Tetramethylammonium and Tetrabutylphosphonium Tetraalkylboron Compounds.—Relatively stable derivatives of sodium and lithium tetraalkylboron compounds were prepared in water solutions by reaction with tetramethylammonium or tetrabutylphosphonium bromide (the latter prepared by the method of Grayson and Keough[29] in 91% yield, m.p. 101–103°, lit.[29] m.p. 99–101°). The following derivative preparation is typical. To a solution of lithium tetrabutylboron (5.9 g., 0.024 mole) in 50 ml. of water was added a solution of 3.9 g. (0.032 mole, 33% excess) of tetramethylammonium bromide in 25 ml. of water. A white precipitate was immediately visible. The mixture was stirred for 0.5 hr., filtered, and washed until the washings showed no trace of bromide ion. The resulting solid was dried at 45° (0.1 mm.) for 1 hr. to yield 6.8 g. (91.4% yield) of tetramethylammonium tetrabutylboron, m.p. 106–112° dec. One recrystallization from ether–pentane raised the melting point to 110–112° dec. Table I summarizes our results from the preparation of stable derivatives.

Hydrolysis of Tetraalkylboron Compounds.—Hydrolysis reactions were performed in 100-ml. three-necked flask equipped with an addition funnel, magnetic stirrer, thermometer, and condenser. An outlet from the condenser led to a 100-ml. gas buret. Gases were collected at room temperature over mercury. The reaction flask was immersed in an oil bath maintained at 35 ± 1° or 60 ± 1°. Approximately 1 g. of tetraalkylboron compound was placed in a flask and allowed to equilibrate for 0.5 hr. Water, base, or acid, preheated to 35 or 60°, then was added in approximately 1 min. Zero time was taken immediately after the addition. During the reactions the volume of gas given off was recorded. After the recorded time interval (Table IV), the reaction mixture was neutralized and extracted with ether; the layers were separated. The ether layer was dried over magnesium sulfate and distilled through a 6-in. Vigreux column. After removal of the ether, tridecane was added and the distillation continued under vacuum until the head temperature reached 75° (1 mm.). The distillate was weighed and the amount of dodecane, from either III or IV, was calculated from the gas chromatographic analysis of the mixture.

The gases collected were examined by infrared and mass spectrometry and gas chromatography. Ethane and butane were separated by gas chromatography using either a silica gel column (10 ft., 60°) or an activated alumina column (Woelm, activity I, 10 ft., 70°).

No evidence for any gases except ethane or butane was obtained. Dodecane, triethylborane, and tributylborane were the only liquids isolated and identified.

Oxidation Procedure.—The following procedure for the oxidation of lithium tetrabutylboron with oxygen in tetrahydrofuran is typical.

A 500-ml. three-necked flask, equipped with a condenser, thermometer, gas inlet, and magnetic stirrer, was immersed in a constant temperature (35 ± 1°) oil bath. The outlet from the condenser led to two gas burets, one of 100-ml. capacity and the other of 500-ml. capacity. Dry tetrahydrofuran, 50 ml., was added to the flask and the apparatus, including the burets, was flushed with oxygen for 30 min. Tetrahydrofuran (25 ml.) was withdrawn and 1.0–1.5 g. of lithium tetrabutylboron dissolved in it. The solution was then introduced into the reaction flask and the system was closed to the atmosphere. Stirring was started and samples were withdrawn periodically by means of a syringe. The peroxide content was measured. No temperature rise was noted during the oxidation. A slight positive oxygen pressure (10–20 mm.) was maintained on the system and the amount of oxygen absorbed was measured by adjusting the burets. After 16 hr. argon was slowly introduced into the flask and the exit gases were passed through two Dry Ice–acetone cooled traps. Assuming all the gases except oxygen to be condensable by the traps, the amount of oxygen absorbed was calculated from the total volume decrease minus the volume of the gas in the traps. A total of 38% of the theoretical amount of oxygen was absorbed, assuming 4 moles of oxygen are required for each mole of lithium tetrabutylboron. The gas in the trap was shown to be butane by infrared and gas chromatography. A total of 15% was recovered.

The liquid layer was hydrolyzed with excess 20% sodium hydroxide solution at 60° for 2 hr. After acidification with HCl, extraction with ether, and separation of layers, the ether layer was dried with magnesium sulfate. The ether was removed by distillation and the resulting liquid was fractionated by distillation and analyzed by infrared and gas chromatography.

A 10-ft. Carbowax 20 M column at 80° was used to identify *n*-butyl alcohol (48%) and *n*-butyraldehyde (3%). The other volatile components totaled 1.4%. Only a trace amount of butyric acid remained in the distillation pot.

The oxidation of lithium tetrabutylboron was also studied in dimethylformamide and ethylene glycol dimethyl ether. Similar results were obtained.

Normal alcohols were also found to be the major products in the oxidation of lithium triethylbutylboron, lithium triethyldodecylboron, and lithium tributyldodecylboron.

Acknowledgment.—The author is indebted to Dr. C. D. Broaddus for his suggestions and stimulating discussions concerning this work. He also wishes to thank Drs. T. J. Flautt and W. L. Courchene for aid in interpreting the n.m.r. and infrared spectra and Mr. Warren Foster for patiently performing most of the work in the laboratory.

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[29] M. Grayson and P. T. Keough, *J. Am. Chem. Soc.*, **82**, 3919 (1960).

Epoxidations with *m*-Chloroperbenzoic Acid

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m-Chloroperbenzoic acid is a convenient reagent for studying epoxidation reactions. When the effect of the solvent upon the rates of epoxidation of *trans*-stilbene and ethyl crotonate was examined, it was found that, with ethyl crotonate, changing the solvent had no effect on the rate of epoxidation so long as the intramolecular hydrogen bonding of the peracid was not disrupted. With one solvent, acetonitrile, an apparent zero-order reaction was observed. A scheme is proposed to account for these results.

While there have been several recent studies of epoxidations with peracids,[1-3] the only olefins examined were those that react rather readily with the peracid. Since *m*-chloroperbenzoic acid recently has become available,[4] and since solutions of this peracid are stable at moderate temperatures for prolonged periods, we were enabled to study the epoxidation of the unreactive α,β-unsaturated esters as well as *trans*-stilbene in a variety of solvents without complications due to side reactions. In all cases, blanks consisting of *m*-chloroperbenzoic acid and the solvent showed less than 2% decomposition after the epoxidation had proceeded to 50–60%. Ethyl β-methylglycidate and *trans*-stilbene epoxide were isolated in good yield from these reactions.

The second-order rate constants for the epoxidation of *trans*-stilbene with *m*-chloroperbenzoic acid at 30°

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[1] R. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955).

[2] G. Berti and F. Bottari, *J. Org. Chem.*, **25**, 1286 (1960).

[3] P. Renolen and J. Ugelstad, *J. Chim. Phys.*, **57**, 634 (1960).

[4] Anon., *Chem. Week*, **92**[14], 55 (April 6, 1963).

TABLE I

RATE CONSTANTS FOR THE EPOXIDATION OF *trans*-STILBENE WITH *m*-CHLOROPERBENZOIC ACID AT 30°

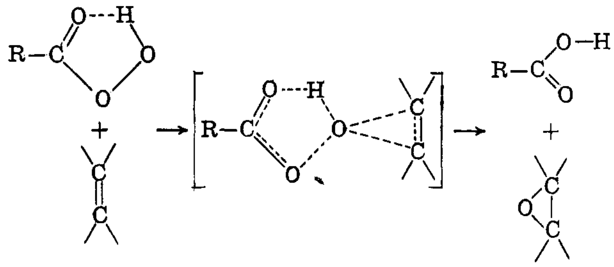
(Reactants at *ca.* 0.05 mole/l.)

Solvent	k_2, l./mole-sec. × 10^4	Dielectric constant (30°)
CCl_4	14.6	2.2
$CHCl_3$[a]	36.0	4.6
CH_2Cl_2	36.1	8.7
$ClCH_2CH_2Cl$[b]	32.7	10.1
$(CH_3)_3COH$	0.42	11.7
C_6H_6	18.9[c]	2.26
C_6H_5Cl	27.3	5.54
o-$C_6H_4Cl_2$	36.3	9.45

[a] 2 mole % CF_3CO_2H/mole of peracid. [b] Rate unaffected by 2 mole % CF_3COOH/mole of peracid. [c] Lynch and Pausacker (ref. 1) give 23.3.

in several solvents are given in Table I. The dielectric constants of the solvents also are tabulated. The only solvent in this series likely to disrupt the intramolecular hydrogen bonding of the peracid is *t*-butyl alcohol (in which, incidentally, the peracid is extremely stable). When the reaction was run in chloroform, a small amount of trifluoroacetic acid was added. The blank in chloroform remained constant in the presence of this strong acid, which did not seem to affect the rate of epoxidation (*cf.* reaction in 1,2-dichloroethane and reactions with ethyl crotonate).

These results indicate that, in agreement with Renolen and Ugelstad,[3] the rates of epoxidation, where intramolecular hydrogen bonding is intact, are roughly parallel to the dielectric constant of the solvent, as would be expected for reactions between unionized molecules if the transition state were more polar than the reactants.[5] The nonionic mechanism shown here has been proposed by several authors[1-3] to account for these observations.



(1)

The effect of solvents which can form intermolecular hydrogen bonds with the peracid, however, reduces the effective concentration of the cyclically bonded peracid and retards the epoxidation rate.

When the epoxidation rates of ethyl crotonate with *m*-chloroperbenzoic acid were determined in a variety of solvents, the solvent effects were somewhat different. In general the rates were much slower than with *trans*-stilbene, and slowest in those solvent systems in which the intramolecular hydrogen bonding of the peracid was disrupted, but, in nonhydrogen bonding solvents, the rate was identical in solvents of widely varying dielectric constant. The second-order rate constants are given in Table II. The reaction in diethyl ether was very slow, and meaningful results could not be obtained owing to decomposition of the peracid.

The recent report by Berti and Bottari[2] that trichloroacetic acid catalyzes the epoxidation of *trans*-stilbene was not confirmed for the epoxidation of ethyl crotonate. When equimolar amounts of *m*-chloroperbenzoic acid, trichloroacetic acid, and ethyl crotonate were allowed to react in 1,2-dichloroethane, the reaction was still second order, but somewhat slower than in the absence of trichloroacetic acid, probably owing to disruption of intramolecular hydrogen bonding of the peracid by trichloroacetic acid.

In the acetic acid–acetic anhydride system, an additional retardation may be due to the formation of peroxides from the peracid.

TABLE II

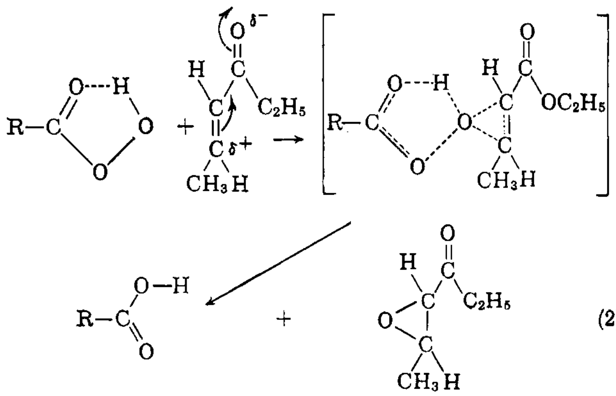
RATE CONSTANTS FOR EPOXIDATION OF ETHYL CROTONATE WITH *m*-CHLOROPERBENZOIC ACID

Solvent	Temp., °C.	k_2, l./mole-sec. × 10^5	Dielectric constant
CH_3COOH (95%) $(CH_3CO)_2O$ (5%)	30	0.075	. . .
CH_3COOH (90%) H_2O (10%)	30	0.53	. . .
$CH_3COOC_2H_5$	25	0.193	6.02
CCl_4	25	1.15	2.23
$CHCl_3$[a]	25	1.15	4.73
CH_2Cl_2	25	1.15	8.89
$ClCH_2CH_2Cl$[b]	25	1.15	10.36
$ClCH_2CH_2Cl$	30	1.73	10.1
C_6H_6	30	1.73	2.26
$ClCH_2CH_2Cl$[c]	25	0.77	10.36

[a] 2 mole % CF_3CO_2H/mole of peracid. [b] Rate unaffected by 2 mole % CF_3CO_2H/mole of peracid. [c] Equivalent amounts of Cl_3CCO_2H, peracid, and ethyl crotonate.

The constancy of the rates in nonhydrogen-bonding solvents of widely varying dielectric constants may be a result of the disruption of the ground state resonance in ethyl crotonate so that there is only a very slight over-all difference in polarity between the ground and transition states.

The constancy of the rate in media of dielectric constants varying from two to ten is evidence against the possibility that the rate-determining step is the formation of a hydrogen-bonded complex between the peracid and ethyl crotonate. In addition, if such a complex were formed to any great extent, the addition of excess peracid should increase the rate, and may even change the order of the reaction, since excess free peracid would then be capable of epoxidizing the complex. This, however, does not occur. The results



(2)

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(5) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 140.

TABLE III

EPOXIDATION OF ETHYL CROTONATE WITH *m*-CHLOROPERBENZOIC ACID IN 1,2-DICHLOROETHANE AT 30°

Peracid, mole	Ethyl crotonate, mole	k_2, l./mole-sec. × 10^5
0.505	0.250	1.75
0.500	0.500	1.73
0.258	0.501	1.75

of changing the ratios of the reactants are shown in Table III.

When ethyl crotonate was epoxidized with *m*-chloroperbenzoic acid in acetonitrile, it was found that, as expected, the initial rate was slower than in the halogenated hydrocarbons, but, to our surprise, the reaction was apparently zero order: the peracid titer decreased linearly with time. These rates are given in Table IV.

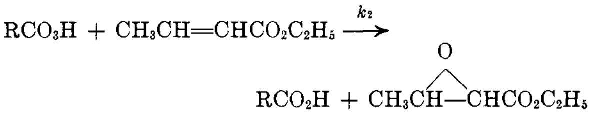
TABLE IV

EPOXIDATION OF ETHYL CROTONATE WITH *m*-CHLOROPERBENZOIC ACID IN ACETONITRILE

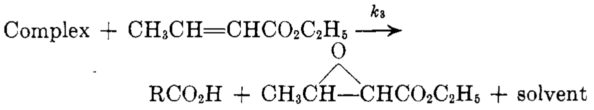
Peracid, mole/l.	Ethyl crotonate, mole/l.	Temp., °C.	k_0, mole-sec. × 10^6
0.5	0.5	25	0.625
0.5	0.5	50	6.95

The following scheme may account for the kinetics of this epoxidation in various solvents.

$$RCO_3H + \text{solvent} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{complex} \quad (3)$$



$$RCO_3H + CH_3CH{=}CHCO_2C_2H_5 \xrightarrow{k_2} RCO_2H + CH_3\overset{O}{CH{-}CH}CO_2C_2H_5 \quad (4)$$



$$\text{Complex} + CH_3CH{=}CHCO_2C_2H_5 \xrightarrow{k_3} RCO_2H + CH_3\overset{O}{CH{-}CH}CO_2C_2H_5 + \text{solvent} \quad (5)$$

If $k_1 > k_{-1}$, $k_2 > k_{-1}$, and $k_2 \gg k_3$, the concentration of free peracid would reach a steady state and the reaction would be independent of initial peracid concentration. If solvation does occur, but k_3 is not negligible with respect to k_2, the reaction would be slower than in the absence of solvation, but still first order in peracid and ethyl crotonate.

There is some evidence for reversible interaction between *m*-chloroperbenzoic acid and acetonitrile. When the nitrile is added to a solution of the peracid in dichloromethane, an increase of 25 cm.$^{-1}$ is observed in the carbonyl frequency of the infrared spectrum. When the solvents are removed under reduced pressure, *m*-chloroperbenzoic acid is recovered quantitatively. The interaction of nitriles with methanolic solutions of aqueous hydrogen peroxide to form peroxycarboximidic acids as postulated by Payne,[6] is presumably different from the interaction observed here, since the formation of the peroxycarboximidic acid probably involves the peroxy anion and subsequent reaction with a hydroxylic solvent. In the present instance, however, hydroxylic compounds, except for the peracid, are absent, and the solution is not basic. The detailed nature of the present interaction is under investigation.

It is stated that monoperphthalic acid reacts more slowly in epoxidations than perbenzoic acid,[7] in contrast to the observation that electron-withdrawing substituents usually increase the rates of epoxidation.[1] The slow rates with monoperphthalic acid may be due to intramolecular hydrogen bonding between the carboxy and percarboxy groups. Kinetic studies with the recently prepared permaleic acid[8] have not been described, but it may be expected the epoxidations with permaleic acid would be slower than with the hypothetical peracrylic acid, if these compounds could be compared in the absence of other carboxylic or hydroxylic compounds. The presence of at least equivalent amounts of water and about 20 mole % maleic acid in the permaleic acid reagent as normally prepared also would tend to reduce epoxidation rates, and would have to be considered in any kinetic study. Trifluoroperacetic acid[9] as normally prepared also has water and trifluoroacetic acid present, and these contaminants may retard epoxidation rates to some extent. Comparisons of the normal trifluoroperacetic acid reagent and pure, anhydrous trifluoroperacetic acid have not been described. Retardation due to water and acetic acid is, however, well established for epoxidations with peracetic acid. It is well known that peracetic acid in aqueous acetic acid is ineffective in the epoxidation of α,β-unsaturated esters,[10] but it was found recently that anhydrous peracetic acid in ethyl acetate or acetone is capable of converting these unsaturated esters to the corresponding glycidates.[11]

Experimental

Materials.—*trans*-Stilbene, Scintillation grade, m.p. 124–125°, was obtained from Matheson Coleman and Bell, and ethyl crotonate was distilled before use, the fraction having $n^{25}D$ 1.4226 being retained. *m*-Chloroperbenzoic acid of 99+% assay was obtained by washing the commercial 85% material (FMC Corporation) with a phosphate buffer of pH 7.5, and drying the residue under reduced pressure. The peracid was assayed iodometrically before use. 1,2-Dichloroethane was fractionated and a center cut retained, and diethyl ether and benzene were distilled from sodium. *t*-Butyl alcohol was treated with potassium and the distillate used. Reagent grade carbon tetrachloride, chloroform, methylene chloride, ethyl acetate, trichloro- and trifluoroacetic acids, acetic anhydride, acetic acid, chlorobenzene, and *o*-dichlorobenzene were used without further purification.

Methods.—In a typical run with ethyl crotonate a sample of 99+% *m*-chloroperbenzoic acid, corresponding to 8.629 g. (0.05 mole) of 100% material was placed in a 125-ml. iodine flask and about 70 ml. of solvent was added. After the peracid dissolved (endothermic reaction), the solution was raised to the desired temperature, transferred to a 100-ml. volumetric flask, and the iodine flask rinsed with three small portions of fresh solvent which were then added to the volumetric flask. Ethyl crotonate, 5.707 g. (0.05 mole), was then added to the volumetric flask with sufficient solvent to fill the flask to the mark. After thor-

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(6) G. B. Payne, P. H. Deming, and P. H. Williams, *J. Org. Chem.*, **26**, 659 (1961).

(7) H. Bohme and G. Steinke, *Ber.*, **70B**, 1709 (1937).

(8) R. W. White and W. D. Emmons, *Tetrahedron*, **17**, 31 (1962).

(9) W. D. Emmons and G. B. Lucas, *J. Am. Chem. Soc.*, **77**, 2287, (1955).

(10) D. Swern, *Chem. Rev.*, **45**, 1 (1949).

(11) D. L. MacPeek, P. L. Starcher, and R. Phillips, *J. Am. Chem. Soc.*, **81**, 680 (1959).

ough mixing, the flask and a blank prepared as above but without ethyl crotonate were placed in a water bath at the desired temperature.

Periodically, 5-ml. aliquots were withdrawn, added to solutions of 3 ml. of acetic acid in 10 ml. of 20% potassium iodide, and the liberated iodine titrated with *ca.* 0.11 N sodium thiosulfate.

Results of a typical run (benzene at 30°) are shown.

Time (hr.)	0	2.5	5.5	21.5	29
[Peracid] (moles/l.)	0.500	0.465	0.425	0.290	0.255

After 30 hr., the blank still had 0.492 mole/l. of peracid.

Experiments with *trans*-stilbene were run in the same way, except that initial concentrations were usually about 0.05 M because of the lower solubility of the *trans*-stilbene.

A Re-examination of the Polymerization of Sterculic Acid. I. Reaction of Sterculene with Acetic Acid

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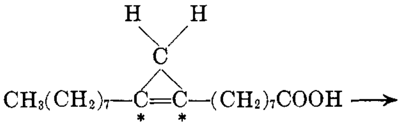
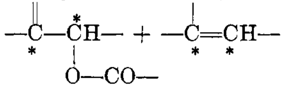
The reaction of sterculene (1,2-di-*n*-octylcyclopropene, V) with acetic acid gave 9-acetoxy-10-methylene-octadecane (VI), 9-acetoxymethyl-9-octadecene (VII), and 9-acetoxy-10-methyl-9-octadecene (VIII).

Sterculic acid (I) polymerizes with destruction of the cyclopropene ring and formation of a polyester.[1-3] A similar reaction occurs with acetic acid, and from permanganate–periodate oxidations of the reaction products, the structures II and III were inferred to be



I

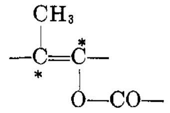


$$-\overset{*}{\underset{}{C}}(=CH_2)-\overset{*}{C}H(O{-}CO{-})- \; + \; -\overset{*}{C}(CH_2{-}O{-}CO{-})=\overset{*}{C}H-$$

II III

present in the mixture as well as in the polymer.[3] The olefinic carbon atoms in I and its reaction products are starred.

Although Faure and Smith[2] noted an increase in the infrared absorption at 7.72 μ, which they attributed to methyl groups, Rinehart, *et al.*,[3] found no chemical or spectroscopic evidence for the enol ester group IV.

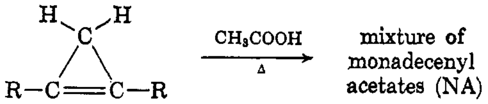


$$-\overset{*}{C}(CH_3)=\overset{*}{C}(O{-}CO{-})-$$

IV

Earlier work in this laboratory on gas chromatography (g.l.c.) of the methyl esters of the acids produced by saponification of the sterculic acid polymer suggested that structure IV is present in the polymer.[4] The availability of sterculene[5] (V) prompted us to reinvestigate the problem because the products expected from V and acetic acid would be more amenable to chromatography and yield simpler compounds on degradation than those derived from I.

When sterculene was heated with acetic acid, a mixture was obtained from which the reaction product was separated by distillation. The product was a mixture of nonadecenyl acetates (NA) that gave two

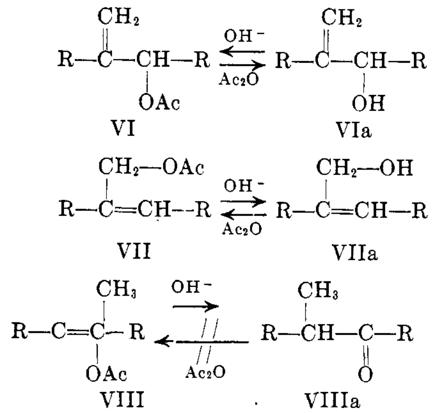


V

R (in this and succeeding diagrams) = n-C_8H_{17}–

peaks on g.l.c. and two spots on thin layer chromatography (t.l.c.). Saponification (calcd. for $C_{19}H_{37}$-OAc, 324; found, 321 and 322) gave a mixture (NA, OH^-) that showed two different peaks on g.l.c. and three different spots on t.l.c. Acetylation of NA,OH^- gave a product (NA,OH^-,Ac) that showed the original two peaks on g.l.c. plus the smaller one in the NA,OH^- diagram (Fig. 1), and the original two spots on t.l.c. plus the smaller one of highest R_f given by the NA,OH^- mixture (Fig. 1). The saponification equivalent of NA,OH^-,Ac (345) indicated that a portion of the saponified nonadecenyl acetate mixture could not be reacetylated to an ester.

These results suggested that at least three components were present in NA: the methyleneacetoxy derivative VI and the acetoxymethyl derivative VII, on the basis of previous results,[3] as well as the enol acetate derivative VIII.



The infrared spectrum of NA,OH^- corroborated this supposition. A small band at 5.83 μ indicated the presence of a ketone such as VIIIa in the mixture of alcohols VIa and VIIa.

NA was ozonized in methylene chloride and the resulting solution decomposed with zinc in aqueous acetic acid. The aqueous fraction from the ozonolysis

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(1) J. R. Nunn, *J. Chem. Soc.*, 313 (1952).

(2) P. K. Faure and J. C. Smith, *ibid.*, 1818 (1956).

(3) K. L. Rinehart, Jr., S. I. Goldberg, C. L. Tarimu, and T. P. Culbertson, *J. Am. Chem. Soc.*, **83**, 225 (1961).

(4) J. C. Masson, Ph.D. thesis, University of Arizona, 1959.

(5) H. W. Kircher, *J. Am. Oil Chemists' Soc.*, **41**, 4 (1964).