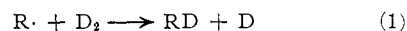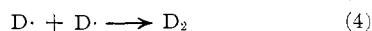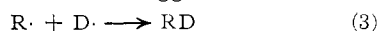ethylene. Evidence for it is based on studies of hydrogen isotope exchange between gaseous deuterium and gamma ray irradiated Marlex-50 polyethylene. Such exchange *during the irradiation* has been studied by Varshavskii, *et al.*[4] These authors postulated a chain reaction

$$R\cdot + D_2 \longrightarrow RD + D \tag{1}$$
$$D + RH \longrightarrow R\cdot + HD \tag{2}$$

Additional reactions can be suggested

$$R\cdot + D\cdot \longrightarrow RD \tag{3}$$
$$D\cdot + D\cdot \longrightarrow D_2 \tag{4}$$
$$R\cdot + R\cdot \longrightarrow RR \tag{5}$$

However, in the Russian work reaction (1) might have involved electronically excited or ionized methylene groups because of the existence of these species rather than the free radical R· during the irradiation. In order to clarify this point we have irradiated Marlex-50 at liquid nitrogen temperature and *in vacuo*, warmed the sample to room temperature, pumped off the evolved hydrogen gas and then introduced deuterium gas subsequent to the irradiation. During this treatment probably two thirds of the free radicals decayed[6]; nevertheless copious exchange up to 25% conversion of D_2 to HD involving the remaining free radicals occurred over a period of about 100 hours. During this period there was less then 0.2% decrease in the total gas pressure; thus reactions (3) and (4) may be considered negligible.[5]

Letting y represent $P_{HD}/P^0_{D_2}$ where $P^0_{D_2}$ is the initial deuterium pressure, it can be shown that for various mechanisms

$$y = \frac{1}{(b/a) - 1}[e^{-\alpha} - e^{-\beta}]$$

where $2b/a$ is the D–H fractionation factor, and α and β have the values:

	α	β
No free radical decay	at	bt
First order R· decay	$(a/k_3)(1-q)$ $q = e^{-k_3 t}$	$(b/k_3)(1-q)$
Second order R· decay	$(a/B)\ln(1+Bt)$	$(b/B)\ln(1+Bt)$

The meaning of the kinetic constants a, b, B and k_3 will be discussed in the complete paper; t is the time. Suffice it to say that for t very small, for the three sets of α and β values Eq. (6) reduces to $y \simeq at$. At long times, however, there is a marked difference between the three possibilities. Our evidence indicates that R· decays by a first order process at least at long times (the mechanism of this will be considered later); the extensive and excellent work of Lawton, Balwit and Powell[6] also demonstrates a first order decay of the alkyl free radical in irradiated Marlex-50.

Referring to Eqs. (1) and (2) it is now evident that these reactions must occur provided that excited or ionized methylene groups no longer

(4) Ya. M. Varshavskii, G. Ya. Vasil'ev, V. L. Karpov, Yu. S. Lazurkin and I. Ya. Petrov, *Doklady Akad. Nauk. S.S.S.R.*, **118**, 315 (1958).

(5) The possibility of a back thermal reaction between molecular hydrogen and irradiated polyethylene suggested by the work of Arvia and Dole, Proc. 2nd Conf. Peaceful Uses of Atomic Energy, United Nations, Geneva, 29, 171 (1958) is being further investigated.

(6) E. J. Lawton, J. S. Balwit and R. S. Powell, *J. Chem. Phys.*, **33**, 395 (1960).

existed in the polyethylene subsequent to the irradiation. It is further evident that the R· of Eq. (2) is not at the same location in the solid polyethylene as the R· of Eq. (1). Thus we have an additional mechanism for free radical migration in solid polyethylene. Increase of deuterium gas pressure should not increase dy/dt, for reasons to be discussed later, but should lower the extent of D–H exchange because of acceleration of R· decay. This prediction of the mechanism postulated here is borne out by the data.

There is a possibility that some of the exchange may be the result of a reaction in which the D-atom replaces the H-atom on the alkyl free radical without free radical migration as suggested by Voevodskii, *et al.*,[7] in a study involving exchange between deuterium gas and ethyl radicals. While such exchanges may occur to a small extent, evidence will be given later that this mechanism cannot account for the major effect.

By R·-decay in this note we include also the possibility of conversion of the alkyl to the allyl free radical.[1,2,3] Because of the greater stability of the allyl free radical, reaction (1) involving it would be less likely by a factor of about 10^{-11}.

This research was supported by the U. S. Atomic Energy Commission.

(7) V. V. Voevodskii, G. K. Lavrovskaya and R. E. Mardaleïshvili, *Doklady Acad. Nauk, S.S.S.R.*, **81**, 215 (1951).

(8) Fulbright travel grantee from the University of Louvain, Belgium.

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THE ACID-CATALYZED ISOMERIC REARRANGEMENT OF *cis* AND *trans*-5-METHYL-2-CYCLOHEXENOL-O[18]

Sir:

Several years ago the acid-catalyzed ($HClO_4$) rearrangement of *cis*- (I) and *trans*-5-methyl-2-cyclohexenol (II) in 35% aqueous acetone was investigated in these laboratories and it was found that with both isomers the pseudo first-order rate of loss of optical activity (k_α) is several times larger than that of geometric isomerization (k_i). This means that the acid-catalyzed allylic rearrangement is stereospecific in the sense that each isomer is converted to its enantiomer faster than to its geometric isomer—in this symmetrical system, allylic rearrangement without geometric isomerization results in the interconversion of enantiomers. It was suggested that the racemization with preservation of geometric configuration may involve either an SNi intramolecular rearrangement of the conjugate acids of the alcohols or an intermolecular stereospecific (*cis*) SN2' process.
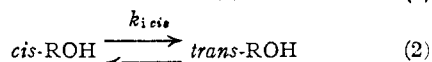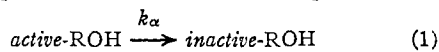

I II
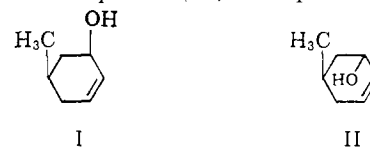
We have now reëxamined this rearrangement and have confirmed the earlier report[1] that $k_\alpha > k_i$
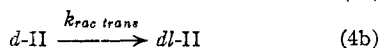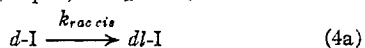
(1) H. L. Goering and E. F. Silversmith, *J. Am. Chem. Soc.*, **79**, 348 (1957).

for both isomers. In addition we have determined the pseudo first-order rate of oxygen exchange for both isomers to learn more about the excess racemization.

The three measured reactions: (a) loss of optical activity (eq. 1), (b) isomerization (eq. 2) and (c)

$$active\text{-}ROH \xrightarrow{k_\alpha} inactive\text{-}ROH \qquad (1)$$

$$cis\text{-}ROH \underset{k_{i\ trans}}{\overset{k_{i\ cis}}{\rightleftarrows}} trans\text{-}ROH \qquad (2)$$

$$RO^{18}H \xrightarrow{k_{exc}} ROH \qquad (3)$$

oxygen exchange (eq. 3), are cleanly pseudo first-order, i.e., these processes are first-order in acid (the concentration of which remains constant) and alcohol. The kinetic behavior is consistent with the interpretation that these processes involve reversible protonation of the alcohols followed by first-order transformations of the conjugate acids of the alcohols.[1] If the three rates are compared at the same acid concentration the relative magnitudes of the pseudo first-order constants correspond to those of the first-order constants for transformations of the conjugate acids of the alcohols. The pseudo first-order constant for the stereospecific racemization (k_{rac}, eq. 4) is $k_\alpha - k_i$.

$$d\text{-}I \xrightarrow{k_{rac\ cis}} dl\text{-}I \qquad (4a)$$

$$d\text{-}II \xrightarrow{k_{rac\ trans}} dl\text{-}II \qquad (4b)$$

Pseudo first-order constants for reactions 1–4 at 30° in 35% aqueous acetone containing 0.095 M HClO$_4$ are given in Table I. Rate constants for isomerization, $k_{i\ cis}$ and $k_{i\ trans}$, were determined from the pseudo first-order rate of equilibration ($k_{i\ cis} + k_{i\ trans}$) and the equilibrium constant for equation 2; $K_{eq} = k_{i\ cis}/k_{i\ trans} = 1.22$. The same values for K_{eq} and ($k_{i\ cis} + k_{i\ trans}$) were obtained with both isomers. The isomerizations were followed by capillary gas chromatography which is superior to the method used in the earlier work (infrared analysis).[1] The rates of O^{18} exchange were determined using labeled I and II. In these experiments samples of alcohol were isolated periodically by gas chromatography without fractionation of the isomers and the O^{18} contents of the alcohol fractions were determined by a previously described method.[2] Rates of loss of optical activity were determined in the usual manner.[1]

TABLE I

PSEUDO FIRST-ORDER RATE CONSTANTS FOR LOSS OF OPTICAL ACTIVITY (k_α) ISOMERIZATION (k_i) RACEMIZATION (k_{rac}) AND OXYGEN EXCHANGE (k_{exc}) FOR I AND II IN 35% AQUEOUS ACETONE ([HClO$_4$] = 0.095) at 30.2°

Isomer[a]	I	II
10 k_α, hr.$^{-1}$	1.46[b]	3.64[b,c]
10 k_i, hr.$^{-1}$	0.15 ± 0.02	0.19 ± 0.02
10 k_{rac}, hr.$^{-1}$	1.31	3.45
10 k_{exc}, hr.$^{-1}$	0.23 ± .03	1.5 ± .3

[a] Substrate concentration is 0.5 M. [b] Taken from reference 1 and corrected for acid concentration of 0.095 M. [c] This value was reconfirmed in the present work.

The data presented in Table I reveal a most

(2) H. L. Goering and M. Pombo, J. Am. Chem. Soc., **82**, 2515 (1960).

interesting phenomenon. In the cis system, the rate of oxygen exchange (k_{exc}) is far smaller than that of loss of optical activity and in fact corresponds quite closely to that of isomerization. Since isomerization undoubtedly involves exchange, this means that the excess racemization (k_α/k_i = 10) is almost completely intramolecular, i.e., an SNi' process. Such schemes have been proposed earlier[1,3] for acid-catalyzed rearrangements of allylic alcohols, however, this appears to be the first demonstration of an intramolecular allylic rearrangement of this charge type.

The trans system behaves in a completely different way. In this case k_{exc} is much larger than k_i and nearly half as large as k_α. Or to put it another way, there is substantial exchange associated with the stereospecific excess racemization. If racemization involved an SN2' displacement, k_{exc} would equal k_i plus $1/2k_{rac}$ or 1.9 hr.$^{-1}$. The value is nearly this large, which shows that in this case racemization is substantially an intermolecular or SN2'-type process with a small contribution from the intramolecular process.

The reason for the different behavior of the two isomers is not clear. It seems unlikely that the conjugate acids of the isomeric alcohols react by fundamentally different mechanisms. If the rearrangement involves a carbonium ion mechanism it is obvious that the geometric isomers give rise to different intermediates. However, this difference may be in the conformation of the symmetrical 4-methyl-2-cyclohexenyl carbonium ion or in the way that the ion is solvated.

This work was supported by a grant (G-6285) from the National Science Foundation.

(3) W. G. Young, K. Nozaki and R. Warner, ibid., **61**, 2564 (1939); E. A. Braude, Ann. Rept. Chem. Soc., **47**, 114 (1949); Quart. Rev., **4**, 404 (1950).

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MICROBIOLOGICAL ESTERIFICATION OF STEROIDS

Sir:

While many types of reactions may occur in fermentation processes,[1] the microbiological transformation of steroids most frequently involves oxidative, reductive or hydrolytic reactions.[2] Acetylation of steroids by biological systems has been reported only recently. The isolation of 11-dehydrocorticosterone acetate from normal peripheral human plasma[3] implies the presence of a C$_{21}$-acetyl transferase in mammals. Testosterone acetate has been obtained by fermentation of androstenedione with a strain of Saccharomyces fragilis.[4] The same ester was isolated from the fermentation of progesterone with Cladosporium resinae,[5] but in

(1) L. L. Wallen, F. H. Stodola and R. W. Jackson, "Type Reactions in Fermentation Chemistry," ARS 71-13, May 1959 (U. S. Department of Agriculture).

(2) E. Vischer and A. Wettstein, "Advances in Enzymology," Vol. XX, Interscience Publishers, Inc., New York, N. Y., 1958, p. 237. Earlier reviews are cited in this reference.

(3) T. E. Weichselbaum and H. W. Margraf, J. Clin. Endocrinol. and Metabolism, **20**, 1341 (1960).

(4) J. S. McGuire, E. S. Maxwell and G. M. Tomkins, Biochim. et Biophys. Acta, **45**, 392 (1960).