Observations on the Ozonolysis of Allylic Compounds. The Structure of Geraniol.

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Geranyl acetate has been found to give less than 3% of formaldehyde on ozonolysis. It is concluded that the acetate and hence geraniol itself have predominantly the *iso*propylidene structure, in agreement with the infrared data. The ozonolysis of allylic compounds is discussed with reference to the general applicability of the Doeuvre–Naves method for the estimation of Δ^1-unsaturation.

THE infrared spectrometric studies of Barnard, Bateman, Harding, Koch, Sheppard, and Sutherland (*J.*, 1950, 915) and of Carrol, Mason, Thompson, and Wood (*ibid.*, p. 3457) have shown that simple acyclic terpenes such as geraniol (I) (for this and other formulæ see Table) and citronellol (II) exist predominantly, if not completely, in the *iso*propylidene form. This conclusion, which confirmed the interpretation of the Raman spectra by Naves, Brus, and Allard (*Compt. rend.*, 1935, **200**, 1112), is not in agreement with evidence obtained by oxidative degradation (cf. Simonsen and Owen, " The Terpenes," Vol. I, Cambridge, 1947) and has been criticized by Simonsen and Owen (*op. cit.*, Vol. III, 1952, p. 481) on the grounds that no parallel oxidation experiments were carried out. Naves (*Bull. Soc. chim. France,* 1951, **18**, 506) compared the infrared and the ozonolytic method for the estimation of *iso*propenyl structures and obtained excellent agreement between them for citronellol, citronellal, citral, citronellic acid and its ethyl ester, rhodinol, farnesal, and farnesyl acetate, but not for the allylic alcohols, linaloöl (III), 6 : 7-dihydrolinaloöl, and nerolidol (IV). In order to complete the comparison we have measured the yields of formaldehyde obtained on ozonolysis of geraniol, geranyl acetate, and some related compounds.

In the determination of the structure of ethylenic compounds by ozonolysis the so-called " ozonide " is often degraded by either an oxidative or a reductive procedure, and the yields of fission products are usually considerably less than the theoretical (cf. Young, McKenzie, Webb, and Roberts, *J. Amer. Chem. Soc.*, 1946, **68**, 293). For quantitative purposes it must then be assumed that the relative yields of the various fission products parallel the proportions of structural types present in the starting material. This is not very satisfactory but fortunately in the case of terminal ethylenic unsaturation formaldehyde is produced without the necessity of decomposing the " ozonide " chemically, and may be estimated directly. This forms the basis of the method originally proposed by Doeuvre (*Bull. Soc. chim. France,* 1936, **3**, 612) and recently modified by Naves (*Helv. Chim. Acta*, 1949, **32**, 1151). This procedure involves treating the ozonized solution with Schiff's reagent in dilute hydrochloric acid (Denigès, *Compt. rend.*, 1910, **150**, 529). Formaldehyde gives a *stable* red colour with this reagent, whereas other aliphatic aldehydes do not; acraldehyde and glyoxylic acid are reported to interfere (see Walker, " Formaldehyde," Reinhold Publ. Corpn., New York, 1944, p. 244). The results summarized in the Table were obtained by using the method as described by Naves, but with precautions taken to prevent over-ozonization.

Three samples of geraniol were obtained from different commercial sources and were purified as indicated on p. 2833; all three then exhibited infrared spectra similar to those reported by Barnard *et al.* and by Carrol *et al.* (*locc. cit.*). Two samples (*a* and *c*) showed weak absorption bands at 916 and 881 cm.$^{-1}$ which are conceivably attributable to the presence of not more than 2% of structures containing CH$_2$:CHR and CH$_2$:CR$_2$ end-groups respectively. On ozonolysis, however, both samples gave formaldehyde in about 20% yield. The other geraniol sample exhibited bands at 905 and 884 cm.$^{-1}$ and probably contained about 7% of *iso*propenyl-type structures; this sample gave formaldehyde in about 25% yield. Similarly 3-methylbut-2-enol (VII), prepared by lithium aluminium hydride reduction of 3-methylbut-2-enoic acid (VI), and containing less than 2% of 3-methylbut-3-enol according to its infrared spectrum, gave about 23% of formaldehyde. On the other hand, geranyl acetate (V) and 3-methylbut-2-enyl acetate (VIII), prepared from the alcohols by methods unlikely to give rise to allylic rearrangement, both gave less than 5% of formaldehyde. It is thus clear that geranyl acetate and hence geraniol itself must exist predominantly in the *iso*propylidene form and that geraniol, like other allylic alcohols (cf. Young *et al.*, *loc. cit.*), gives anomalous products on ozonization.

Summary of ozonolysis results

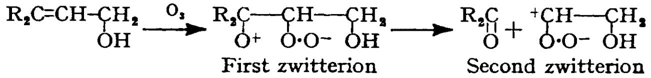
	CH$_2$O (%)	CH$_2$:CR$_2$ (%), detd. by infrared spectrum
CMe$_2$:CH·CH$_2$·CH$_2$·CMe:CH·CH$_2$·OH (I*a*)	19, 20, 21	<2
(I*b*)	23, 25·5, 26	~7
(I*c*)	20, 22·5, 24	<2
CMe$_2$:CH·CH$_2$·CH$_2$·CMe:CH·CH$_2$·OAc (V)	<3, <3	<2
CMe$_2$:CH·CH$_2$·CH$_2$·CHMe·CH$_2$·CH$_2$·OH (II) [a]	~5	4—5
CMe$_2$:CH·CO$_2$H (VI)	1·5, 2	—
CMe$_2$:CH·CH$_2$·OH (VII)	23, 23·5	<2
CMe$_2$:CH·CH$_2$·OAc (VIII)	3	—
CHMe:CH·CH$_2$·OH (XI)	12, 14	—
CHMe:CH·CHO (X)	2·5, 3·5	—
CMe$_2$:CH·CH(OH)·CH$_3$ (IX) [b]	7, 8·5	~5
CHMe:CH·CH(OH)·C$_2$H$_5$ (XII)	<2, <2	—
CMe$_2$:CH·CH$_2$·CH$_2$·CMe(OH)·CH:CH$_2$ (III) [a]	50—56	0
CMe$_2$:CH·CH$_2$·CH$_2$·CMe:CH·CH$_2$·CH$_2$·CMe(OH)·CH:CH$_2$ (IV) [a]	49—62	4—5
CH$_2$:CH·CH(OH)·C$_2$H$_5$ (XIII)	50·5, 60·5	—
CH$_2$:CH·CH(OH)·C$_5$H$_{11}$ (XIV)	48, 52·5	>98 [c]
CH$_2$:CMe·CH$_2$Bu^t (XV)	99	>99

[a] Data from Naves (*Bull. Soc. chim. France*, 1951, **18**, 506). [b] The sample contained ~5% of 4-methylpenta-1 : 3-diene. [c] CH$_2$:CHR (%).

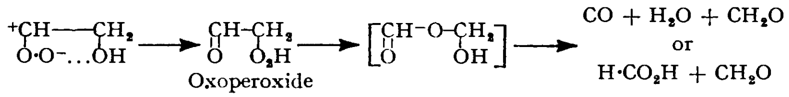
Mechanism of the Abnormal Ozonolysis.—Simonsen and Owen (*op. cit.*) suggested that large yields of formaldehyde or formic acid might be obtained from compounds such as geraniol if the *iso*propenyl and *iso*propylidene forms were in equilibrium, with the latter predominating but the former reacting more quickly with ozone. This explanation cannot be correct since the substitution of acetoxyl for hydroxyl should not affect the mobility or reactivity of such a system and yet the acetate gives very little formaldehyde on ozonolysis. Young *et al.* (*loc. cit.*) showed that ozone-catalysed, anionotropic rearrangements to linaloöl-type structures do not occur. They found that partial ozonolysis of crotyl alcohol or but-3-en-2-ol gives rise to abnormal products but that the recovered alcohol is not isomerized. This observation also indicates that prototropic rearrangements, *e.g.*, of crotyl alcohol to but-3-en-1-ol, do not occur.

Young *et al.* (*loc. cit.*) suggested that formaldehyde arises anomalously from an unexpected reaction of the " ozonide," and the mechanism which they proposed may be modified slightly, after the recent work of Criegee (*Fortschr. Chem. Forsch.*, 1950, **1**, 508). According to Criegee, addition of ozone to an ethylenic bond results in the formation of a zwitterion which splits to give a carbonyl compound and a second zwitterion.

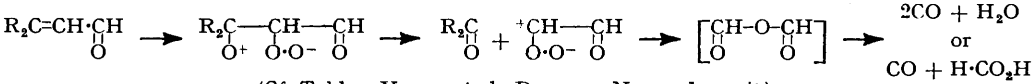
Normally the latter entity will polymerize or undergo reaction with the solvent, but if it contains a hydroxyl or oxo-group in the α-position it may undergo a rearrangement :



Abnormal reaction :

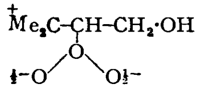


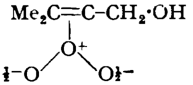
Young *et al.* found that allylic amines and ethers also undergo the abnormal ozonolysis but that esters do not. These workers suggested that in the presence of water the abnormal reaction might give rise to two molecules of formaldehyde, but this cannot be correct since a secondary alcohol such as 4-methylpent-3-en-2-ol, would then also give formaldehyde on ozonolysis, whereas in fact it does not. It will be obvious that for αβ-unsaturated aldehydes and ketones, the zwitterions themselves will be oxoperoxides which may rearrange as before, and that formic acid, but not formaldehyde, may be produced.

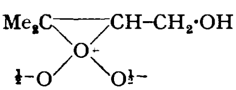


(Cf. Table; Young *et al.*, Doeuvre, Naves, *locc. cit.*)

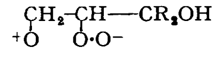
It will be seen from the Table that the yields of formaldehyde are in the order : 3-methylbut-2-enol ~ geraniol > but-2-enol; and further, that for alcohols of linaloöl type ($CH_2{:}CH{\cdot}CR_2{\cdot}OH$), the yields are considerably lower than theoretical. It thus appears that substituent alkyl groups at the double bond affect the course of the ozonolysis. If the mechanism proposed above is correct, this must result from an alteration in the structure of the first zwitterion. Ozone is an electrophilic reagent (cf. Wibaut, Sixma, Kampschmidt, and Boer, *Rec. Trav. chim.*, 1950, **69**, 1355); hence it may not attack the carbon–carbon double bond in, for example, 3-methylbut-2-enol initially only at $C_{(2)}$, but probably forms a π-complex, as Badger (*ibid.*, 1952, **71**, 468) has suggested, or a three-membered ring intermediate ("ozonium ion") similar to that originally proposed by Roberts and Kimball (*J. Amer. Chem. Soc.*, 1937, **59**, 947) for halogen addition to ethylenic compounds :

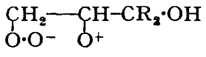






Such intermediates would then rearrange to give either or both possible zwitterions, which in the case of an alcohol of the linaloöl type may be represented by (A) and (B). It will be seen that a zwitterion of type (*A*) can decompose to formaldehyde and may also undergo the

(*A*) 

 (*B*)

abnormal reaction (cf. Young *et al.*, *loc. cit.*) but that a zwitterion of type (*B*) cannot undergo the abnormal reaction; further, the products derived from $^{+}CH_2{\cdot}O{\cdot}O^{-}$ should not decompose to formaldehyde under the Doeuvre–Naves ozonolysis conditions. Hence, if the reaction proceeds at least partly *via* zwitterion (*B*), less than the theoretical yield of formaldehyde will be obtained. In allylic alcohols about equal amounts of the two structures must be formed (see Table), but in alk-1-enes, *e.g.*, 2 : 4 : 4-trimethylpent-1-ene, which give nearly theoretical yields of formaldehyde under these conditions, only the zwitterion of type (*A*) can be formed. This is at least in qualitative agreement with what might be expected by considering the relative charge distributions at $C_{(1)}$ and $C_{(2)}$ in the "ozonium ions" derived from such types of compounds.

The possible duality of reaction routes will affect the reliability of the Doeuvre–Naves method, but not procedures based on oxidative or reductive fission of the " ozonides." The former method is clearly trustworthy only when control experiments with model structures can be shown to give satisfactory results (cf. Adams, Wolff, Cain, and Clark, *J. Amer. Chem. Soc.*, 1940, **62**, 2215; Karrer and Kebrle, *Helv. Chim. Acta*, 1952, **35**, 862).

EXPERIMENTAL

Ozonolysis Technique.—Ozonized oxygen was passed through three tubes containing (i) the allylic compound (0·001—0·01 mole) in a 2 : 3 v/v mixture (5 ml.) of acetic acid and ethyl acetate at $-20°$ to $-10°$, (ii) the solvent alone (2 ml.) at $-20°$ to $-10°$, and (iii) potassium iodide in aqueous acetic acid. The iodine liberated in (iii) was titrated with standard sodium thiosulphate solution at intervals of one minute, ozonization being stopped when three successive titrations were the same to within $\pm 0·1$ ml. The contents of (i) and (ii) were treated with Schiff's reagent in dilute hydrochloric acid as described by Naves (*Helv. Chim. Acta*, 1949, **32**, 1151), and the solution made up to 50 ml. and kept at 30° for exactly 2 hr. The amount of formaldehyde produced was determined with a Hilger " Spekker " colorimeter, a calibration curve being set up with standard formaldehyde solutions.

Infrared Spectra.—The spectra for pure liquid films were determined by Mr. R. L. Erskine using a Grubb–Parsons S 4 double-beam spectrometer with rock-salt optics. Estimates of the amounts of *iso*propenyl structures present were made from the intensity of the absorption band near 890 cm.$^{-1}$, a molecular extinction coefficient (ε) of 155 being assumed for a pure *iso*propenyl compound (cf. Barnard *et al.*, *loc. cit.*).

Geraniol (I).—(*a*) A sample obtained from L. Light and Co. Ltd. was converted into the calcium chloride adduct which was washed well with ether and *n*-hexane. Decomposition of the adduct with warm water followed by distillation gave geraniol, b. p. 118°/16 mm., n_D^{19} 1·4744, $[\alpha]_D^{20}$ 0·06° (Simonsen and Owen, *op. cit.*, give b. p. 229—230°/757 mm., 114—115°/12 mm., n_D^{20} 1·4766).

(*b*) A sample obtained from A. Boake Roberts and Co. Ltd. was purified as above; it had b. p. 74—74·5/1·0 mm., n_D^{19} 1·4710, $[\alpha]_D^{20}$ 0·00°.

(*c*) Another sample had b. p. 229—230°, n_D^{19} 1·4730, $[\alpha]_D^{20}$ 0·00°. The infrared spectra of samples (*a*) and (*c*) were very similar to those reported by Barnard *et al.* and Carrol *et al.* (*locc. cit.*) with the exception of a weak band due to a trace of a carbonyl compound (citral ?) in (*a*) (cf. p. 2831).

Geranyl Acetate (V).—A mixture of geraniol (I*a*) (5 g.), acetic anhydride (5 g.), and pyridine (4 g.) was heated at 60—70° for 3 hr., then distilled, giving geranyl acetate (5 g.), b. p. 128—130°/21 mm., n_D^{19} 1·4590, $[\alpha]_D^{20}$ 0·00 (lit., b. p. 130—132°/22 mm., n_D^{15} 1·4620).

3-*Methylbut*-2-*enoic Acid* (VI).—This was prepared by oxidizing mesityl oxide with sodium hypochlorite solution (Vogel, " Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 448) and on redistillation had m. p. 69·5—70·5° (Vogel, *loc. cit.*, gives m. p. 68°).

3-*Methylbut*-2-*enol* (VII).—Reduction of the acid (VI) (10 g.) with lithium aluminium hydride (4·7 g.) in ether gave the alcohol (VII) (4·7 g.), b. p. 50—51°/13 mm., $n_D^{21·5}$ 1·4385 (Braude and Timmons, *J.*, 1950, 2007, give b. p. 84—86°/80 mm., n_D^{20} 1·4382).

3-*Methylbut*-2-*enyl Acetate* (VIII).—The alcohol (VII) (1·0 g.), acetyl chloride (1·0 g.), and pyridine (5 ml.) were kept below 35° for 15 min. After being worked up in the usual manner, the acetate (VIII) (0·8 g.) had b. p. 148—149°, n_D^{22} 1·4245 (Courtot, *Bull. Soc. chim. France*, 1906, **35**, 662, gives b. p. 149—150°, n_D^{25} 1·4233).

4-*Methylpent*-3-*en*-2-*ol* (IX).—Mesityl oxide (10 g.), on treatment with lithium aluminium hydride (2 g.) in ether, gave the alcohol (IX) (4 g.), b. p. 138—139°, n_D^{19} 1·4330 (Found: C, 72·1; H, 12·1. Calc. for $C_6H_{12}O$: C, 72·0; H, 12·1%). The infrared and ultraviolet spectra ($\lambda_{max.}$ 2260 Å, ε 1400, in EtOH) indicate the presence of $\sim$5% of 4-methylpenta-1 : 3-diene.

Pent-1-*en*-3-*ol* (XIII).—Acraldehyde (5 g.) and ethylmagnesium bromide in ether yielded the product (XIII) (1·4 g.), b. p. 97·5—98·5°/50 mm., n_D^{18} 1·4238 (Delaby, *Compt. rend.*, 1922, **175**, 967, gives b. p. 114—116°, n_D^{27} 1·4182).

Hex-4-*en*-3-*ol* (XII).—Crotonaldehyde (5 g.) and ethylmagnesium bromide in ether gave the hexenol (2 g.), b. p. 129—130°, n_D^{19} 1·4318 (Auwers and Westerman, *Ber.*, 1921, **54**, 2993, give b. p. 135—135·5°, n_D^{25} 1·4325).

Oct-1-*en*-3-*ol* (XIV).—A commercial sample, when redistilled, had b. p. 174—175°, n_D^{19} 1·4369.

Crotonaldehyde (X).—The commercial product was redistilled and dried ($MgSO_4$); it had b. p. 103—103·5°, n_D^{19} 1·4322.

cis-*Crotyl Alcohol* (XI).—A sample prepared by semi-hydrogenation of but-2-ynol, for which we thank Dr. L. Crombie and Mr. C. K. Warren, had b. p. 63—64°/16 mm., n_D^{25} 1·4290.

2 : 4 : 4-*Trimethylpent*-1-*ene* (XV).—The sample used contained >99% of 2 : 4 : 4-trimethylpent-1-ene.

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