This oil was chromatographed on basic alumina IV. The material was eluted with petroleum ether (trace of ether) solvent to yield 0.6 g (92%) of 2-methyl DMAMF (4). Nmr data: δ 1.95 (s, 3.0), 2.13 (s, 6.0), 3.26 (AB quartet, 2.1, $\nu_1 = 3.21$, $\nu_2 = 3.30$, $J = 13.0$), 4.00 (m, 8.0).

Registry No.—**1**, 38744-26-2; **2**, 38641-31-5; **2a**, 12214-99-2; **4**, 12111-28-3; **5**, 38641-34-8; **5a**, 38641-35-9; **5b**, 12111-89-6; **6**, 38641-37-1; **7**, 38641-38-2; **8**, 38641-39-3.

Oxidation of Olefins by Palladium(II). VI. Ethylene Oxidation by Palladium(II) Acetate in Acetic Acid Promoted by Various Oxidants[1]

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Palladium(II) salts alone in acetic acid oxidize ethylene to vinyl acetate. It has been previously reported that $CuCl_2$ and NO_3^- increase the rate of oxidation and change the product from vinyl acetate to 1,2-disubstituted ethanes such as ethylene glycol mono- and diacetate and 2-chloroethyl acetate. The present study was undertaken to determine the generality of this new reaction. A number of oxidants, including $K_2Cr_2O_7$, $NaNO_2$, $CuBr_2$, MnO_2, $Pb(OAc)_4$, $Tl(OAc)_3$, $TlCl_3$, and $HAuCl_4$, were also found to be active in this reaction. Others which had little or no activity include *p*-quinone, $FeCl_3$, $Fe(OAc)_3$, $Hg(OAc)_2$, $MoCl_5$, and $MoOCl_4$. $CuBr_2$ gave 2-bromoethyl acetate. In addition to the 1,2-disubstituted ethanes, $Tl(OAc)_3$, $TlCl_3$, and $HAuCl_4$ also formed appreciable quantities of ethylidene diacetate. The reaction probably proceeds by a mechanism similar to that of the previously studied aromatic substitution reaction. This mechanism involves formation of an intermediate with a palladium(II)–carbon bond. This intermediate reacts with the oxidant to give the observed products.

In the absence of other oxidants palladium(II) salts in acetic acid oxidize ethylene to vinyl acetate[3] and other olefins to mixtures of vinyl and allylic acetates.[4] A study of the product distributions obtained from oxidation of 1 and 2 olefins with palladium(II) acetate

$$C_2H_4 + Pd^{2+} + 2OAc^- \xrightarrow{HOAc} C_2H_3OAc + HOAc + Pd^0 \quad (1)$$

$$Pd(OAc)_2 + C_2H_4 \longrightarrow \underset{\mathbf{1}}{AcOPdCH_2CH_2OAc} \xrightarrow{-HPdOAc} CH_2{=}CHOAc \quad (2)$$

indicated that the reaction proceeds by way of an acetoxypalladation–Pd(II)-hydride elimination.[5]

Addition of copper(II) chloride to these reaction mixtures causes the rate of olefin oxidation to increase. In addition the main product changes from vinyl acetate to 1,2-disubstituted alkanes.[6] It has been demonstrated that both $PdCl_2$ and $CuCl_2$ are required for this reaction

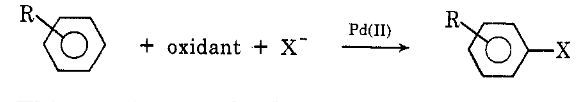
$$C_2H_4 + CuCl_2 + OAc^- \xrightarrow[HOAc\ +\ H_2O]{PdCl_2} \left\{\begin{array}{l} AcOCH_2CH_2Cl \\ AcOCH_2CH_2OAc \\ AcOCH_2CH_2OH \end{array}\right. + CuCl \quad (3)$$

to take place.[6b] On the basis of studies with the butenes[6b] and cyclohexene[1] the mechanism for this reaction has been postulated to involve the interception of the acetoxypalladation intermediate, **1**, by oxidant to give saturated products (X = OAc, Cl, or OH).

$$\mathbf{1} + 2CuCl_2 + X^- \longrightarrow AcOCH_2CH_2X + PdCl_2 + 2CuCl + OAc^- \quad (4)$$

The reaction is not limited to $CuCl_2$, as it has been demonstrated that nitrate can replace $CuCl_2$.[7] The present study is aimed at defining the scope of this new reaction. In particular a number of oxidants will be surveyed to determine what types of oxidants are effective in interacting with Pd(II).

A related reaction is the Pd(II)-catalyzed aromatic substitution reaction, which also requires a second oxidant[8] ($X^- = OAc^-, N_3^-, Cl^-, NO_2^-, Br^-, CN^-$, or SCN^-).



(5)

This reaction very likely proceeds by way of a Pd(II)-aryl intermediate analogous to **1** although Pd(IV) species cannot be eliminated by the experimental evidence.

Results

A number of oxidants were tested for their ability to change the nature of the oxidation of olefins in the same fashion as $CuCl_2$ or nitrate. In the present work ethylene was the olefin used. There are two criteria for a given reagent to be capable of interacting with Pd(II): first, the rate of ethylene oxidation in the presence of this reagent and Pd(II) as compared to the rate of oxidation in the absence of Pd(II); and second, the product distributions obtained in the oxidations containing Pd(II) and the reagent. Of course, Pd(II) alone gives only vinyl acetate.

Gas Uptake Experiments.—In Table I are listed the results of a series of experiments in which the $Pd(OAc)_2$

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[1] Paper V: P. M. Henry, *J. Amer. Chem. Soc.*, **94**, 7305 (1972).

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[3] (a) I. I. Moiseev, M. N. Vargaftik, and Ya. K. Sirkin, *Dokl. Akad. Nauk SSSR*, **133**, 377 (1960); (b) E. W. Stern and M. L. Spector, *Proc. Chem. Soc.*, 370 (1961).

[4] (a) M. N. Vargaftik, I. I. Moiseev, and Ya. K. Sirkin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 930 (1962); (b) I. I. Moiseev, A. P. Belov, and Ya. K. Sirkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1527 (1963).

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[6] (a) D. Clark, P. Hayden, and R. D. Smith, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14** (2), B10 (1969); (b) P. M. Henry, *J. Org. Chem.*, **32**, 2575 (1967).

[7] M. Tamura and T. Yahui, *Kogyo Kagaku Zasshi*, **72**, 578, 581 (1969).

[8] P. M. Henry, *J.Org.Chem.*, **36**,1886 (1971).

TABLE I

EFFECT OF VARIOUS OXIDANTS ON THE RATE OF ETHYLENE UPTAKE BY $Pd(OAc)_2$ SOLUTIONS IN ACETIC ACID AT 25° AND ATMOSPHERIC PRESSURE[a]

Oxidant	Initial rate, M hr^{-1}
None	0.017
p-Quinone[b]	0.015
$Pb(OAc)_4$	0.09
$CuBr_2$	0.047
MnO_2	2.0[c]
$FeCl_3$	<0.001
$Fe(OAc)_3$	<0.001
$Hg(OAc)_2$	Very fast[d]
$K_2Cr_2O_7$	0.73
$KMnO_4$	0.004
$NaNO_3$	0.1
$NaNO_2$	0.011
$MoCl_5$	0.005
$MoOCl_4$	0.005

[a] For all solutions $[Pd(OAc)_2] = 0.04\ M$ and $[LiOAc] = 1\ M$; concentration of oxidant is also 1 M. Most reaction mixtures were heterogeneous. [b] Concentration of this oxidant is 0.25 M. [c] After ethylene uptake reached 0.04 M the uptake stopped. [d] Gas uptake-mass transfer controlled. Uptake stopped after 1 M ethylene concentration was reached.

and LiOAc concentrations are kept constant but contain various oxidants at a concentration of 1 M.

The initial ethylene uptake as measured by gas burets is given for all oxidants. The initial rate is used since in almost all cases the rate of ethylene uptake decreases rapidly with time. For all the oxidants listed in Table I the initial ethylene uptake in the absence of palladium(II) acetate was less than 0.005 M hr^{-1}.

In some cases the oxidant in the absence of $Pd(OAc)_2$ oxidized ethylene at an appreciable rate under the reaction conditions. Three such oxidants are $Tl(OAc)_3$, $TlCl_3$, and $HAuCl_4$. The initial rates of oxidation and product distributions in the presence and absence of $Pd(OAc)_2$ are given in Table II.

Product Distributions.—The reactions listed in Table I were allowed to run under atmospheric ethylene pressure at 25° for 24 hr and then analyzed for the type of products found in the $CuCl_2$-promoted reaction. Results are listed in Table III. Because of the inaccuracy in refilling the gas burets, the total ethylene uptake was not measured. Thus yields could not be calculated, so total concentrations of products are given. For two-electron oxidants such as $Pb(OAc)_4$, the maximum total concentration of oxidation products would be 1 M, and for one-electron oxidations, it would be 0.5 M. For oxidants such as $K_2Cr_2O_7$, which have lower oxidizing states, the maximum expected concentration of products is uncertain. In the case of $CuBr_2$ the main product (*ca.* 0.5 M) was 2-bromoethyl acetate, the product expected by analogy with the reaction of $CuCl_2$ and $PdCl_2$.

Two oxidants, p-quinone and $FeCl_3$, which did not give the promoted oxidation at 25° and atmospheric pressure, were tested under more vigorous conditions. The $FeCl_3$ run was carried out at 100° under an ethylene pressure of 500 psig for 24 hr. Only traces (0.015 M) of vinyl acetate were found in the reaction mixture.

The p-quinone run was carried out under the conditions described in a patent[9] claiming to produce saturated esters. These include 0.007 M $PdCl_2$, 2 M p-quinone, 1.4 M LiCl, and 0.1 M LiOAc. The reaction was run at 69° under 300 psig ethylene pressure for 12 hr. Only vinyl acetate was detected in the reaction mixture.

A control run was carried out to determine if the ethylidene diacetate in the $Tl(OAc)_3$ run could result from further reaction of vinyl acetate. The reaction was carried out in the same fashion as the first run in Table II except that the reaction mixture was initially 0.1 M in vinyl acetate. At the conclusion of the run the reaction mixture still contained 0.1 M vinyl acetate.

Discussion

The most important result of the present study is the demonstration that oxidants other than $CuCl_2$ and nitrate will act as cocatalyst with Pd(II) in the oxidation of olefins. On the basis of oxidation rates for the oxidants listed in Table I, $K_2Cr_2O_7$, $Pb(OAc)_4$, $CuBr_2$, $NaNO_2$, and $NaNO_3$, included for purposes of comparison, definitely give the reaction. MnO_2 gave a rapid initial rate but is a doubtful case because the total ethylene uptake was 1 mmol. The data in Table II indicate that $Tl(OAc)_3$, $TlCl_3$, and $AuCl_4^-$ also give the reaction, although the result is obscured by the fact that they oxidize ethylene in the absence of $Pd(OAc)_2$. However, rates are faster in the presence of $Pd(OAc)_2$, and product distributions are different than in its absence.

A number of oxidants, including p-quinone, $FeCl_3$, $Fe(OAc)_3$, $NaNO_2$, $MoCl_5$, $KMnO_4$, and $MoOCl_4$, gave initial rates slower than the rates with $Pd(OAc)_2$ alone, so by this criterion are not effective. $Hg(OAc)_2$ gave a rapid ethylene uptake, but no oxidation resulted. The only reaction was the well-known mercuration reaction.[10]

$$Hg(OAc)_2 + C_2H_4 \xrightarrow{HOAc} AcOHgCH_2CH_2OAc \qquad (6)$$

The product distribution data, samples of which are given in Tables II and III, tend to confirm the ethylene uptake results, since the active cocatalysts gave saturated products. In addition, $NaNO_2$ and $KMnO_4$, which gave a slow ethylene uptake, produced detectable amounts of saturated products. The other oxidants, which gave slow initial rates, also gave no detectable amounts of saturated products. The case of quinone is worthy of special mention because it has been used as a reoxidant for Pd(0) in kinetic studies of olefin oxidation at temperatures close to room temperature.[11] The present results confirm that quinone is suitable for this purpose, since it does not change either the rate or product of the oxidation.

The fact that an oxidant gives little or no activity under the reaction conditions used in this study does not eliminate it as a candidate under more vigorous conditions. Thus $KMnO_4$ gives the aromatic substitution reaction at 90° and almost certainly would give appreciable rates of ethylene oxidation at this temperature. Its slow activity at 25° probably results from low solubility. For this reason two oxidants which gave negative results and are of special interest in Pd(II) chemistry were tested under more vigorous conditions. $FeCl_3$, used as reoxidant for Pd(II) in several patents, still

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[9] H. B. Copelin and M. J. Freamo, Canadian Patent 761,018 (1967).

[10] J. Chatt, *Chem. Rev.*, **48**, 7 (1951).

[11] I. I. Moiseev, A. P. Belov, V. A. Igoshin, and Ya. K. Sirkin, *Dokl. Akad. Nauk SSSR*, **173**, 863 (1967).

TABLE II

INITIAL RATES AND PRODUCT DISTRIBUTIONS WITH $TlCl_3$, $Tl(OAc)_3$, AND $HAuCl_4$ IN THE PRESENCE AND ABSENCE OF $Pd(OAc)_2$[a]

	Reaction Mixtures							
$[Pd(OAc)_2]$, M	0.04		0.04		0.04		0.04	
[LiOAc], M	1.0	1.0			1.0	1.0	1.0	1.0
[NaOAc], M			0.1	0.1				
Oxidant	$Tl(OAc)_3$	$Tl(OAc)_3$	$Tl(OAc)_3$	$Tl(OAc)_3$	$TlCl_3$	$TlCl_3$	$HAuCl_4$	$HAuCl_4$
Concentration of oxidant, M	1.0	1.0	0.4	0.4	1.0	1.0	1.0	1.0
	Initial Rate, M hr^{-1}							
	0.1	0.026	0.103	0.019	0.15	0.0094	0.07	0.011
	Product Distribution, M[b]							
Vinyl acetate	0.006	ND	ND	ND	0.012	ND	0.027	ND
2-Chloroethyl acetate	ND	ND	ND	ND	0.0025	0.013	0.08	0.01
Ethylidene diacetate	0.14	ND	0.2	ND	0.105	ND	0.07	ND
Ethylene glycol diacetate	0.145	0.057	0.082	0.051	0.004	0.033	0.08	0.02
2-Hydroxyethyl acetate	0.023	0.075	0.067	0.045	ND	0.03	ND	0.02

[a] All reactions run for 24 hr before product analysis. [b] ND = not detected (<0.001 M).

TABLE III

PRODUCT DISTRIBUTIONS FOR THE OXIDATION OF ETHYLENE BY $Pd(OAc)_2$ IN THE PRESENCE OF OTHER OXIDANTS[a]

Oxidant	$Pb(OAc)_4$	*p*-Quinone	MnO_2	$KMnO_4$	$K_2Cr_2O_7$	$NaNO_3$	$NaNO_2$
Vinyl acetate	0.003	0.03	ND[b]	0.004	0.017	ND	ND
Ethylidene diacetate	ND	ND	ND	ND	0.031	0.0017	0.011
Ethylene glycol diacetate	0.08	ND	0.029	0.017	0.43	0.013	0.0031
2-Hydroxyethyl acetate	0.15	ND	ND	ND	0.13	ND	ND
Total	0.233	0.03	0.029	0.021	0.608	0.0147	0.0141

[a] All reaction mixtures 0.04 M in $Pd(OAc)_2$ and 1.0 M in LiOAc. Concentration of oxidant is 1.0 M; reaction run for 24 hr under 1 atm ethylene pressure at 25°. [b] ND = not detected (<0.001 M).

gave no saturated products, and quinone gave only vinyl acetate under conditions previously reported to produce saturated products.[9]

The saturated product distributions deserve comment in some cases. In the case of $CuBr_2$ the main product, as expected in analogy to oxidations by $CuCl_2$, is 2-bromoethyl acetate. The appreciable yields of ethylidene diacetate found with $Tl(OAc)_3$, $TlCl_3$, and $AuCl_4^-$ were not observed with these oxidants in the absence of $Pd(OAc)_2$ or with the other oxidants in the presence of $Pd(OAc)_2$. Control experiments demonstrated that this product was not formed by a secondary reaction of vinyl acetate. Finally, detection of 2-hydroxyethyl acetate in some reaction mixtures was unexpected inasmuch as the reaction mixtures were dried with acetic anhydride, and formation of this acetate would usually require the presence of water. Thus either water is introduced into the reaction in some manner or an intermediate is formed which can react with acetic acid to give this product. An example of the latter could be Cr–O–C bonds in the $K_2Cr_2O_7$ reaction.

The present results do not justify a detailed mechanistic analysis but do emphasize one difference between the aromatic and olefin oxidations previously noted in the study of the aromatic oxidation. This is the fact that the aromatic oxidation requires stronger oxidants than the olefin oxidation. Thus $CuCl_2$ and $Tl(OAc)_3$ give the olefin oxidation but not the aromatic substitution. As mentioned in the introduction, there is good evidence that the $CuCl_2$-promoted oxidation proceeds *via* a Pd(II) species, but there are no definitive experiments to distinguish between mechanisms involving Pd(II) and Pd(IV) species in the case of aromatic substitution. Likewise, the ethylene oxidation with stronger oxidants may proceed through Pd(IV) species. Certainly more mechanistic work is required on both oxidations to distinguish between the two possibilities. Any mechanism will have to explain the formation of ethylidene diacetate in some oxidations.

The properties which cause an oxidant to be a cocatalyst with Pd(II) are certainly not well defined by this study. In general the oxidants with higher redox potentials in aqueous solution appear to give the oxidation; but $CuCl_2$ is certainly an exception with a potential in the range of Fe(III), Mo(VI), and *p*-quinone. Other factors, such as solubility, may be important. The fact that MnO_2 oxidized only 1 mmol of ethylene may mean that an impurity is the actual active reagent.

Experimental Section

Reagents.—Palladium(II) chloride was purchased from Engelhardt Industries Inc. The thallic acetate was prepared as described earlier.[12] The *p*-quinone (Aldrich) was recrystallized from ethanol before use. The acetic acid was dried by refluxing over $B(OAc)_3$.[13] Water content was less than 0.01% as determined by Karl Fischer. The lead tetraacetate was purchased from K & K Laboratories, Inc. All other chemicals were of reagent grade.

Experimental Procedure.—All runs at 25° and atmospheric pressure were carried out on a 25-ml scale using creased flasks. The gas uptake was measured by gas burets. The procedure has been described previously.[14] The various reagents were mixed and diluted to 25 ml with acid. Then 0.3 ml of acetic

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(13) W. C. Eichelberger and V. K. La Mer, *ibid.*, **55**, 3633 (1933).

(14) P. M. Henry, *ibid.*, **86**, 3246 (1964).

anhydride was added and the reaction mixture was heated gently on a steam bath. After cooling the reaction mixture was put in a 25° bath for 0.5 hr before the run was begun. Because of limited solubility of reactants in acetic acid almost all reaction mixtures were heterogeneous.

Analysis of Reaction Mixtures.—All analyses were carried out by vapor phase chromatography using a 6-ft column packed with 20% Carbowax 20M on a 70–80 mesh ABS support. The temperature was programmed from 80 to 200° at a rate of 7.5°/min. The helium flow rate was 60 ml/min. Standards of vinyl acetate and all the saturated products were prepared and used to calculate the concentration of the various products.

Registry No.—Ethylene, 74-85-1; $Pd(OAc)_2$, 3375-31-3; $Tl(OAc)_3$, 2570-63-0; $HAuCl_4$, 16903-35-8; $TlCl_3$, 13453-32-2.

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(+)-Limonene Oxidation with Selenium Dioxide–Hydrogen Peroxide

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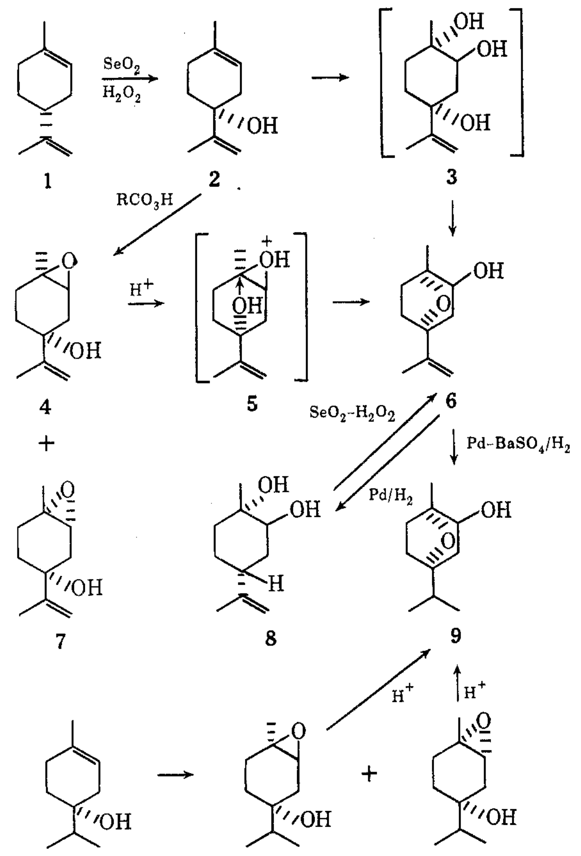
(+)-Limonene oxidation with selenium dioxide–hydrogen peroxide has afforded (+)-1-hydroxyneodihydrocarveol (8) as the main product plus (−)-carvone, (−)-*cis*-carveol, (−)-*trans*-carveol, (−)-1,8-*p*-menthadien-4-ol (2), and three other alcohols. One of the alcohols, (−)-1,4-epoxyneoisodihydrocarveol (6), is a new compound whose structure was determined and whose mechanism for formation was explored. (−)-1,8-*p*-Menthadien-4-ol (2) was oxidized with *m*-chloroperbenzoic acid to produce the previously unreported (−)-4-hydroxy-*trans*-8-*p*-menthene oxide (4), and (−)-4-hydroxy-*cis*-8-*p*-menthene oxide (7). The trans oxide 4, but not the cis isomer 7, was converted to 6 with acetic acid. Terpinen-4-ol (10) was similarly oxidized with peracid, and both the cis and trans isomers (11 and 12) afforded a 1,4-epoxide (9) upon treatment with dilute sulfuric acid.

Selenium dioxide oxidation of (+)-limonene has been studied by several workers,[2a–d] and the products identified involved oxidation at all allylic positions except carbon-3 (menthol series). Most of these oxidation products are constituents of natural products such as citrus essential oils,[2e] of which (+)-limonene is the major constituent. As part of a program to explore conversion of (+)-limonene to more valuable fine chemicals, we studied (+)-limonene oxidation with hydrogen peroxide and only a catalytic amount of selenium dioxide.[3] Among the oxidation products was a new 1,4-epoxide derivative (6 in Scheme I) whose structure was determined and whose mechanism for formation was explored.

Table I lists the products identified from selenium dioxide–hydrogen peroxide oxidation of (+)-limonene under four sets of reaction conditions. Increasing the proportion of oxidizing agents increased the yield of most products (reaction 2). Decreasing the catalytic amount of selenium dioxide (reaction 3) decreased the percentage of all oxidation products except (−)-*cis*-carveol, (+)-1-hydroxyneodihydrocarveol (8), and 1,8-*p*-menthadien-7-ol. Stopping the reaction at the end of the initial exothermic period (reaction 4) resulted in decreased yield of all oxidation products. For most products yield was best with high proportions of oxidizing agents and a long reaction time (reaction 2).

SCHEME I



One of the main oxidation products of this reaction is a previously unreported compound, (−)-1,4-epoxyneoisodihydrocarveol[4] (6 in Scheme I). The ir spectrum suggested that this compound contained either two hydroxyl groups or one hydroxyl group and an ether linkage [1045 (C–OH), 1118 cm^{-1} (C–O–C or *t*-OH)].[5] A high-resolution mass spectrum showed the empirical formula to be $C_{10}H_{16}O_2$. The low-resolution mass spectrum showed a major fragment due to loss of one water molecule (M − 18), but a second molecule

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(1) One of the laboratories of the Southern Region, Agricultural Research Service, U. S. Department of Agriculture. References to specific commercial products do not constitute endorsement.

(2) (a) J. Verghese, *Perfum. Essent. Oil Rec.*, 876 (1968); (b) Y. Sakuda, *Bull. Chem. Soc. Jap.*, **42**, 3348 (1969); (c) A. F. Thomas and W. Bucher, *Helv. Chim. Acta*, **53**, 770 (1970); (d) E. N. Trachtenberg and J. R. Carver, *J. Org. Chem.*, **35**, 1646 (1970); (e) G. L. K. Hunter and M. G. Moshonas, *J. Food Sci.*, **31**, 167 (1966).

(3) M. Fieser and L. Fieser, "Reagents for Organic Synthesis," Vol. 2, Wiley, New York, N. Y., 1969, p 362.

(4) See E. E. Royals and J. C. Leffingwell, *J. Org. Chem.*, **31**, 1937 (1966), for nomenclature.

(5) R. N. Jones, "National Research Council Bulletin," No. 6, Ottawa, Canada.