbonyl yields of only 69%. This lower yield results probably from steric factors associated with this tertiary alcohol.

When reduction was carried out catalytically, carbonyl yields were much lower, ranging from 66 to 86%. As with chemical reduction, no overall trend was detected for a correlation of yield to structure or reactivity of solvent used. There are two values which should be mentioned as exceptions: the yields in 2-methyl-2-propanol and 2-methoxyethanol, which were quite low. As with chemical reduction, steric effects can be used to explain the low yield in 2-methyl-2-propanol. Evidently, compared to good results by chemical reduction, low yields by catalytic hydrogenation in 2-methoxyethanol are due to the structural configuration of the alkoxy hydroperoxide.

Because pyridine (11) reportedly improved yields when used during ozonization and reduction in methanol, it was tried at a 10% level in several of the primary alcohols, and carbonyl yields were raised to

TABLE II  
Correction Factors for GLC Analysis Compared to Dimethyl Azelate

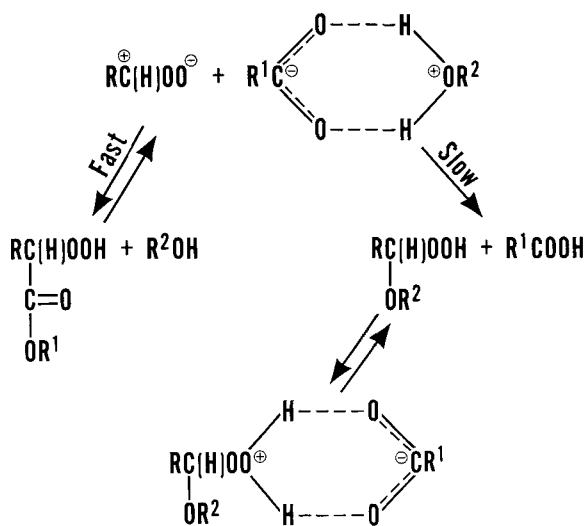
Methyl oleate	1.36
Methyl azelaaldehyde	1.15
Methyl azelaaldehyde	
di(2-methoxyethyl) acetal	1.96
Methyl 2-methoxyethyl azelate	1.14

90–94%. With 2-methoxyethanol, however, the carbonyl yield was only 69% and free acid was formed. The same low yields were obtained when Lindlar catalyst (6, 11, 12), a poisoned Pd/CaCO<sub>3</sub>, was used with 2-methoxyethanol.

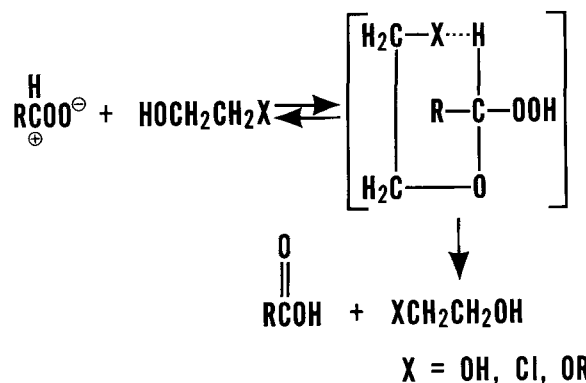
A possible source of free acid might be from the hydrolysis of the 2-methoxyethyl esters formed, under the basic conditions, during reduction. By structural consideration it would appear that these esters could be easily hydrolyzed owing to predicted neighboring-group participation of the ethereal oxygen in the alcohol portion of the ester. The reaction medium is basic, owing to pyridine or CaCO<sub>3</sub> from Lindlar catalyst, and contains water resulting from the reaction in which esters are formed from the alkoxy hydroperoxide. A sample of 2-methoxyethyl pelargonate was carried through a series of steps duplicating conditions found during ozonization, reduction and isolation. No free acid resulted. Evidently the ester is not a precursor of the acid.

The use of an alcohol of similar size, 1-butanol, in place of 2-methoxyethanol yielded no free acid in the presence of pyridine or Lindlar catalyst. Therefore, it was postulated that the ethereal oxygen in the 2-position was involved in the breakdown of the alkoxy hydroperoxide leading to formation of free acid under basic conditions. In an attempt to substantiate the role of the ethereal oxygen, acetic acid was substituted for pyridine. The acetic acid was added to protonate the ether oxygen so that it would no longer be available for hydrogen bonding. The resulting yields were better than those obtained when 2-methoxyethanol was used by itself, and no free acid was formed.

Experiments with acetic acid were carried out to determine the conditions giving the best yields of carbonyl compounds. When 7 mole % of acetic acid (based on moles of 2-methoxyethanol) was present during reduction only, carbonyl yield increased from 74 to 81%. When the same amount was present both during ozonization and reduction, the yield was 86%. The mole percent of acetic acid was varied to determine the optimum ratio of acid to alcohol (Fig. 1). An apparent maximum occurred at a 1:1 molar ratio. Overall yields of 98% were realized when an equimolar solution of acetic acid and 2-methoxyethanol was used for both the ozonization and reduction steps. When a stronger acid such as formic was substituted for acetic, no improvement in yield of carbonyl was



EQUATION 5: Formation of a protonated alkoxy hydroperoxide in acid-alcohol solvents.



EQUATION 6: Hydrogen-bridged intermediate leading to acid formation.

found over that with the same level of acetic acid; however, acetal formation was more pronounced. Substitution of propionic acid for acetic gave yields comparable to those obtained with acetic.

When 1-butanol and other simple primary alcohols were used in equimolar mixtures with either acetic or propionic acid comparable yields (94–98%) were obtained (Table I).

An explanation for the exceptionally high yields obtained in an equimolar mixtures of alcohol and acid can be developed based on the reactions possible in the solvent cage. The alcohol and acid are probably present in an associated form. During ozonization, the reaction of the zwitterion with the acyl portion of the solvent may be fast but reversible and would serve to stabilize the zwitterion until reaction with the alcohol portion could occur in a probably slow but irreversible manner (Equation 5). During catalytic hydrogenation, the alkoxy hydroperoxide in its associated form with the acid would give heterolytic cleavage of the peroxidic oxygen bond. Heterolytic cleavage was the explanation previously given for improved yields when hydrogenation was carried out in the presence of pyridine (11). In the absence of pyridine, homolytic cleavage could occur on the catalyst surface. Homolytic cleavage to  $\text{RC(H)(OR}^2\text{)O}\cdot$  and  $\cdot\text{OH}$  was postulated as the origin of the by-product ester  $\text{RCOOR}^2$ .

The data obtained with 2-methoxyethanol explain some of the other lower yields when solvents of the same type (ethylene glycol, diethylene glycol, 2-hydroxyethylacetate, 2-(2-methoxyethoxy)ethanol and possibly 2-chloroethanol) were used. Each of these solvents has a substituent in the 2-position which has electrons available for hydrogen bonding. The structure of the postulated alkoxy hydroperoxide from these solvents can easily assume a six-member ring as in Equation 6. Present data point to this structure

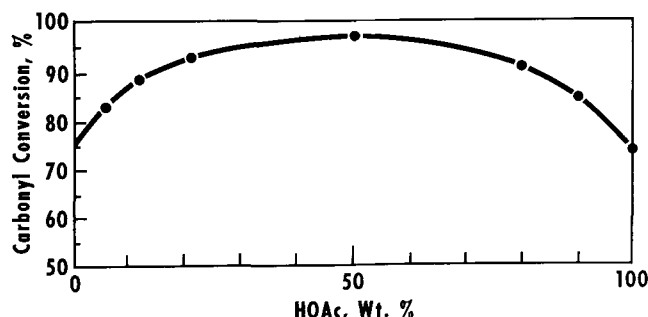


FIG. 1. Carbonyl conversions in mixtures of 2-methoxyethanol and acetic acid.

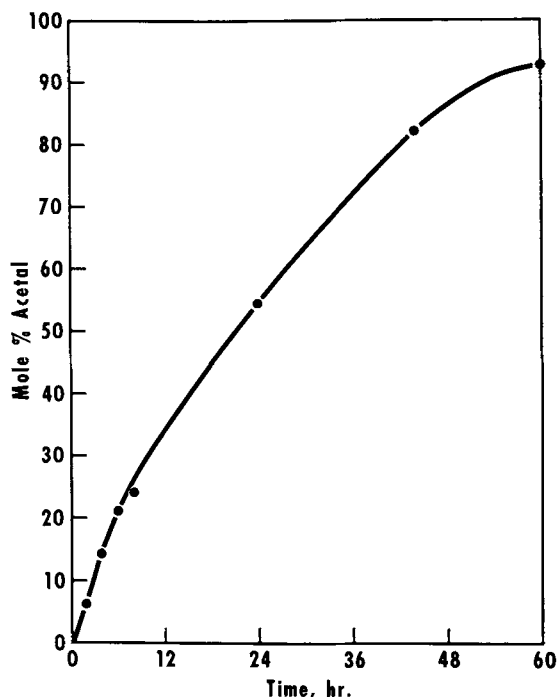


FIG. 2. Formation of methyl azelaaldehyde acetal as a function of time at room temperature.

as being the source of the free acids found under basic conditions during catalytic reductions.

In the mixed solvent system of acid and alcohol, there is an apparent correlation between structure and carbonyl yield based upon steric effects. As the alkoxy hydroperoxide becomes more hindered, the yield decreases from 98% for the simple primary alcohols to 79% for 2-methyl-2-propanol. The yield in 2-methyl-2-propanol/propionic acid is higher (79%) than either chemical or catalytic reduction in the alcohol alone (66–69%). No reason for the magnitude of this enhanced yield is evident.

TABLE III  
Effect of Hydrogenation Conditions in 1:1  
2-Methoxyethanol/Glacial Acetic Acid

Temp., C	Catalyst concn., <sup>a</sup> Pd g/mole	Hydrogen flow, liters/hr	Reduction time, hr	Methyl azela- aldehyde recovered, %
25–30	0.176	30	3 ½	79
25–30	0.588	300	< ¾	86
10–15	0.588	300	< ½	98

<sup>a</sup> Catalyst concentration based upon initial amount of double bond.

In the study of the alcohol/acid solvent system, three new variables affecting the yield of carbonyl by catalytic hydrogenation were found: temperature of reduction, catalyst concentration and hydrogen flow. As the temperature is lowered, the acetal formation is lowered; but ester formation is somewhat increased. By combining both increased catalyst concentration and hydrogen flow with lower temperatures, the formation of esters and reduction time decrease considerably. The time of free aldehyde contact with the solvent system is also decreased. Table III summarizes some results obtained when these factors were varied. Our best conditions for obtaining pure aldehyde free from acetal and ester in this alcohol/acid solvent system are reduction at 10–15°C with a hydrogen flow  $\approx$  300 liters/hr (finely dispersed) and a catalyst concentration of 1 g Pd metal per 1.7 mole of unsaturation. Under these conditions, yields of methyl azelaaldehyde of 98% of theory were realized.

As this investigation proceeded, it became evident that the yield of aldehyde, free of acetal, became less as the solubility of the alcohol in water decreased. Detailed analysis of this problem led to the discovery that acetal was being formed during drying of the aldehyde. When methyl azelaaldehyde stood at room temperature in presence of 1-butanol, methylene chloride, and Drierite, the conversion to acetal was pronounced. Figure 2 gives data for change in acetal content (GLC) with time. For maximum yields of free aldehydes, the drying step should be eliminated if alcohol is present. This route to acetals also allows their preparation from carbonyl compounds that are sensitive to acid or heat.

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#### REFERENCES

1. Criegee, R., *Record Chem. Progr. (Kresge-Hooker Sci. Lib.)* 18, 110–120 (1957).
2. Fischer, F. G., H. Düll and L. Ertel, *Ber.* 65B, 1467 (1932).
3. Harries, C., *Ibid.* 39, 3728 (1906).
4. Harries, C., and C. Thieme, *Ibid.* 39, 2844 (1906).
5. Jones, E. P., and V. L. Davison, *JAOCs* 42, 121–126 (1965).
6. Lindlar, H., *Helv. Chim. Acta* 35, 446–450 (1952).
7. Molinari, E., and E. Soncini, *Ber.* 39, 2735 (1906).
8. Noller, C. R., and R. Adams, *JAOCs* 48, 1074 (1926).
9. Otsuki, H., and H. Funahashi, *Japan Patent* 8417 (1954); U.S. Patent 2,862,940 (1958).
10. Pryde, E. H., D. E. Anders, H. M. Teeter and J. C. Cowan, *J. Org. Chem.* 25, 618 (1960).
11. Pryde, E. H., D. E. Anders, H. M. Teeter and J. C. Cowan, *Ibid.* 27, 3055 (1962).
12. Pryde, E. H., R. A. Awl and J. C. Cowan, *JAOCs* 42, 549–553 (1965).
13. Stoll, M., and H. Rouvé, *Helv. Chim. Acta* 27, 950 (1944).

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