3e conformation. *It is this conformational effect which is responsible for the non-Markownikoff opening and subsequent Wagner–Meerwein rearrangement actually observed.*[7]

The structure of maaaliol (I) has been deduced from the following degradations: Acetylation of I with ketene gave the acetate (XI), m.p. 36°, found: C, 77.36; H, 10.60. Pyrolysis of XI at 300° produced mainly VIII, b.p. 121° (11 mm), found: C, 87.75; H, 11.72; 3.35 6.11, 11.34 μ. On catalytic hydrogenation of VIII over Pd/C II was formed which did *not* show infrared absorption due to methylene in a cyclopropane.[8] Osmylation of VIII led to a single diol which was oxidized with lead tetraacetate to formaldehyde and a norketone (IX), m.p. 58°, found: C, 81.47; H, 10.82; 5.87 μ, which was stable to base; 2.95 D introduced with NaOD in EtOD. Oxidation of IX with perbenzoic acid gave lactone XII, m.p. 113°, found: C, 75.67; H, 9.79; 5.82 μ. The corresponding hydroxycarboxylic acid (XIII), m.p. 120°, found: C, 70.06; H, 10.07, on Sarett oxidation was converted to X, m.p. 64°; 5.85, 5.90, 9.92 μ; λ max. 215 mμ ε 2650. Light absorption of X is characteristic of cyclopropyl ketones.[9] We have established the presence and location of a cyclopropane ring in I by a second sequence to be discussed in the full paper. Dehydrogenation of I over Pd/C at 330° gave eudalene (50%) and vetivalene (1%). The presence of a geminal dimethyl in I was established by destructive oxidation of I with permanganate which led to α-hydroxyisobutyric acid.

I, R = OH
II, R = H

III

IV, R = CH²
V, R = O

VI, R = CH₂
VII, R = O

VIII, R = CH₂
IX, R = O

X
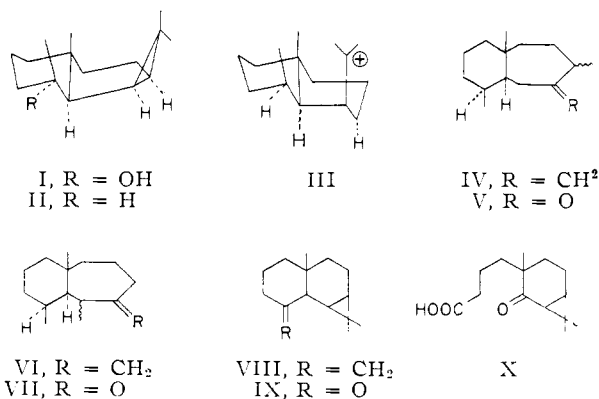
The relative configurations of four out of the five asymmetric centers present in I is evident from the facts presented above. The formation of epimaaliol (XIV); m.p. 59°, found: C, 81.12; H, 11.71 exclusively on treatment of IX with methylmagnesium bromide points to an equatorial hydroxyl in I.

Acknowledgments.—We are indebted to Firmenich and Co., Geneva, for financial support, to the N.I.H. for a fellowship to D. M. W. and to

(7) A similar effect seems to cause the abnormal behavior of aromadendrene (A. J. Birch and F. N. Lahey, *Australian J. Chem.*, **6**, 379 (1953)).

(8) A. R. H. Cole, *J. Chem. Soc.*, 3807, 3810 (1954).

(9) R. H. Eastman and S. K. Freeman, THIS JOURNAL, **77**, 6642 (1955).

Dr. Alida Hosking-Wind for the maaliol which was made available to us by Prof. O. Jeger, Zürich.

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A COMPARISON OF THE RADIOLYSIS AND MASS SPECTROMETRY OF SEVERAL DEUTERATED ETHANOLS

Sir:

The formation of acetaldehyde and 2,3-dihydroxybutane during the radiolysis of ethanol with ionizing radiation has been generally attributed to attack on the ethanol molecule at the $-CH_2-$ position.[1] Substantial proof of this mechanism together with a more detailed insight into it has now been obtained by means of the isotopic tracer technique. CD_3CH_2OH, CH_3CD_2OH, CH_3CH_2OD, and C_2D_6O have been prepared by standard methods,[2] and have been irradiated in the liquid phase with Co^{60} gammas to total dosages of about 5×10^{20} e.v. per gram.[3]

The measurements obtained from these irradiations have been (a) the rate of hydrogen (= hydrogen + deuterium) production, expressed as molecules of hydrogen produced per 100 e.v. absorbed ($G(H_2)$), and (b) the deuterium content of the hydrogen so obtained. These data are shown in Table I. In addition, the mass patterns of the

TABLE I

Substance	$G(H_2)$[a]	% Deuterium in radiolytic hydrogen[b]
CH_3CH_2OH	3.66 ± 0.26	...
CD_3CH_2OH	3.90 ± 0.15	4.27
CH_3CD_2OH	2.81[c]	42.0
CH_3CH_2OD	3.67 ± 0.08	34.2
CD_3CD_2OD[d]	2.98 ± 0.04	93–95[e]

[a] These are the averages and average deviations obtained from two or three independent irradiations. [b] Mass spectrometer analysis. [c] Single experiment. [d] Sample furnished by Tracerlab, Inc. [e] This low value must reflect contamination or exchange during work-up and analysis.

first two deutero-ethanols have been obtained in a Nier-type spectrometer; the pertinent portions of these patterns are shown in Table II.
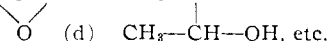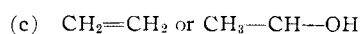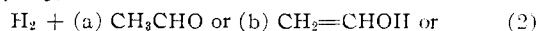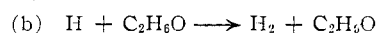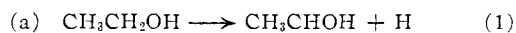
From the data in Table I, it may be concluded that $G(H_2)$ is lowered from the value observed in ethanol (3.66) to that observed in perdeutero-ethanol (2.98) by deuterium substitution only in the $-CH_2-$ group; $G(H_2)$ is unaffected by deuterium

(1) *Cf.* for example, W. McDonnell and A. S. Newton, THIS JOURNAL, **76**, 4651 (1954).

(2) The isotopic purity of these materials was 95–100% as measured by examination of the infrared spectra. These purities were confirmed by examination of the mass patterns and the nuclear magnetic resonance lines. The materials were chemically pure within the limits detectable with a Perkin–Elmer Vapor Fractometer. Infrared examination of the recovered, redistilled, irradiated alcohols showed that no randomization of the label occurred during the irradiation. No exchange between molecular hydrogen and substrate alcohol occurred (*cf.* J. G. Burr, Jr., *J. Chem. Phys.*, **25**, 587 (1956)) under the conditions of these irradiations.

(3) These doses are on the linear portion of the yield curve for hydrogen; *cf.* A. S. Newton and W. McDonnell, THIS JOURNAL, **78**, 4554 (1956),

substitution in either the CH₃– or the –OH groups. Thus the formation of radiolytic hydrogen from ethanol must be primarily a radical process (1) since molecular hydrogen formation by a monomolecular process (2) would necessarily be affected by deuterium substitution in at least two of these groups; bimolecular processes (such as (2d)) are excluded by the observed distribution of deuterium in the radiolytic hydrogen (Table I).[4]

$$(a) \quad CH_3CH_2OH \longrightarrow CH_3CHOH + H \quad (1)$$

$$(b) \quad H + C_2H_6O \longrightarrow H_2 + C_2H_5O$$

$$CH_3CH_2OH \longrightarrow$$

$$H_2 + (a) \ CH_3CHO \ or \ (b) \ CH_2{=}CHOH \ or \quad (2)$$

$$(c) \quad CH_2{=}CH_2 \ or \ CH_3{-}CH{-}OH$$
$$\underset{O}{\diagdown\diagup} \quad (d) \quad CH_3{-}CH{-}OH, \ etc.$$

In the radical process (1), the hydrogen atoms must originate almost exclusively from –CH₂–. A similar conclusion may be deduced from the mass patterns of these deuteroethanols (Table II). In the patterns of both CH₃CH₂OH and in CD₃CH₂OH the peak corresponding to the loss of one hydrogen atom is about twice the size of the parent mass peak. In the pattern for CD₃CH₂OH the peak corresponding to the loss of a deuterium atom is small—*but in the pattern for CH₃CD₂OH the peak corresponding to the loss of one hydrogen atom is very small while the peak corresponding to the loss of a deuterium atom is as large as the parent mass peak.* Thus here also the loss of a hydrogen atom from CH₃CD₂OH occurs largely from the –CD₂– group, despite the opposition offered to this preference by the deuterium isotope effect.[5]

The deuterium content of the radiolytic hydrogen produced from these three alcohols considered in conjunction with the selectivity in hydrogen atom formation (1a) discussed above demonstrates that there must also be a pronounced selectivity in the ensuing abstraction reactions (1b).[4]

It is thus apparent that the production of these radiolysis products from ethanol is not a random process even under conditions where the random process is most favored. *i.e.*, for the formation of hydrogen atoms from carbon–hydrogen bonds

(4) For the alcohol CH₃CD₂OH. a pure radical process involving only D atoms from the –CD₂– and involving only abstraction from the CH₃– and –OH would produce gas with a maximum H percentage of 50%. Any contribution by the bimolecular process (2d) or by abstraction from the –CD₂– would decrease the percentage of H. The observed percentage of H was 58% (explained by assuming a small contribution of H atoms from the CH₃ and OH). Similar deductions may be made from the data on CH₃CH₂OD radiolyses.

(5) Examination of the mass spectra of CH₃CHDCH₃ (Turkevich, Friedman, Solomon and Wrightson, THIS JOURNAL, **70**, 2638 (1948)), of CH₃CD₂CH₃ (Condon, McMurray and Thornton, *J. Chem. Phys.*, **19**, 1010 (1951)), and of CD₃CH₂CD₃ (Condon, THIS JOURNAL, **73**, 4675 (1951)) shows that electron impact removes a secondary hydrogen 13–17 times as readily as a primary hydrogen. Similarly electron impact removes a tertiary hydrogen 55 times as readily as a primary hydrogen from 2-methylpropane (Condon, McMurray and Thornton, *loc. cit.*). Finally the mass spectra of CH₃CDOHCH₃ (*idem., ibid.*), of CH₃CHODCH₃ and CH₃CDODCH₃ (Friedman and Turkevich, THIS JOURNAL, **74**, 1666 (1952)) shows that the secondary C–H bond is ruptured more frequently than either the primary C–H bonds or the O–H bond. These data, in conjunction with the data of the present paper, suggest that selectivity in C–H bond rupture is not confined to alcohols (*i.e.*, molecules containing highly electronegative atoms) and that a similar selectivity will be found in gamma irradiation of liquid propane, isobutane, and isopropyl alcohol.

which differ only slightly in bond energy, and in the liquid phase where the high collision frequency should prevent equilibration of energy among the various molecular degrees of freedom. It is further apparent that the primary processes leading to loss of hydrogen atoms are similar in the con-

TABLE II

Mass number	46 CH₃CH₂OH	49 CD₃CG₂OH	48 CH₃CD₂OH
50		4.75	
49		100.00	7.18
48		248.80	100.00
47	2.74	46.00	12.50
46	100.00	98.40	100.00
45	205.00	49.25	15.45
44	9.37	28.75	18.40
43	37.80	12.12	17.15
42	12.30	4.94	4.55
41	3.65	2.06	3.68
40	1.60	1.56	1.46
39			2.36
38			3.05

densed phase and in the gas phase at 10^{-5} mm. pressure. This suggests that the other primary processes observed in the gas phase also occur in the liquid phase but since the corresponding final stable products do not appear[6] these processes must be altered by the influence of the medium, *i.e.*, by a "cage effect" of some sort.

(6) W. McDonnell and A. S. Newton. THIS JOURNAL **76**, 4651 (1954).

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INFRARED SPECTRUM OF IRON DODECACARBONYL

Sir:

The infrared spectrum of iron dodecacarbonyl, Fe₃(CO)₁₂, has been studied previously by Sheline.[1] He reported two strong absorptions at 2020 and 2043 cm.⁻¹ attributable to C–O stretching of ordinary (end-group[2]) carbon monoxide groups; a third band at 1833 cm.⁻¹ was considered to be associated with the presence of ketone-like bridging carbon monoxide group(s) in the molecule. The validity of three possible models for the molecule was considered in the light of these data and it was concluded from symmetry arguments that the most likely structure was a linear one, which, in the nomenclature used previously,[2] would be 4-2-2-4, the two groups of two carbon monoxides forming ketonic bridges.

We have reinvestigated the infrared spectrum of Fe₃(CO)₁₂ in the C–O stretching region using both rock salt and lithium fluoride optics and also in the cesium bromide region; our observations are sum-

(1) R. K. Sheline, THIS JOURNAL, **73**, 1615 (1951).

(2) F. A. Cotton, A. D. Liehr and G. Wilkinson, *J. Inorg. Nucl. Chem..* **2**, 141 (1956).