indication of contamination by the low-melting (33°) stereoisomer.

Nitration of Other Arylalkenes.—The remaining arylalkenes mentioned in the text were nitrated according to the general nitration procedure,[3] using several drops of sulfuric acid as a catalyst. The products were separated by chromatography and purified in much the same manner as in the examples already given. The results are summarized in Table I.

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Selective Hydrogenation of Methyl Oleate Ozonolysis Products by Palladium in Pyridine–Methanol Solvent[1]

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Decomposition of the ozonolysis products formed by ozonization of methyl oleate in methanol gave dimethyl azelate as a major by-product when reductive decomposition to aldehydes was carried out by hydrogenation over palladium on charcoal. The presence of pyridine during hydrogenation resulted in significantly reducing the amounts of dimethyl azelate and other by-products formed and poisoned the catalyst for hydrogenation of olefinic unsaturation. Thus, yield and purity of aldehyde ester were improved and unused methyl oleate could be recovered. Hydrogenation was under ambient conditions. Reaction mechanisms are suggested that explain the contrasting results obtained with certain nonreactive solvents.

Catalytic hydrogenation of ozonolysis products to produce aldehydes has never given yields comparable to those obtained by reduction with zinc and acetic acid or similar reducing agents.[3–7] In none of these investigations was a reactive solvent (*e.g.* methanol)[8] used in the ozonization step. We have reported on the superior yields of methyl azelaaldehydate obtained by ozonization of methyl oleate in methanol as compared to those obtained in nonreactive solvents.[9] However, catalytic hydrogenation over palladium on charcoal still gave low yields even when methanol was used in both ozonization and reduction steps. Use of a reactive solvent in both steps has been described in the patent literature, and, where reported, the yields were low (54%).[10–12]

We have now discovered that the presence of pyridine improves the yield of methyl azelaaldehydate substantially when the ozonolysis products are hydrogenated. The effect of pyridine on the course of ozonolysis has been described previously,[13–15] but its effect during catalytic hydrogenation has not. In our experiments with methanol–pyridine, the pyridine reduced the amounts of dimethyl azelate and other by-products formed, poisoned the catalyst for hydrogenation of olefinic unsaturation, and prevented acetal formation. Thus, yield and purity of aldehyde–ester were improved and unused olefinic ester could be recovered. We believe that this technique will also be of considerable value in preparing unsaturated aldehydes by partial ozonization of polyunsaturates (now under investigation at this laboratory) and in reducing hydroperoxide compounds in general without hydrogenation of olefinic unsaturation.

Results of this technique are illustrated by chemical and gas-liquid chromatographic (GLC) analyses of the product solutions after hydrogenation, as well as of the isolated products. Chemical analyses by oximation on the product solutions were possible only in the absence of pyridine, and these indicated 75% conversions to carbonyl compounds. (In contrast, 93% conversions were obtained when reduction was carried out with zinc and acetic acid).[11] GLC analyses were possible on product solutions both with and without pyridine present (Table I).

Three major and two minor peaks were found for the bifunctional portion of the products. The major peaks were identified as methyl azelaaldehydate, its dimethyl acetal (which was resolved from methyl azelaaldehydate only at a lower column temperature), and dimethyl azelate. The

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(1) Presented before Division of Organic Chemistry, American Chemical Society Meeting, Chicago, Illinois, September 7, 1961.

(2) One of the laboratories of the Northern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

(3) F. G. Fisher, H. Düll, and L. Ertel, *Ber.*, **65B**, 1467 (1932).

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(6) M. Stoll and A. Rouvé, *Helv. Chim. Acta*, **27**, 950 (1944).

(7) R. Lukes and J. Kovar, *Chem. Listy*, **50**, 272 (1956).

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(9) E. H. Pryde, D. E. Anders, H. M. Teeter, and J. C. Cowan, *J. Org. Chem.*, **25**, 618 (1960).

(10) E. E. Fisher, U.S. Patent 2,733,270, January 31, 1956.

(11) G. W. Rigby, U.S. Patent 2,657,239, October 27, 1953.

(12) A. S. Carpenter and F. Reeder, British Patent 743,491, January 18, 1956.

(13) F. W. Heyl, A. P. Centolella, and M. E. Herr, *J. Am. Chem. Soc.*, **69**, 1957 (1947).

(14) G. Slomp, Jr., and J. L. Johnson, *ibid.*, **80**, 915 (1958).

(15) R. B. Bates, E. J. Eisenbraun, and S. M. McElvain, *ibid.*, **80**, 3420 (1958).

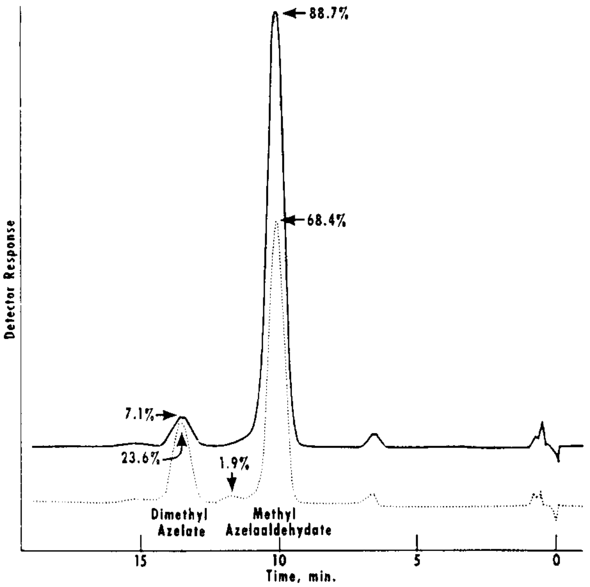

Fig. 1.—Gas-liquid chromatogram of methyl azelaaldehydate fractions obtained from methanol (......) or from pyridine–methanol (———) solvents.

TABLE I

GAS-LIQUID CHROMATOGRAPHIC ANALYSES ON PRODUCT SOLUTIONS (COLUMN TEMPERATURE 165°)

Reaction conditions		GLC analyses, area per cent			
Pyridine concentration, wt. %	Catalyst g./g. methyl oleate, $\times 10^3$	Methyl azelaaldehydate	Dimethyl azelate	Unknown No. 1	Unknown No. 2
0	2.0	80.2	14.2	1.4	4.2
0	40.0	78.9	14.0	2.0	5.1
1	1.7	85.7	8.7	1.4	4.2
10	7.4	92.6	3.2	1.3	2.9

two minor peaks were unidentified. The first three are C_9 compounds and total about 94% of the product. Hence, not more than about 6% chain degradation occurred as a result of carrying out ozonization and hydrogenation in the reactive solvent methanol. Excessive formation of dimethyl azelate was the principal cause for poor yields of methyl azelaaldehydate. Because the presence of pyridine during hydrogenation minimized this formation, improved yields of methyl azelaaldehydate were obtained. Over-ozonization was not the cause of dimethyl azelate formation, since ozone consumption was the same as that in experiments in which reduction was with zinc and acetic acid. Ozone consumption is normally 115–120% of theory as a result of some attack of ozone on the methanol.

For the most part, analyses were made on the isolated product, on which both chemical and GLC analyses were possible. Isolation of the methyl azelaaldehydate product was accomplished by fractional distillation under vacuum and by collection of the fraction boiling over a range of about 10°. The dimethyl azelate could not be separated from methyl azelaaldehydate by the type of fractional distillation employed. Identical procedures were followed for all experiments, except where noted in Table II, and the methyl azelaaldehydate fraction gave an average of 80% of crude product, calculated as methyl azelaaldehydate. Ozonization on a larger scale than the 0.07 molar scale given in Table II resulted in higher (92%) yields of distilled products. Since we did not separate dimethyl azelate from methyl azelaaldehydate in most of these experiments, the actual yields of methyl azelaaldehydate must be calculated from the purity and yield of crude distilled product.

Analytical results for the isolated products are given in Table II. Chemical analysis by oximation confirmed GLC analyses for the higher purity obtained in the presence of pyridine. In general, chemical analyses gave higher results than indicated by GLC analyses. However, the total of the aldehyde ester, its acetal, and unknown as determined by GLC agreed fairly well with the results obtained by oximation, indicating that the unknown may have an aldehyde functionality. The unknown was not isolated in sufficient quantity for identification. In the absence of pyridine, dimethyl azelate content of the isolated product was 22–24%. When 1% pyridine was present, the dimethyl azelate content was 10%; with 9% pyridine, the dimethyl azelate content was about 7% (Fig. 1). Differences in degree of dimethyl azelate formation possibly may result from using one lot of catalyst for experiments in Table I and another lot for those in Table II. Amount of catalyst used had no significant effect (Table I).

Since dimethyl azelate could not be separated from methyl azelaaldehydate for identification purposes by fractional distillation, means for chemically removing the aldehyde ester were sought. The separation was successfully accomplished by forming the pentaerythritol acetal[16] in an essentially quantitative reaction, and distilling dimethyl azelate from the acetal.

Partial ozonization of methyl oleate resulted in good recovery of methyl oleate when from 1 to 9% pyridine was present. However, with 1% pyridine, recovery of methyl oleate was less if the hydrogenation was allowed to continue after the methoxy hydroperoxides were reduced. Apparently reduction of the peroxide and the unsaturation occurred in consecutive processes, rather than simultaneously. Experiments with the hydrogenation of methyl oleate, with no ozonization having been carried out previously, indicated optimum pyridine concentration was about 9% (Table III).

Ozonization in nonreactive solvent combinations, methylene chloride–pyridine and pentane–hexane–pyridine, resulted in low yields of aldehyde products and relatively large quantities of acidic materials. GLC analyses of these indicated chain degradation had occurred. Relatively large

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(16) E. H. Pryde, R. A. Awl, H. M. Teeter, and J. C. Cowan, *J. Org. Chem.*, **25**, 2260 (1960).

TABLE II

ANALYSES OF METHYL AZELAALDEHYDATE FRACTIONS

Experimental conditions				Analyses of methyl azelaaldehydate fractions[a]							Methyl oleate-stearate recovered	
		Pyridine		Chemical analyses, wt. %		GLC analyses, %[b]						
Ozonization solvent	Ozone consumed, % of theory	Present during hydrogenation	Concentration, wt. %	Carbonyl	Acidity[c]	MAZ	MAZ acetal	Dimethyl azelate	Pelargonaldehyde	Unidentified	Per cent of starting material	Methyl oleate content, wt. %
Methanol	114	No	0	74.8	4.8	68.4	1.9	23.6	1.3	4.8	0	
Methanol[d]	117	No	18.0	74.6	3.3	58.8	8.5	22.2	1.4	9.2	0	.
Methanol–pyridine[e]	49	Yes	1.0	...	...	89.8	0	10.1	...	...	54.5	96.4
Methanol–pyridine[f]	45	Yes	1.0	...	...	84.0	0	6.2	0	4.6	56.0	86.2
Methanol–pyridine	118	Yes	9.0	88.3	2.9	88.7	0	7.1	1.1	3.1	0	...
Methanol–pyridine	50	Yes	9.0	90.0	2.6	84.1	0	6.8	2.7	6.4	53	96.0
Methanol–pyridine	118	Yes	90.0	...	...	54.5	...	...	...	21.0	23.5	56.0
Methanol	111	Yes	9.0	89.4	0	72.2	8.8	7.0	3.3	8.6	0	...
Methylene chloride–pyridine[g]	157	Yes	6.0	65.8	37.4	56.6	...	...	1.8	41.6	17	...
Pentane–hexane–pyridine	166	Yes	12.0	46.5	63.5	35.9	...	...	0	64.1	0	...

[a] Average product yield 80%, except for pentane–hexane–pyridine which gave 54% yield. [b] Column temperature, 140°. [c] Calculated as monomethyl azelate. [d] Product solution washed with pyridine and water. [e] Hydrogenated for 2 hr. until peroxide test was negative. [f] Hydrogenated for 2 hr. after peroxide test was negative for a total of 4 hr. [g] Methylene chloride displaced by methanol by distillation before hydrogenation.

TABLE III

EFFECT OF PYRIDINE ON THE HYDROGENATION OF METHYL OLEATE

Pyridine concentration, wt. %	Product		Recovery of methyl oleate, %
	Recovery, wt. %	Specific iodine number[a]	
0	98	0	0
4.5	93	3.01	90
9	98	3.17	95

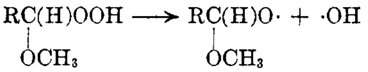
[a] The specific iodine number, N_I, is defined as the number of mmoles of Wijs reagent consumed per gram of sample.[22] For pure methyl oleate $N_I = 3.37$.

amounts of ozone were consumed compared to the ozone consumption in methanol. With methanol, about 1.1 moles of ozone was consumed for each mole of unsaturation whether 2 or 4 moles of pyridine were present. With methylene chloride or pentane–hexane, 1.6 and 1.7 moles of ozone were consumed for each mole of unsaturation when 4 moles of pyridine were present. In pentane–hexane, a second liquid phase, probably pyridine oxide, separated from solution as ozonization proceeded. The second phase did not appear when methylene chloride, a more polar solvent, was used. Recovery of 17% of unchanged methyl oleate from the methylene chloride–pyridine experiment, even at 189% of theory ozone absorption, indicated that pyridine oxide formation was a competing and not a consecutive reaction.

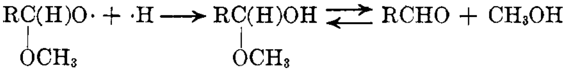
Although the literature indicates that pyridine oxide can by hydrogenated only with difficulty in neutral solution,[17] the two-phase system formed in pentane–hexane was hydrogenated successfully over a 24-hr. period. Several additions of catalyst were required, but the second phase gradually disappeared until a homogeneous solution was once again present, and the test for peroxides was negative. Attempted hydrogenation in methylene chloride solution was unsuccessful, confirming a previous report that methylene chloride inhibited hydrogenation.[4] Consequently, methylene chloride was removed by distillation after addition of methanol, and hydrogenation was done in the methanolic solution.

Reaction mechanisms operating in these two different types of ozonization media are obviously quite different.

For the mechanism involving methanol, the formation of dimethyl azelate may be explained by assuming homolytic cleavage of a methoxy hydroperoxide on the catalyst surface (equation 1). (The methoxy hydroperoxide is formed because of the methanol, a reactive solvent.) Reaction of the cleavage product with atomic hydrogen, or an activated form of the hydrogen on the catalyst surface, would produce an aldehyde as in equation 2. On the other hand, reaction of the cleavage product with a hydroxyl radical would produce the ester (equation 4) in an over-all dehydration reaction.[18]

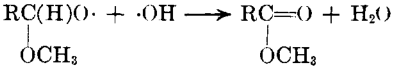


$$\underset{\mathrm{OCH_3}}{\mathrm{RC(H)OOH}} \longrightarrow \underset{\mathrm{OCH_3}}{\mathrm{RC(H)O\cdot}} + \cdot\mathrm{OH} \qquad (1)$$

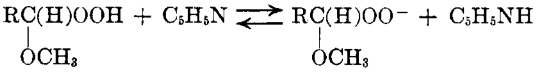


$$\underset{\mathrm{OCH_3}}{\mathrm{RC(H)O\cdot}} + \cdot\mathrm{H} \longrightarrow \underset{\mathrm{OCH_3}}{\mathrm{RC(H)OH}} \rightleftarrows \mathrm{RCHO} + \mathrm{CH_3OH} \qquad (2)$$

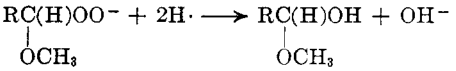
$$\mathrm{H\cdot} + \cdot\mathrm{OH} \longrightarrow \mathrm{H_2O} \qquad (3)$$



$$\underset{\mathrm{OCH_3}}{\mathrm{RC(H)O\cdot}} + \cdot\mathrm{OH} \longrightarrow \underset{\mathrm{OCH_3}}{\mathrm{RC{=}O}} + \mathrm{H_2O} \qquad (4)$$



$$\underset{\mathrm{OCH_3}}{\mathrm{RC(H)OOH}} + \mathrm{C_5H_5N} \rightleftarrows \underset{\mathrm{OCH_3}}{\mathrm{RC(H)OO^-}} + \mathrm{C_5H_5NH^+} \qquad (5)$$



$$\underset{\mathrm{OCH_3}}{\mathrm{RC(H)OO^-}} + 2\mathrm{H\cdot} \longrightarrow \underset{\mathrm{OCH_3}}{\mathrm{RC(H)OH}} + \mathrm{OH^-} \qquad (6)$$

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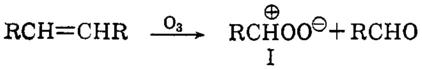
(17) E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).

(18) D. B. Sharp and T. M. Patrick, Jr., *ibid.*, **26**, 1389 (1961).

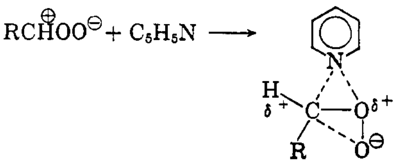
Pyridine may be effective because of association with the hydroperoxide to form a salt, which probably is less subject to homolytic cleavage (equation 5). (A stronger base than pyridine should have even a more pronounced effect, but the aldehydes formed would then be subject to aldol-type condensations.[19]) The hydroperoxide anion then could be reduced to the aldehyde, probably in the form of the hemiacetal (equation 6).

An alternative route involving production of an acid followed by esterification does not seem likely since, under the conditions of ozonolysis, esterification would not proceed to an appreciable extent.

A second mechanism is necessary to explain the results when pyridine is used in the absence of methanol or other reactive solvent. Reportedly, pyridine functions as a reducing agent, forming pyridine oxide, when methylene chloride is the solvent.[14] Our data suggest that this report is not correct, but that relatively stable complexes between pyridine and the ozonolysis products are formed instead. Ozone consumption indicates that at least 1 mole of pyridine remains unaffected by ozone and could be in association with the ozonolysis products or could have reacted with them. If pyridine were the reducing agent, the yield should not be affected by the method of reduction, *i.e.*, chemical or catalytic. We confirmed the good yields obtained by chemical reduction in the presence of pyridine.[14] Our current data illustrate the poor yields obtained by catalytic hydrogenation.

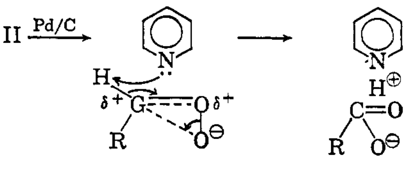


$$\mathrm{RCH{=}CHR} \xrightarrow{\mathrm{O_3}} \underset{\mathrm{I}}{\mathrm{RC\overset{\oplus}{H}OO^{\ominus}}} + \mathrm{RCHO} \qquad (7)$$

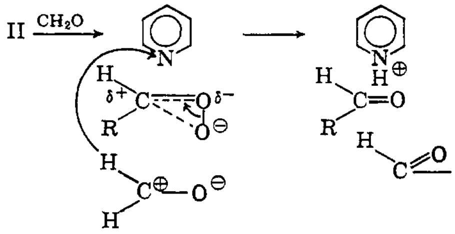


(8)

II



(9)



(10)

Furthermore, aldehydes produced are not affected by the catalyst. Accordingly, a complex such as II formed between the zwitterion (I) postulated by Criegee,[8] and pyridine is suggested. In the presence of a catalyst, pyridine may abstract a proton from the zwitterion complex to form a pyridinium salt (equation 9). In the presence of a chemical reducing agent, like formaldehyde, pyridine abstracts a proton from the reducing agent to form pyridinium formate and an aldehyde (equation 10).

The lack of pyridine oxide formation in methanol under the conditions of the reaction strongly suggest that an addition complex between the pyridine (not associated with the zwitterion) and the solvent is formed. A recent report has indicated that intramolecular hydrogen bonding in OH—N is even stronger than OH—O.[20]

Experimental

Gas-Liquid Chromatography.—A Pye-Argon[21] chromatographic analyzer with a radium D ionization detector and an integrator was used. The column was 4 ft. × 1/4 in. glass tubing packed with 10% Craig polyester succinate on Chromosorb W 60/80 mesh. The volume injected was 0.1 μl., temperature 140°, pressure drop approximately 315 mm., gas flow 50 cc./mm. Relative retention volumes for the compounds involved in this paper are as follows: methyl azelaaldehydate, 1.00; methyl azelaaldehydate dimethyl acetal, 1.14; dimethyl azelate, 1.32.

Representative GLC analyses are given in Fig. 1.

Ozonization Procedures.—The general procedure employed for ozonization has been described previously in some detail.[9] For all the experiments summarized in Table II, two will illustrate the advantages of carrying out ozonization and catalytic hydrogenation in the presence of pyridine. A third will describe partial ozonization.

Ozonization and Reduction in Methanol.—Methyl oleate (obtained from Applied Science Laboratories, I.V. 85.3, n^{30}_D 1.4483), 20.8 g. (0.07 mole of unsaturation), was dissolved in 250 ml. of absolute methanol. Oxygen containing 0.915 mmole of ozone per liter of oxygen was passed through the solution at the rate of about 2.12 l./min. for 42.5 min. at room temperature. The end of the reaction was determined by a Welsbach ozone meter. The amount of unreacted ozone passing through the reactor was 3.5% of the ozone theoretically expected to be absorbed by the reaction mixture. The amount of ozone absorbed by the reaction was 114% of theory.

The ozonolysis solution and the reactor flask were flushed with nitrogen, and 0.1 g. of 10% palladium-on-charcoal catalyst was added. Hydrogen was bubbled through the solution for 90 min. at atmospheric pressure and room temperature. At the end of this time, a solution of potassium iodide in glacial acetic acid gave a negative test for peroxide. The product solution was filtered, and 10-ml. aliquots were taken for carbonyl analysis (by the hydroxylamine hydrochloride method). The filtrate contained 106 mmoles of carbonyl for a conversion of 76% of aldehydic products before isolation. Our previous work with reduction by zinc and acetic acid had shown that conversions of aldehydic products before isolation were of the order of 93%.[9]

Solvent was removed from the aldehydic products by distillation on a steam cone under a slight vacuum, and the

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[19] Preliminary work by Mr. R. A. Awl of this laboratory indicates that almost equally good results can be obtained by the use of Lindlar catalyst or by impregnating the catalyst support with sodium hydroxide.

[20] H. H. Freeman, *J. Am. Chem. Soc.*, **83**, 2900 (1961).

[21] Mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

[22] J. S. Showell, *J. Am. Oil Chemists' Soc.*, **36**, 343 (1959).

residue distilled under reduced pressure through a 1 in. × 6 in. column packed with 3 mm. i.d. glass helices. From 20.8 g. of methyl oleate, two main fractions were recovered: A pelargonaldehyde fraction (8.09 g., 81%) boiling 94–103° (25 mm.), $n^{30}\text{D}$ 1.4185, purity 71% by the hydroxylamine hydrochloride method; and a methyl azelaaldehydate fraction (10.49 g., 80%) boiling 94–106° (0.28 mm.), $n^{30}\text{D}$ 1.4340 (lit., $n^{20}\text{D}$ 1.4384), and having a purity of 75% by the hydroxylamine hydrochloride method, 68.4% by GLC.

Ozonization and Reduction in Methanol–Pyridine.—Methyl oleate (20.8 g., 0.07 mole of unsaturation) was dissolved in a solution of 250 ml. of absolute methanol and 22.8 g. (0.28 g. mole) of pyridine. Oxygen containing 0.966 mmole of ozone per liter of oxygen was passed through the solution at the rate of approximately 2.41 l./min. for 36 min., at room temperature. The amount of unchanged ozone was 1.23 mmoles, amounting to 1.8% of the absorption theoretically expected. The amount of ozone absorbed was 118% of theory. The ozonolysis solution and the reactor flask were flushed with nitrogen, and 0.1 g. of 10% palladium-on-charcoal catalyst was added. Hydrogenation was carried out for 100 min. at room temperature and atmospheric pressure. The solution was filtered and the methanol removed by distillation on a steam bath under a slight vacuum. The temperature was kept as low as possible during distillation to reduce the possibility of aldol condensation because of the basic compound pyridine. The possibility of condensing the aldehydes was minimized in other experiments by washing the reduced solution with dilute hydrochloric acid, extracting the aldehydic products in methylene chloride, and washing with water until free of acid. The residue was distilled under reduced pressures through a 1 in. × 6 in. glass helices-packed column, and two main aldehydic fractions were collected. The pelargonaldehyde fraction (7.34 g., 74%) boiling 94–96° (22 mm.), $n^{30}\text{D}$ 1.4189, had a chemical purity (by the hydroxylamine hydrochloride method) of 82%. The methyl azelaaldehydate fraction (10.02 g., 76%) boiling 97–100° (0.34 mm.), $n^{30}\text{D}$ 1.4346, had a chemical purity 88.3% and a GLC purity of 88.7%.

Addition of pyridine after ozonization but before reduction reduced dimethyl azelate formation but gave no appreciable increase in aldehyde ester because acetal formation was not prevented. Use of pyridine after reduction in the wash solution had no beneficial effect. Accordingly, pyridine was not effective in washing out by-products.

Ozonization was also carried out on a larger scale to reduce the relative proportion of handling losses. Methyl oleate (148.25 g., 0.50 mole) was dissolved in 700 ml. of absolute methanol containing 5 ml. of pyridine (1% by weight of the solvent). Oxygen containing 0.98 mmole of ozone per liter of oxygen was passed through the solution at the rate of about 2.57 l./min. for 241 min. The amount of ozone passing through the solution was 1.7% of the absorption theoretically expected, and the amount of ozone absorbed was 120% of theory. Hydrogen was bubbled through the solution at a rate of about 2.3 l./min. with 0.25 g. of 10% palladium on charcoal present. When the solution temperature reached 35° as a result of the exotherm, the reaction flask was immersed in a water bath to maintain the solution temperature at about 25°. After 4 hr. the peroxide test was negative. GLC analysis of this solution showed the following relative composition of the high-boiling constituents: methyl azelaaldehydate, 85.7%; dimethyl azelate, 8.7%; unknowns, 5.6% (Table I). The solution was filtered and distilled through a Vigreux column under vacuum on a water bath at 35°. Methylene chloride was added to the residue, and the solution was washed with 1 *N* hydrochloric acid to remove pyridine then with water until neutral. Each wash was backwashed three times. Isolation of the products by distillation gave 85.5 g. (91.8%) of a fraction boiling 85–105° at 0.15 mm. GLC analysis of this fraction indicated it to contain 79.6% methyl azelaaldehydate and 10.8% dimethyl azelate. No acetal was detected. Thus, pyridine at the 1% level was effective in eliminating acetal and lowering dimethyl azelate content to a considerable extent.

Redistillation of this fraction through an 8 mm. × 60 cm. concentric tube column at 0.4 mm. and with a 50:1 reflux ratio gave 41% of a fraction having a methyl azelaaldehydate content of 92% and a dimethyl azelate content of about 7%. A 23% loss of product resulted from condensation or polymerization reactions which occurred in the distillation pot during the prolonged heating period.

Partial Ozonization and Reduction in Methanol–Pyridine.—Methyl oleate (148.25 g., 0.50 mole) was dissolved in 540 g. of methanol and 60 g. of pyridine. Ozonization was carried out as before except that the reaction was stopped at the half-way point. The solution was flushed with nitrogen and hydrogen, 0.3 g. of 10% palladium on charcoal dispersed in methanol was added, and hydrogen was bubbled through the solution for 4 hr. until the peroxide test was negative. After standing overnight under a hydrogen atmosphere, the solution was filtered and distilled through a Vigreux column under vacuum on a water bath at 35° to remove methanol. The residue was dissolved in methylene chloride, and this solution was washed with 2 *N* hydrochloric acid until free of pyridine then with water until neutral. Each wash was backwashed three times. Distillation through a 1 in. × 6 in. glass helices-packed column gave 34.5 g. (48.6% conversion, 89.6% yield) of pelargonaldehyde boiling 66–74° at 8 mm., 46.1 g. (49.6% conversion, 91.6% yield) of methyl azelaaldehydate boiling 76–82° at 0.07 mm., and 68.0 g. (45.9% recovery) of methyl oleate boiling 116–140° at 0.05 mm. GLC analyses of the methyl azelaaldehydate fraction indicated a methyl azelaaldehydate content of 87.9% and dimethyl azelate content of 6.8%. GLC analysis of the methyl oleate fraction indicated a methyl oleate content of 91.1% and a methyl stearate content of 8.0%. Thus, pyridine at the 10% level was effective in eliminating acetal, lowering dimethyl azelate content and preventing hydrogenation of unozonized unsaturation.

Isolation and Identification of Dimethyl Azelate.—Attempts to separate the dimethyl azelate impurity from the aldehyde ester or its acetal by fractional distillation were unsuccessful. However, the impurity was successfully concentrated and isolated by forming the pentaerythritol acetal of the aldehyde ester acetal. Methyl azelaaldehydate dimethyl acetal[11] of 80.2% purity (100.7 g., 0.35 mole) and pentaerythritol (29.3 g., 0.215 mole) were heated in the presence of potassium acid sulfate. GLC analysis of the dimethyl acetal showed about 16.8 % of the major impurity was present. The reaction product, after washing, was distilled at reduced pressure. There was obtained a fraction (16.6 g.) boiling at 100–150° and 0.5 mm., with the pentaerythritol acetal obtained in subsequent fractions. The 100–150° fraction was redistilled through a Podbielniak spinning band column, and a heart cut (36% of the total) boiling 123–125° was taken for analysis, $n^{30}\text{D}$ 1.4328, $d^{24}{}_{24}$ 1.0029. The dibasic acid obtained upon saponification gave no depression in a mixed melting point determination with azelaic acid.