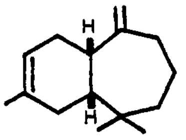
total diene product), identical in retention time and infrared spectrum with the synthetic material; β-himachalene (8%) with retention time and infrared spectrum identical with the natural material's; and a third hydrocarbon, ν_{max} 3070, 3025, 1635, 1448, 1390, 1380, 1366, 890 cm^{-1}, which is probably i (70%).



i

Acid-Catalyzed Rearrangement of α-Himachalene.—(−)-α-Himachalene (17 mg) was dissolved in 30% formic acid–ether (*ca.* 50 μl) in a capillary tube. The tube was sealed and kept at 60° for 50 hr. Glpc then showed that one substance represented 85% of the material and this was identified by retention time and by isolation and infrared spectrum as β-himachalene.

Acid-Catalyzed Rearrangement of *trans*-α-Himachalene. i.—The hydrocarbon, obtained from 95 mg of the dihydrochloride, was dissolved in 30% formic acid–ether (300 μl) in a capillary tube. The tube was sealed and heated at 80° for 24 hr. Separation of the contents by glpc gave β-himachalene identified by retention time and infrared spectrum.

ii.—The change in composition on heating such a mixture was followed with time: 2 hr, 70° (2% β, 4% *trans*-γ); 6 hr, 80° (65% *trans*-α-, 2% β, 25% *trans*-γ); 18 hr, 80° (40% *trans*-α, 5% β, 50% *trans*-γ + others). The *trans*-γ-himachalene was isolated by glpc.

Registry No.—**2**, 18766-90-0; **3**, 18766-91-1; **4**, 18791-06-5; **5**, 18766-92-2; **6**, 18791-07-6; **7**, 18766-93-3; **8**, 18766-94-4; **9** dione, 18766-95-5; cyclopentane-1,3-dione enol acetate 18766-96-6; cyclopentane-1,3-dione enol acetate in cyclopentene, 18766-97-7; **10**, 18766-98-8; **11** stereoisomers, 18766-99-9; **20**, 18767-00-5; **28**, 18767-01-6; **30**, 18767-02-7; **37**, 3883-57-6; **40**, 17894-21-2; **44**, 18791-08-7; **45**, 18766-73-9; **46**, 18766-74-0; **47**, 18766-75-1; **49**, 17928-70-0; **51**, 18791-09-8; **53**, 18791-10-1; **54**, 18791-11-2; diol A, 18766-77-3; diol B, 18766-78-4; diol C, 18766-79-5; diol D, 18766-80-8; alcohol E, 18766-81-9; hydrocarbon G, 18766-82-0; **55**, 17928-72-2; **56**, 18766-84-2; **60**, 18067-37-3.

The Mechanism of the Sulfuric Acid Catalyzed Rearrangement of Methyl and Carbonyl Carbon-14-Labeled 3,3-Dimethyl-2-butanone[1]

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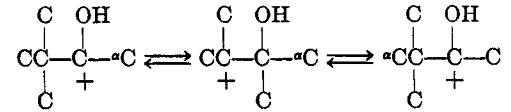
The rates of the arrangements of 3,3-dimethyl-2-butanone-1-^{14}C to 3,3-dimethyl-2-butanone-4-^{14}C and of 3,3-dimethyl-2-butanone-2-^{14}C to 3,3-dimethyl-2-butanone-3-^{14}C have been studied as a function of sulfuric acid concentration in the range from 65 to 101.5%. Rearrangement rates for both compounds are proportional to the fraction of ketone present as conjugate acid. Methyl rearrangement takes place about ten times as fast as oxygen function rearrangement in acid concentrations below 90%. At higher acid concentrations, oxygen function rearrangement becomes relatively more important. No oxygen function rearrangement mechanism *by itself* can account for this difference; the results are interpreted in terms of carbonium ion rearrangements of the ketone conjugate acid. Since the rate of the oxygen function rearrangement does not decrease in high acid concentrations where water activity is very low, the reversible pinacol formation mechanism seems to be ruled out.

Although considerable research on the scope and mechanisms of acid-catalyzed rearrangements of aliphatic and aromatic ketones has been carried out in recent years,[2] many of the mechanistic details of the reactions remain unresolved. One of the most studied compounds is pinacolone, 3,3-dimethyl-2-butanone.

3,3-Dimethyl-2-butanone-1-^{14}C has been shown[3] to rearrange reversibly to 3,3-dimethyl-2-butanone-4-^{14}C upon treatment with sulfuric acid at 30°. A careful search was made, and none of the activity originally present in the α methyl group was found in C-2 or C-3. The simplest mechanism which can account for this rearrangement is the *concerted or stepwise* interchange, **1a** ⇄ **1b**, of a labeled ($^{\alpha}$C) and an unlabeled methyl group in the conjugate acid of the ketone (eq 1).[4,5]



1a **2a** **1b**

$$\mathrm{C\overset{C}{\underset{C}{C}}\!-\!\overset{OH}{\underset{+}{C}}\!-\!{}^{\alpha}C \rightleftharpoons C\overset{C}{\underset{+}{C}}\!-\!\overset{OH}{\underset{C}{C}}\!-\!{}^{\alpha}C \rightleftharpoons {}^{\alpha}C\overset{C}{\underset{C}{C}}\!-\!\overset{OH}{\underset{+}{C}}\!-\!C} \qquad (1)$$

Parnes, Vitt and Kursanov[6] have concluded from the results of exchange experiments between D_2SO_4 and 3,3-dimethyl-2-butanone that ion **2** is not formed at low temperatures, or is short-lived and does not have time to react with D_2SO_4. However, in exchange experiments

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[1] Supported by U. S. Atomic Energy Commission Contract AT-(40-1)-3234; taken from the Ph.D. dissertation of K.B. and presented in part at the 16th Annual Midwest Chemistry Conference, Kansas City, Mo., Nov 19, 1964.

[2] For leading references to recent work, see W. H. Corkern and A. Fry, *J. Amer. Chem. Soc.*, **89**, 5888 (1967).

[3] T. S. Rothrock and A. Fry, *ibid.*, **80**, 4349 (1958).

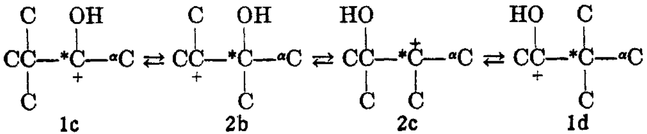
[4] This is a simplified interpretation of the mechanism given by T. E. Zalesskaya, *Zh. Obshch. Khim.*, **16**, 1813 (1946).

[5] Arabic numerals represent specific chemical species; different letters identify isotopic isomers of these species. The counterion, specific solvation and general medium effects are undoubtedly important in these reactions, but for simplicity are omitted for the present from these mechanistic formulations.

[6] Z. N. Parnes, S. D. Witt, and D. N. Kursanov, *Zh. Obshch. Khim.*, **28**, 410 (1958).

at 100°, they found deuterium in the *t*-butyl group and this points out the excellent possibility for reversible formation of ion **2**. These authors, however, propose that the 3,3-dimethyl-2-butanone rearrangement occurs by concerted interchange of two methyl groups.

Alternate mechanisms combine the alkyl shifts of eq 1 with *concerted or stepwise* transfer of the oxygen function from one carbon to another (**2b** ⇄ **2c**) by hydroxyl migration,[7] epoxide conjugate acid formation,[8]



$$\mathrm{C}\overset{\mathrm{C}}{\underset{\mathrm{C}}{\mathrm{C}}}\text{—}\overset{\mathrm{OH}}{\underset{+}{{}^{*}\mathrm{C}}}\text{—}{}^{\alpha}\mathrm{C} \rightleftarrows \mathrm{C}\overset{\mathrm{C}}{\underset{+}{\mathrm{C}}}\text{—}\overset{\mathrm{OH}}{\underset{\mathrm{C}}{{}^{*}\mathrm{C}}}\text{—}{}^{\alpha}\mathrm{C} \rightleftarrows \mathrm{C}\overset{\mathrm{HO}}{\underset{\mathrm{C}}{\mathrm{C}}}\text{—}\overset{+}{\underset{\mathrm{C}}{{}^{*}\mathrm{C}}}\text{—}{}^{\alpha}\mathrm{C} \rightleftarrows \mathrm{C}\overset{\mathrm{HO}}{\underset{+}{\mathrm{C}}}\text{—}\overset{\mathrm{C}}{\underset{\mathrm{C}}{{}^{*}\mathrm{C}}}\text{—}{}^{\alpha}\mathrm{C}$$

1c **2b** **2c** **1d**

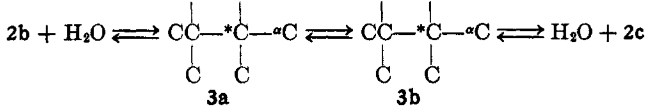
(2)

or reversible pinacol formation.[3] It should be noted that oxygen function rearrangement (eq 2, *C) is inevitably accompanied by methyl (${}^{\alpha}$C) rearrangement, but that a distinction between the two types of mechanisms could be made utilizing a carbonyl labeled (*C) compound. The oxygen function rearrangement mechanism was first demonstrated by such an experiment on carbonyl carbon-14 labeled benzopinacolone,[9] after Barton and Porter had shown[10] by a similar tracer study that it was not an important path in the rearrangement of 2,2,4,4-tetramethyl-3-pentanone to 3,3,4,4-tetramethyl-2-pentanone.

In a preliminary communication, Davis and Fry reported[11] that 3,3-dimethyl-2-butanone-2-^{14}C rearranged to 3,3-dimethyl-2-butanone-3-^{14}C in 70% perchloric acid at 100° for 3 hr, but that the labeled ketone failed to rearrange in concentrated sulfuric acid at 100° for 90 min. Further experiments have now shown that this reported failure of the oxygen function rearrangement in sulfuric acid is in error.[12]

The primary purpose of the present research was to attempt to determine the role of water in the oxygen function rearrangement of 3,3-dimethyl-2-butanone-2-^{14}C to 3,3-dimethyl-2-butanone-3-^{14}C, and to study the relative rates of rearrangement of 3,3-dimethyl-2-butanone-1-^{14}C and 3,3-dimethyl-2-butanone-2-^{14}C in solutions of varying sulfuric acid concentration.

If ion **1c** rearranged to ion **1d** by reversible pinacol formation through ion **2**, the rate of the reaction would be expected to be proportional to the activity of water as well as to the fraction, $(\mathrm{BH^+})/[(\mathrm{B}) + (\mathrm{BH^+})]$, of ketone, B, present as the conjugate acid, $\mathrm{BH^+}$ (eq 3).



$$\mathbf{2b} + \mathrm{H_2O} \rightleftarrows \mathrm{C}\overset{\mathrm{H_2\overset{+}{O}}}{\underset{\mathrm{C}}{\mathrm{C}}}\text{—}\overset{\mathrm{OH}}{\underset{\mathrm{C}}{{}^{*}\mathrm{C}}}\text{—}{}^{\alpha}\mathrm{C} \rightleftarrows \mathrm{C}\overset{\mathrm{HO}}{\underset{\mathrm{C}}{\mathrm{C}}}\text{—}\overset{\mathrm{\overset{+}{O}H_2}}{\underset{\mathrm{C}}{{}^{*}\mathrm{C}}}\text{—}{}^{\alpha}\mathrm{C} \rightleftarrows \mathrm{H_2O} + \mathbf{2c}$$

3a **3b**

(3)

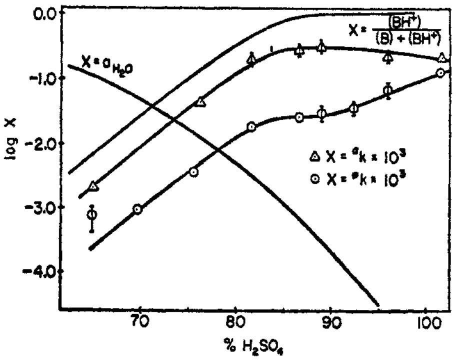


Figure 1.—A comparison of the rates of rearrangement of 3,3-dimethyl-2-butanone-1-^{14}C (${}^{\alpha}k$) and 3,3-dimethyl-2-butanone-2-^{14}C (${}^{*}k$) with the activity of water and the ratio $(\mathrm{BH^+})/[(\mathrm{B}) + (\mathrm{BH^+})]$ as a function of sulfuric acid concentration.

On the other hand, if the mechanism of the reaction involved stepwise or concerted hydroxyl migration or epoxide conjugate acid formation, other than general medium effects, no such kinetic dependence on the activity of water should be observed.

The rates of rearrangement of 3,3-dimethyl-2-butanone-1-^{14}C and 3,3-dimethyl-2-butanone-2-^{14}C were determined as a function of sulfuric acid concentration as described in the Experimental Section, and the kinetic results are summarized in Table I.

TABLE I

COMPARISON OF THE RATE CONSTANTS FOR THE REARRANGEMENT OF 3,3-DIMETHYL-2-BUTANONE-1-^{14}C AND 3,3-DIMETHYL-2-BUTANONE-2-^{14}C IN VARIOUS SULFURIC ACID CONCENTRATIONS

	$k \times 10^5$ sec^{-1}		
% $\mathrm{H_2SO_4}$	${}^{\alpha}k$ (methyl C-14)	${}^{*}k$ (carbonyl C-14)	${}^{\alpha}k/{}^{*}k$
64.9	0.215	0.0224[a]	9.6
69.9	0.81[a]	0.088	9.2
75.5	3.40[a]	0.352	9.6
76.4	4.27	0.44[a]	9.7
81.7	19.9	1.81	11.0
86.6	28.6	2.60	11.0
88.9	30.5	2.88	10.6
92.5	30.0[a]	3.50	8.6
96.0	23.3	6.72	3.5
101.5	23.6	12.82	1.9

[a] Obtained from the curves in Figure 1 so that ${}^{\alpha}k/{}^{*}k$ could be calculated.

When the logarithms of ${}^{\alpha}k$ and ${}^{*}k$ were plotted against log $(\mathrm{BH^+})/[(\mathrm{B}) + (\mathrm{BH^+})]$, straight lines of unit slope were obtained, showing, as was observed by Stiles and Mayer[13] for the rearrangement of 2,2,4,4-tetramethyl-3-pentanone to 3,3,4,4-tetramethyl-2-pentanone, that the rearrangements are first order with respect to ketone conjugate acid, $\mathrm{BH^+}$, ion **1**. The values of $(\mathrm{BH^+})/[(\mathrm{B}) + (\mathrm{BH^+})]$ used were calculated from the value of −7.1 for the pK_a of 3,3-dimethyl-2-butanone reported by Campbell and Edwards,[14] and of H_0 reported by Jorgenson and Hartter.[15]

A comparison of the rates of rearrangement of 3,3-dimethyl-2-butanone-1-^{14}C (${}^{\alpha}k$) and 3,3-dimethyl-2-butanone-2-^{14}C (${}^{*}k$) with the activity of water and the

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[7] S. Barton, F. Morton, and C. R. Porter, *Nature*, **169**, 373 (1952).

[8] H. D. Zook, W. E. Smith, and J. L. Greene, *J. Amer. Chem. Soc.*, **79**, 4436 (1957).

[9] A. Fry, W. L. Carrick, and C. T. Adams, *ibid.*, **80**, 4743 (1958).

[10] S. Barton and C. R. Porter, *J. Chem. Soc.*, 2483 (1956).

[11] C. T. Davis and A. Fry, *Chem. Ind.* (London), 277 (1960).

[12] The original notebooks and data sheets upon which the earlier report was based have been reexamined carefully, and although it is clear that there were some experimental difficulties with the degradation and derivative preparation, the results clearly indicate that the sample of ketone recovered from the sulfuric acid experiment did not contain activity in the *t*-butyl group. In view of the present results, we can offer no explanation for the earlier observation other than the possibility that a sample of starting material was accidentally mislabeled as recovered product.

[13] M. Stiles and R. P. Meyer, *Chem. Ind.* (London), 1357 (1957).

[14] H. J. Campbell and J. T. Edwards, *Can. J. Chem.*, **38**, 2109 (1960).

[15] M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, **85**, 878 (1963).

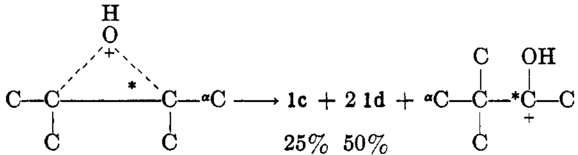
ratio $(BH^+)/[(B) + (BH^+)]$ as a function of sulfuric acid concentration is presented in Figure 1. Values of $\log X$ are plotted *vs* sulfuric acid concentration, where X is the ratio $(BH^+)/[(B) + (BH^+)]$, the activity of water, or the specific rate constant $^{\alpha}k$ or $^{*}k$. The values of the activity of water used are those reported by Giauque, Horning, Kunzler and Rubin,[16] and are in terms of hypothetically molal solutions with the activity of pure water taken to be unity. When the circles or triangles drawn to represent points are not large enough to include errors which would arise from 2% errors in activity measurements, vertical lines representing such error limits are shown (see Experimental Section).

While the general shapes of the curves for a_{H_2O} and the ratio $(BH^+)/[(B) + (BH^+)]$ *vs.* sulfuric acid concentration are bound to be approximately correct, the exact shapes and positions on the acid scale may be subject to considerable question, since the actual reaction medium, being about 20% ketone, is considerably different from that in which the H_0 and pK_a values were measured. For this reason, in the subsequent arguments, no quantitiative correlations between exchange rates, BH^+ concentrations, or a_{H_2O} values were attempted; the arguments depend only on the general parallelism, or lack of parallelism in the shapes of the curves.

It is noted from Figure 1 that as the sulfuric acid concentration increases, the ratio $(BH^+)/[(B) + (BH^+)]$ for 3,3-dimethyl-2-butanone gradually increases up to the point where the ketone is completely protonated, and then remains approximately constant, whereas the activity of water gradually decreases, and, at very high acid concentrations, becomes practically negligible. If water is not involved in or prior to the rate-determining step of the rearrangement, the plot of $\log {}^{\alpha}k$ or $\log {}^{*}k$ *vs.* sulfuric acid concentration should be parallel to that for $\log (BH^+)/[(B) + (BH^+)]$ *vs.* sulfuric acid concentration. On the other hand, if water is involved in or prior to the rate-determining step, the plot of $\log {}^{\alpha}k$ or $\log {}^{*}k$ should be parallel to that for $\log (BH^+)/[(B) + (BH^+)]$ only in lower acid concentrations (where the activity of water is sufficiently high to be considered constant) while in very high concentrations of sulfuric acid (where the activity of water is sufficiently low) the rate would decrease, giving a curve with a maximum.[17]

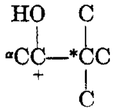
The plot of the log of the specific rate constant for 3,3-dimethyl-2-butanone-1-C^{14} ($^{\alpha}k$) *vs.* sulfuric acid concentration has the same shape as that for $\log (BH^+)/[(B) + (BH^+)]$ *vs.* sulfuric acid concentration, up to ~92% sulfuric acid, and beyond that the rate decreases somewhat. Thus the rate of rearrangement of the methyl group is not influenced by the activity of water, except, perhaps, in ~92% or more concentrated sulfuric acid. The plot of the log of the specific rate constant for 3,3-dimethyl-2-butanone-2-^{14}C ($^{*}k$) *vs.* sulfuric acid concentration also has the same shape as that for $\log (BH^+)/[(B) + (BH^+)]$ *vs.* sulfuric acid concentration up to ~92%, but beyond that the rate rapidly increases. The slopes of the lines at the lower sulfuric acid concentrations are the same (1.18) for the three plots. The fact that the rate of oxygen function rearrangement does not decrease in high concentrations of sulfuric acid is strong evidence against any mechanism, such as reversible pinacol formation, eq 3, in which water is involved in or prior to the rate-determining step.

The cause for the lack of parallelism between the plots of $\log {}^{\alpha}k$, $\log {}^{*}k$ and $\log (BH^+)/[(B) + (BH^+)]$ *vs.* sulfuric acid concentration in the high acid concentration region is best discussed in terms of the ratio of rate constants, $^{\alpha}k/^{*}k$ (see Table I). At acid concentrations up to about 90%, the ratio is nearly constant at about 10, but at higher acid concentrations, it decreases markedly. If any of the concerted or stepwise oxygen function rearrangement paths indicated by eq 2 or 3 were the *only* rearrangement mechanism, the ratio $^{\alpha}k/^{*}k$ would be 3/2. This is easily seen since some chemically symmetrical species (pinacol, the conjugate acid of the epoxide, or the hydroxyl migration transition state **4a**—which must resemble closely the epoxide conjugate acid) must be involved between ions **2b** and **2c.** In the initial stages of reaction of any such species, neglecting isotope effects, there must be an equal migration probability for each of the four methyl groups.



4a **1e**, 25%

There is no way to form the isotopic isomer **1f**



1f

in the initial reaction, although it could form later from **1e.** Initially then, the ratio $^{\alpha}k/^{*}k$ will be given by $(\mathbf{1d} + \mathbf{1e})/\mathbf{1d} = 75\%/50\% = \frac{3}{2}$. Furthermore, at equilibrium three-fourths of the labeled methyl groups will be in the *t*-butyl groups, and one-half of the activity initially present in the carbonyl group will have rearranged to the *t*-butyl group; so $^{\alpha}k/^{*}k = (\frac{3}{4})/(\frac{1}{2}) = \frac{3}{2}$. A more detailed kinetic analysis[18] shows that the $\frac{3}{2}$ ratio holds throughout the course of the reaction. Clearly then, since the ratio is about 10 instead of $\frac{3}{2}$, some additional mechanism such as eq 1 (concerted or stepwise), which leads to methyl interchange without oxygen function rearrangement, must be operative. The methyl interchange, eq 1, is about six times as probable as hydroxyl interchange (or oxygen function rearrangement by any other mechanism), eq 2, in sulfuric acid solutions up to about 90% concentration. Perhaps this much greater migration tendency for methyl than hydroxyl is related to the likely high degree of interaction of the solvent with the unshared electron pairs of the hydroxyl group compared to the nearly unsolvated methyl group. Alternatively, methyl interchange might be a fast concerted reaction (transi-

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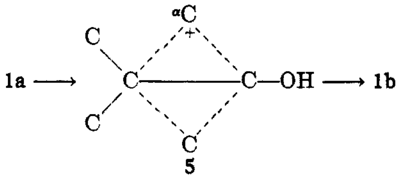
[16] W. F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, *J. Amer. Chem. Soc.*, **82,** 62 (1960).

[17] W. M. Schubert and R. C. Zahler, *ibid.*, **76,** 1 (1954).

[18] K. Bhatia, Ph.D. Dissertation, University of Arkansas, Fayetteville, Ark., 1965.

tion state **5**) in competition with a slower stepwise oxygen function rearrangement.



5

The ratio ${}^{\alpha}k/{}^{*}k$ decreases with increasing acid concentration above about 90% sulfuric acid (Table I and Figure 1). At these high acid concentrations, essentially all of the ketone is present as the conjugate acid. It is clear that the decrease in ${}^{\alpha}k/{}^{*}k$ arises more from an increase in ${}^{*}k$ than a decrease in ${}^{\alpha}k$, and it is tempting to think that it is caused by the incursion of a concerted epoxide conjugate acid mechanism at high acid concentrations as the hydroxyl group and the adjacent positive carbon become less encumbered by tightly bound solvent molecules as the water concentration becomes negligible. If this is so, the path represented by eq 2, with stepwise migration of the hydroxyl group (**2b** → **2c**), would be the main mechanism for oxygen function rearrangement in sulfuric acid below about 90%, with epoxide conjugate acid formation becoming more important in competition with it at higher acid concentrations. (As pointed out above, the transition state for hydroxyl migration, **4**, resembles the epoxide conjugate acid very strongly, differing only in the degree of bonding of oxygen to carbon. A decrease in solvation of the hydroxyl group and the adjacent positive carbon should permit the hydroxyl group to approach the carbon atoms more closely.) No distinction can be made on the basis of the present evidence between concerted or stepwise methyl migration (**1a** → **1b**), but since ion **2** appears to be involved in the oxygen function rearrangement, it is appealing to think that it is also involved in the methyl rearrangement.

Bimolecular reaction products (disproportionation products) are known to be formed from some ketones upon treatment with acid.[19] It is conceivable that some such reaction could account for the rearrangements being studied here, so a careful gas chromatographic search was made for disproportionation products, especially 4,4-dimethyl-3-pentanone. It was estimated that any disporportionation products present in as much as 1% concentration could be detected, but no trace of them was found. In view of other work on the disproportionation reaction,[20] none would be expected from a ketone such as 3,3-dimethyl-2-butanone.

Experimental Section

Activity Determinations.—Activity determinations were carried out by the method described previously.[21] Activity balances obtained by comparing the sums of the activities of degradation products to the activity of the starting ketone were generally good, indicating that no side reactions affecting the molar activity of the ketone has occurred during the rearrangement.

Preparation and Radiochemical Purity of 3,3-Dimethyl-2-butanone-1-^{14}C and 3,3-Dimethyl-2-butanone-2-^{14}C.—3,3-Dimethyl-2-butanone-1-^{14}C and 3,3-dimethyl-2-butanone-2-^{14}C were prepared[22] by the methods described previously.[3,11] Final purification of the labeled compounds was by preparative gas chromatography. In order for meaningful results to be obtained from the rearrangement experiments, it was necessary to demonstrate that the labeled starting materials were radiochemically pure, and that they were labeled exclusively in the indicated positions. Activity results (millicuries/mol) on the ketones, ketone derivatives, and degradation products (using the procedure described below) follow: 3,3-dimethyl-2-butanone-1-^{14}C (neat, 0.5329 ± 0.018); 2,4-dinitrophenylhydrazone recrystallized once from ethanol–water [mp 126–127° (lit.[23] mp 126–127°), 0.5360 ± 0.012]; 2,4-dinitrophenylhydrazone recrystallized twice from ethanol–water and once from petroleum ether (mp 126–127°, 0.5531 ± 0.006); acetanilide from degradation [mp 113° (lit.[24] mp 113–114°), 0.5497 ± 0.008]; 2,4-dinitrophenylsulfenyl derivative of *t*-butyl alcohol from degradation [mp 118–119° (lit.[25] mp 118–119°), 0.000]; 3,3-dimethyl-2-butanone-2-^{14}C (neat, 0.6858 ± 0.01); 2,4-dinitrophenylhydrazone recrystallized once from ethanol–water (mp 126–127°, 0.6996 ± 0.01); 2,4-dinitrophenylhydrazone recrystallized twice from ethanol–water and once from petroleum ether (mp 126–127°, 0.7146 ± 0.0075); acetanilide from degradation (mp 113°, 0.7106 ± 0.01); 2,4-dinitrophenylsulfenyl derivative from *t*-butyl alcohol from degradation (mp 118–119°, 0.000). The slightly lower activities of the neat ketones than of their derivatives is due to the presence, as shown by gas chromatography, of about 1% of an inactive impurity which was present in the inactive ketone used to dilute the originally prepared active compounds. Since it was removed in the derivative preparation and degradation procedures, this impurity caused no serious problems. It is clear that no radioactive impurities were present. Furthermore, since the activities of the acetanilide samples agree with those of the ketone 2,4-dinitrophenylhydrazones, and since no activity was found in either *t*-butyl alcohol derivative, it is clear that the two starting materials were uniquely labeled as indicated.

Degradation of 3,3-Dimethyl-2-butanone-X-^{14}C.—The procedure used previously for degradation of 3,3-dimethyl-2-butanone-X-^{14}C was rather long and involved, and exactly reproducible results proved to be difficult to obtain. Accordingly, an alternate, simple, reliable procedure was developed involving peroxybenzoic acid oxidation of the ketone to *t*-butyl acetate, from which acetic acid and *t*-butyl alcohol derivatives were prepared for carbon-14 analysis. For either labeled ketone any methyl or oxygen function rearrangement would result in the presence of activity in the *t*-butyl alcohol derivative, and a corresponding reduction in the activity of the acetic acid derivative.

Peroxybenzoic Acid Oxidation of 3,3-Dimethyl-2-butanone-X-^{14}C.—A solution of 5.85 g (0.0424 mol) of peroxybenzoic acid in 80 ml of methylene chloride was added to 4.0 g (0.040 mol) of 3,3-dimethyl-2-butanone-X-^{14}C and the reaction mixture was maintained at 40.5 ± 0.5° for 28 hr. Distillation using a short Vigreux column yielded 6 g of a fraction, bp 60–94°, containing about 90% *t*-butyl-X-^{14}C acetate-X-^{14}C and 10% methylene chloride. Careful analysis of this material by gas chromatography on triethylene glycol, 1,2,3-tris-2-cyanoethoxypropane, β,β'-oxydipropiontrile, and Carbowax columns demonstrated[18] the complete absence of the starting ketone and of methyl pivalate. In accordance with the observations of Hawthorne, Emmons, and McCallum,[26] it is clear that the *t*-butyl group migrates to the practical exclusion of the methyl group in the peroxybenzoic acid oxidation of 3,3-dimethyl-2-butanone.

Hydrolysis of *t*-Butyl Acetate and Preparation of Acetic Acid and *t*-Butyl Alcohol Derivatives.—The 6-g *t*-butyl-X-^{14}C acetate-X-^{14}C fraction from the peroxybenzoic acid oxidation was refluxed for 18 hr with 7 g of barium hydroxide in 15 ml of water. Distillation, using a short Vigreux column, yielded 3 g of a fraction, bp 40–48°, containing mostly *t*-butyl-X-^{14}C alcohol and a small amount of methylene chloride.

The residue in the distillation flask was evaporated to dryness,

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[22] We are indebted to Mr. Robert Barnes for carrying out these syntheses.

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[24] Reference 23, Vol. I, p 6.

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TABLE II

KINETIC AND DEGRADATIVE DATA FROM THE REARRANGEMENT OF 3,3-DIMETHYL-2-BUTANONE-1-^{14}C IN 76.4% SULFURIC ACID AND OF 3,3-DIMETHYL-2-BUTANONE-2-^{14}C IN 75.5 AND 86.6% SULFURIC ACID AT 100 ± 2°

Reaction time, min × 10^{-3}	Degradation product molar activities, mCi/mol: Acetanilide	$(NO_2)_2C_6H_3SOC(CH_3)_3$	Σ
76.4% Sulfuric Acid, 3,3-Dimethyl-2-butanone-1-^{14}C, 0.3420 mCi/mol			
1.20	0.1785	0.1661	0.3446
3.16	0.1087	0.2339	0.3426
4.40	0.0957	0.2490	0.3447
75.5% Sulfuric Acid, 3,3-Dimethyl-2-butanone-2-^{14}C, 0.5838 mCi/mol			
6.15	0.4375	0.1416	0.5791
15.23	0.3525	0.2281	0.5806
24.00	0.3189	0.2615	0.5804
30.60	0.3076	0.2725	0.5801
86.6% Sulfuric Acid, 3,3-Dimethyl-2-butanone-2-^{14}C, 0.7146 mCi/mol			
1.25	0.5100	0.2062	0.7162
2.50		0.2767	
3.30	0.3927	0.3178	0.7105
4.20		0.3345	
4.90	0.3639	0.3476	0.7115

and treated carefully with 10 ml of phosphorus oxychloride at 0°. The reaction mixture was left overnight in a closed container at 0–5°, and 0.3 g of acetyl-X-^{14}C chloride was distilled from the reaction mixture. This was treated with aniline to form the acet-X-^{14}C-anilide, mp 113° (lit.[24] mp 113–114°), used for carbon-14 analysis.

The 3-g sample of *t*-butyl-X-^{14}C alcohol was diluted with 10 ml of methylene chloride, dried overnight with magnesium perchlorate, and treated with 1 g of 2,4-dinitrophenylsulfenyl chloride. The solution was warmed, treated with 1 ml of dry pyridine, allowed to stand at room temperature for 15 min, and filtered. The filtrate was evaporated to dryness using a water suction pump, and the yellow residue was washed five times with water and recrystallized twice from absolute alcohol to give the 2,4-dinitrophenylsulfenyl derivative of *t*-butyl-X-^{14}C alcohol, mp 118–119° (lit.[25] mp 118–119°), which was used for carbon-14 analysis.

Kinetics of Rearrangement of 3,3-Dimethyl-2-butanone-1-^{14}C and 3,3-Dimethyl-2-butanone-2-^{14}C in Sulfuric Acid.—Sulfuric acid solutions of various accurately known concentrations were prepared by standard methods. In a typical kinetic experiment, 43 g of 3,3-dimethyl-2-butanone-2-^{14}C was added to 220 g of 75.5% sulfuric acid while the temperature was maintained at 20° using a water bath. The two components were mixed thoroughly and the reaction mixture was divided into four fractions of 47, 58, 72 and 89 g which were left in an oil bath at 100 ± 2° for 10.25, 25.38, 40.00, and 51.00 hr, respectively. The reaction mixtures were poured on cracked ice, made alkaline with 8 *M* sodium hydroxide, and extracted with methylene chloride. The methylene chloride layer was washed with water, dried and distilled using a short Vigreux column to yield 3,3-dimethyl-2-butanone-X-^{14}C, which was degraded and analyzed for carbon-14 content as described above. Other complete kinetic experiments were conducted with 3,3-dimethyl-2-butanone-2-^{14}C in 86.6% sulfuric acid, and on 3,3-dimethyl-2-butanone-1-^{14}C in 76.4% sulfuric acid. The kinetic and degradative data for these experiments are given in Table II. It is to be noted that the agreement between the activity of the starting ketone and the sum of the activities of the degradation products from the recovered rearranged ketones is excellent in all cases. Additional rearrangement reactions were carried out at 100 ± 2° with the two labeled ketones at various other sulfuric acid concentrations. The ketone/acid solution ratio was the same for all experiments. The results are given in Table III.

Calculation of Rate Constants.—For reversible isotopic isomerization reactions it can be shown[3,18] that the rate law for the loss of activity from the original position has the form of eq 4,

$$\log (A_0 - A_e)/(A - A_e) = (k_f + k_r)t \qquad (4)$$

where A_0, A_e, and A are initial, equilibrium, and instantaneous concentrations (proportional to molar activities) of the labeled species, and k_f and k_r are the specific rate constants for the forward and reverse reactions. The similar expression for the gain of activity in the isomeric position is eq 5.

$$\log (A_0 - A_e)/(A_e - A) = (k_f + k_r)t \qquad (5)$$

Plots of the logarithmic functions of eq 4 and eq 5 were made for the data in Table II, and excellent straight lines were obtained. Similar "two point" plots were made for the data in Table III. It is to be noted that the points for $\log (A_0 - A_e)/(A - A_e)$ and $\log (A_0 - A_e)/(A_e - A)$ for a given experiment are complementary, but are derived from different experimental measurements. That the two points generally fall together[18] adds weight to the validity of using these "two point" plots for rate constant calculations. The slopes of all these lines were computed by the

TABLE III

RESULTS OF REARRANGEMENT REACTIONS AT 100 ± 2° OF 3,3-DIMETHYL-2-BUTANONE-1-^{14}C AND 3,3-DIMETHYL-2-BUTANONE-2-^{14}C AT VARIOUS SULFURIC ACID CONCENTRATIONS

Acid concn, %	Reaction time, min × 10^{-3}	Molar activities, mCi/mol: Starting ketone	Acetanilide	$(NO_2)_2C_6H_3SOC(CH_3)_3$	Σ
3,3-Dimethyl-2-butanone-1-^{14}C					
64.9	5.40	0.5531	0.4628	0.0917	0.5545
81.7	0.45	0.3420	0.1358		
86.4	0.36	0.3420	0.1251		
88.9	0.30	0.3420	0.1330	0.2108	0.3438
96.0	0.40	0.5531	0.2116	0.3401	0.5517
101.5	0.46	0.5531		0.3590	
3,3-Dimethyl-2-butanone-2-^{14}C					
64.9	4.20	0.5838	0.5538	0.0247	0.5785
69.9	24.00	0.5838	0.1607	0.4208	0.5815
81.7	3.05	0.5838	0.3507	0.2325	0.5832
81.7	3.30	0.5838	0.3431		
88.9	3.30	0.5838	0.3032	0.2711	0.5743
92.5	1.25	0.5838	0.3733	0.2054	0.5787
96.0	0.95	0.5838	0.3242	0.2509	0.5751
101.5	0.30	0.5838	0.3736	0.1955	0.5681

least-squares method, yielding values for $(k_f + k_r)$. In general, $K_e = k_f/k_r$, where K_e is the isotopic equilibrium constant. Ordinarily, as in the present case, if isotope effects are neglected, these equilibrium constants involve only statistical factors. Thus, at equilibrium, for 3,3-dimethyl-2-butanone-1-^{14}C, K_e = **1b**/**1a** = 3 and $(k_f + k_r) = \frac{4}{3}k_f$. The experimental rate constant, $^{\alpha}k$, is equal to k_f, and is obtained by dividing the least squares slope by $\frac{4}{3}$. Similarly, for 3,3-dimethyl-2-butanone-2-^{14}C, $K_e = 1$, and $^{*}k$ is obtained by dividing the least squares slope by 2. The values for $^{\alpha}k$ and $^{*}k$ calculated in this manner are tabulated in Table I. Sample calculations, assuming 2% errors in activity measurements, give values for $^{\alpha}k$ and $^{*}k$ which fall within the circles or triangles in Figure 1, or which are specifically indicated by the vertical lines on the points in Figure 1. The usual activity measurement error is more like 0.5–1.0%. These calculations reflect only errors resulting from variations in counting data, which is probably the largest source of error, but other errors such as in the determination of the sulfuric acid concentration, the time of reaction, errors in the work-up procedure, etc., might cause some additional uncertainties in the rate constant values. These are probably not very important since the points in Table II fall very nicely on straight line kinetic plots.

Registry No.—Sulfuric acid, 7664-93-9; 3,3-dimethyl-2-butanone-1-^{14}C, 17032-76-7; 3,3-dimethyl-2-butanone-2-^{14}C, 17032-75-6.

Photochemical Addition of 4,4-Dimethyl-2-cyclohexenone to Tetramethylethylene[1]

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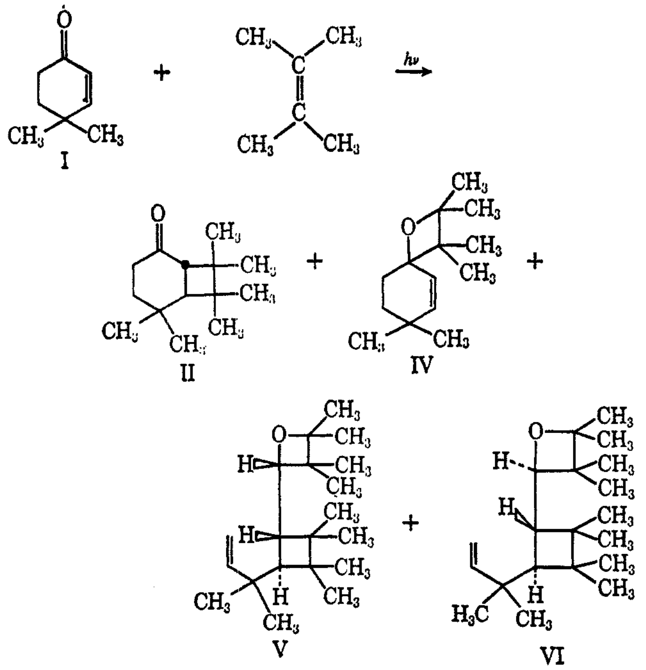
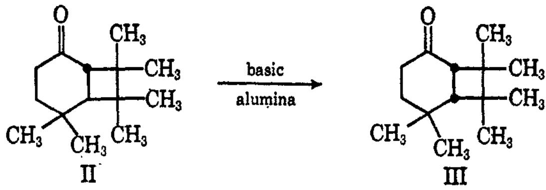
Irradiation of 4,4-dimethyl-2-cyclohexenone in the presence of tetramethylethylene gives *trans*-5,5,7,7,8,8-hexamethylbicyclo[4.2.0]octan-2-one and an oxetane as major products. In addition, two novel secondary photoproducts are isolated and characterized.

Photochemical addition of cycloalkenones to olefins has found substantial use in synthesis since the initial investigations by Corey[3] and Eaton.[4] We wish to describe the photochemical addition of 4,4-dimethyl-2-cyclohexenone to tetramethylethylene which has three special features. First, only *trans*-cyclobutane adduct is formed, second the oxetane is a major product, and third two novel minor products are formed.

Scheme I



Irradiation of 4,4-dimethyl-2-cyclohexenone (I) in neat tetramethylethylene or in *t*-butyl alcohol containing tetramethylethylene in a Pyrex vessel using a Rayonet reactor with 3500-Å lamps gives two major products and several minor products (Scheme I). The products isolated are shown below. The major products account for 89% of the starting material destroyed. The *trans* adduct II shows the expected spectroscopic properties, molecular weight, and elemental analysis (see Experimental Section) and is isomerized by basic alumina to *cis*-5,5,7,7,8,8-hexamethylbicyclo[4.2.0]octan-2-one (III). Vapor chromatography of the crude product from the irradiation showed the absence of *cis* adduct III. The oxetane IV showed no infrared carbonyl absorption but did show double bond absorption. The nmr spectrum (see Experimental Section) showed the presence of six methyl groups on saturated carbon, two olefinic protons as an AB pattern, $^3J_{AB} = 10.3$ Hz, and four methylene protons. Elemental analysis was consistent with the formula $C_{14}H_{24}O$. The mass spectrum did not show a significant parent ion but did show intense ions at m/e 150 $(M - C_3H_6O)$ and 135 $[(M - C_3H_6O) - CH_3]$. These fragment ions correspond to sequential loss of acetone and a methyl group from the parent ion. The minor oxetane products (V and VI) were first isolated from the crude reaction mixture but were more easily prepared by a reaction described in Scheme II.



The minor oxetane products (V and VI) were best prepared by irradiation of *trans*-5,5,7,7,8,8-hexamethylbicyclo[4.2.0]octan-2-one in the presence of tetramethylethylene in *t*-butyl alcohol (Scheme III). They

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(1) Photochemical Transformations. XXX. Portions of this work were described at the 2nd Midwest Regional Meeting of the American Chemical Society, Lawrence, Kansas, Oct 1966.

(2) National Science Foundation Undergraduate Research Participant, summer 1967.

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