mmoles) of *m*-chloroperbenzoic acid. This mixture was heated at 70° for 10 min and then poured into 50 ml of water. The water was extracted with 50 ml of ether. The ether was washed with water and with 10% sodium carbonate solution and was then dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation, and the resulting solid was recrystallized from 95% ethanol to give 280 mg (90%) of XIV, mp 224–225°.

The pmr spectrum of XIV in deuteriochloroform showed doublets at $\tau$ 5.23 (two protons, $J_{12}$ = 4.6 cps) and at 5.64 (one proton, $J_{15}$ = 7.2 cps), a doublet of triplets centered at $\tau$ 6.23 (one proton), and a multiplet due to aromatic protons from $\tau$ 1.9 to 3.0 (18 protons).

*Anal.* Calcd for $C_{28}H_{22}O_4S_2$: C, 69.12; H, 4.56. Found: C, 69.29; H, 4.60.

Oxidation of the thioether XIII with excess hydrogen peroxide in acetic acid followed by the usual work-up but omitting the 10% sodium carbonate wash gave results identical with those obtained with the *m*-chloroperbenzoic acid oxidation.

When 90 mg of the sulfone XIV was heated in 3 ml of glacial acetic acid-O-*d* (90% monodeuterated) at 70° for 10 min, then poured into 5 ml of deuterium oxide (99.5% minimum assay), and then extracted with 10 ml of anhydrous ether, a pmr spectrum of the resulting solid showed no deuterium incorporation into XIV.

Deuterium exchange of the benzylic protons was carried out in the same manner as the exchange reactions with the methyl ether VIII and the thioether XIII. *syn*-2,*syn*-8-Dideuterio-*anti*-2,*anti*-8-bis(phenylsulfonyl)-*cis*-dibenzobicyclo[3.3.0]-3,6-octadiene (XV) was obtained in 88% yield and was recrystallized from 95% ethanol, mp 224–225°, undepressed with XIV. The pmr spectrum in deuteriochloroform showed doublets (one proton each) at $\tau$ 5.64 and at $\tau$ 6.23 ($J_{15}$ = 7.2 cps) and a multiplet due to 18 aromatic protons from $\tau$ 1.9 to 3.0.

Treatment of 150 mg of the bis(phenyl sulfone) XIV for 10 min in a refluxing solution of 50 mg of sodium metal dissolved in 1 ml of dioxane and 7 ml of absolute ethanol gave no reaction. Only starting material (130 mg) was recovered, mp and mmp 224–225°.

**Oxidation of the Thioether XIII with Hydrogen Peroxide in Methanol.** To a solution of 50 mg (0.1 mmole) of XIII in 10 ml of methanol held at reflux was added 1 ml of 30% hydrogen peroxide. This mixture was heated at reflux for 1 hr whereupon an additional 1 ml of 30% hydrogen peroxide was added. The resulting solution was heated at reflux for an additional 2 hr, cooled, and poured into 50 ml of a 5% sodium bisulfite solution. The mixture was extracted well with ether, and the ether extracts were combined and dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation, and a pmr spectrum of the resulting oil showed no starting material present and indicated the presence of only XIV. The sample was crystallized from 95% ethanol to give 30 mg (60%) of XIV, mp and mmp 224–225°.

**Attempted Addition of Thiophenol and Methanol to 1-Phenylsulfonyldibenzotricyclo[3.3.0.0$^{2,8}$]-3,6-octadiene (I).** When the cyclopropyl sulfone I was treated under the same reaction conditions as the cyclopropyl sulfone II was treated, neither thiophenol nor methanol reacted with I. The use of higher temperatures (up to 180°) and longer periods of time (up to 3 days) still led to no observable (pmr spectra) reaction although the reaction mixtures became very dark.

**Attempted Nucleophilic Addition of Water to the Cyclopropyl Sulfone II.** When 1 g of II was treated with 190 mg of potassium hydroxide dissolved in 5 ml of water and 5 ml of dioxane in a sealed tube at 180° for 30 hr, no observable (pmr spectra) reaction took place. The use of varying amounts of water and dioxane had no effect upon the reaction. The use of *t*-butyl alcohol in conjunction with water and dioxane still had no effect on the course of the reaction.

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# Reactions of Ketones and Related Compounds with Solid Supported Phosphoric Acid Catalyst. I. The Scope and Mechanisms of Ketone Rearrangements[1a]

**Walter H. Corkern[1b] and Arthur Fry**

*Contribution from the Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701.* *Received December 30, 1966*

**Abstract:** Open-chain aliphatic ketones and some aldehydes can be rearranged easily with a high recovery of fairly extensively rearranged material by passing the carbonyl compound over a bed of solid supported phosphoric acid catalyst at elevated temperature. The rearrangement products are usually accompanied by numerous low retention time materials. It was found that ketones which have branching adjacent to the carbonyl group rearrange at lower temperatures than their straight-chain isomers. However, the branched-chain ketones decompose readily at temperatures which result in good yields of rearrangement products from the straight-chain ketones. Several carbonium ion type mechanisms are suggested for the reaction, and for cases where more than one product might be obtained, the one expected from the path which involves the most stable carbonium ions is always the major rearrangement product.

Most recent research on acid-catalyzed ketone rearrangements has been carried out in homogeneous solutions in sulfuric or perchloric acid.[2] In order to obtain extensive rearrangement in many of these systems, it is necsssary to work at such high temperatures and acid concentrations that most of the starting material is converted to intractable polymeric material. For instance, treatment of 3-pentanone with 72% perchloric acid at 100° for 12 hr resulted in a 1.9% recovery of a mixture of 2- and 3-pentanone containing 12% of the rearranged isomer, 2-pentanone.[3,4]

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(1) (a) Supported by U. S. Atomic Energy Commission Contract AT-(40-1)-3234; taken from the Ph.D. dissertation of W. H. C. and presented in part at the American Chemical Society 20th Southwest Regional Meeting, Shreveport, La., Dec 4, 1964. (b) Monsanto Fellow, 1963–64.

(2) For leading references to recent work, see (a) I. Ookuni and A. Fry, *Tetrahedron Letters*, 989 (1962); (b) T. E. Zalesskaya and T. B. Remizova, *Zh. Obshch. Khim.*, **35**, 31 (1965).

(3) A. Fry, I. Ookuni, G. J. Karabatsos, J. D. Graham, and F. Vane, *J. Org. Chem.*, **27**, 1914 (1962).

**Table I.** Results of Rearrangement of Straight-Chain Ketones over Solid Supported Phosphoric Acid Catalyst

| Run | Starting ketone | Product | Temp, °C | No. of passes | Product in ketonic fraction, % | Ketonic material in recovered material, % |
|---|---|---|---|---|---|---|
| 1 | 3-Pentanone | 2-Pentanone | 300 | 10 | 27.8 | ~50 |
| 2 | 2-Pentanone | 3-Pentanone | 300 | 10 | 15.4 | ~50 |
| 3 | 3-Pentanone | 2-Pentanone | 300 | Many | 68 ± 1 | . . . |
| 4 | 2-Pentanone | 3-Pentanone | 300 | Many | 31 ± 1 | . . . |
| 5 | 3-Hexanone | 2-Hexanone | 300 | 7 | 11 | 85 |
| 6 | 2-Hexanone | 3-Hexanone | 300 | 10 | 23 | 80 |
| 7 | 2-Heptanone | 3-Heptanone | 300 | 10 | 13 | 75 |
|  |  | 4-Heptanone | 300 | 10 | 1.3 | 75 |
| 8 | 3-Heptanone | 2-Heptanone | 300 | 10 | 9.0 | 82 |
|  |  | 4-Heptanone | 300 | 10 | 8.6 | 82 |
| 9 | 4-Heptanone | 3-Heptanone | 300 | 10 | 16.7 | 87 |
|  |  | 2-Heptanone | 300 | 10 | 0.8 | 87 |

In the present work many acidic catalysts were tried in a search for a system which would permit reasonable recoveries of extensively rearranged ketonic material. A flow system utilizing repetitive passes of the ketone over a column of solid supported phosphoric acid[5] at elevated temperature proved to be the best by far of any of the systems tried. For instance, in contrast to the above result, ten passes of 3-pentanone over the catalyst at 300° resulted in 50% recovery of a mixture of 2- and 3-pentanone containing 28% of the rearranged isomer, 2-pentanone.[6] In other cases the recoveries and amounts of rearrangement were even higher. The present paper deals with the scope and mechanisms of rearrangements of ketones utilizing this catalyst system. In previous work,[2] branched-chain ketones were shown to rearrange readily, but straight-chain compounds gave only very small yields of isomeric ketones. A striking result of the catalyst system used here is the extensive rearrangement which takes place with these straight-chain compounds, as shown in Table I.

Interconversion can be accomplished easily between 2- and 3-pentanone, between 2- and 3-hexanone, and between 3-heptanone and 2- and 4-heptanone; however it is generally not possible to obtain the equilibrium mixture starting with either isomer. After ten passes over the catalyst 3-pentanone was converted into 2-pentanone to the extent of 27.8%, and 2-pentanone was converted into 3-pentanone to the extent of 15% (runs 1 and 2). Twenty passes over the catalyst produced very little change in these percentages; however, when fresh ketone was passed over the same catalyst it rearranged readily. During successive passes over the catalyst, low-boiling impurities build up in the product, and it appears that these impurities cause the ketone rearrangement reaction to slow down and eventually stop. Perhaps these materials preferentially absorbed on the active catalyst sites and prevented further rearrangement from occurring.

The equilibrium ratio, 68 ± 1% 2-pentanone and 31 ± 1% 3-pentanone, was obtained from a series of experiments on synthetic mixtures of 2- and 3-pentanone (runs 3 and 4). Fresh ketone was passed over the catalyst 10–20 times and the product was analyzed to determine the amount of isomerization. A synthetic mixture of pure 2- and 3-pentanone was prepared which contained the two ketones in the same ratio as the analyzed product. The mixture was passed over the catalyst, and the more extensively rearranged product was analyzed. This procedure was repeated until there was no further change in the ratio of ketones. Starting with either isomer, it was possible to obtain the equilibrium concentrations stated above.

A word of caution should be given here about measuring the equilibrium composition by the above procedure. For this method to be valid, both compounds must be equally stable in the reaction system. That is, the irreversible destruction of one of the equilibrium members should not occur at a faster rate than that of the other member. In many cases studied, it appears that this condition is not met.

In runs 7–9, 2-, 3-, and 4-heptanone were subjected to the catalyst to see how rapidly the functional group could move along the carbon chain. The possibility of a 1,3 shift of the functional group was also considered. When 2-heptanone was passed over the catalyst (run 7), forming 3-heptanone, only a very small amount of 4-heptanone was produced. The reaction material was analyzed after each catalyst pass, and 4-heptanone was not even detected until a fairly large amount of 3-heptanone was already present in the reaction product. Similarly, in run 9, starting with 4-heptanone, 3-heptanone was formed and only a trace of 2-heptanone was detected. Again the minor product was not detected until a considerable amount of 3-heptanone was already present in the reaction mixture. The results from run 8 indicate that 2- and 4-heptanone are produced in approximately equal amounts from 3-heptanone. These data seem to indicate that the 4-heptanone formed in the 2-heptanone experiment and the 2-heptanone formed in the 4-heptanone experiment were in actuality formed from 3-heptanone. Clearly a 1,3 shift of the oxygen function is not required, and certainly is not predominant.

In the various mechanisms proposed for acid-catalyzed ketone rearrangements, the first and last steps always involve reversible equilibria between ketones and their conjugate acids, RCOR + $A^+ \rightleftarrows RC^+(OA)R$. The rearrangement step may then simply consist of concerted

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[4] In most ketone rearrangements, it is easy to visualize the relationship between reactants and products as involving interchange of a group attached directly to the carbonyl carbon on one side with one attached to the $\alpha$ carbon on the other side, $RCR_2'COR'' \rightarrow R''CR_2'COR$. The interchange is accomplished without actual exchange of the two groups by some mechanisms.

[5] We are indebted to Dr. Michel Blanchard for suggesting this type of catalyst.

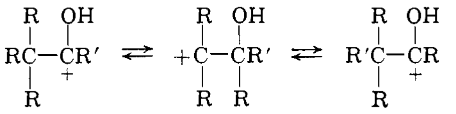
[6] The expected 3-pentanone disproportionation reaction[2a] products, butanone and 3-hexanone, were obtained from this experiment, but the yields were very small.

Table II. Results of Rearrangement of Branched-Chain Ketones over Solid Supported Phosphoric Acid Catalyst

| Run | Starting ketone | Product | Temp, °C | No. of passes | Product in ketonic fraction, % | Ketonic material in recovered material, % |
|---|---|---|---|---|---|---|
| 10 | 2-Methyl-3-pentanone | 3-Methyl-2-pentanone | 230 | 10 | 11.3 | 95 |
| 11 | 3-Methyl-2-pentanone | 2-Methyl-3-pentanone | 230 | 10 | 15.8 | 95 |
| 12 | 2-Methyl-3-pentanone | 3-Methyl-2-pentanone | 300 | 5 | 31 | Extensive dec |
|  |  | 4-Methyl-2-pentanone | 300 | 5 | 0.0 | Extensive dec |
| 13 | 4-Methyl-2-pentanone | 2-Methyl-3-pentanone | 300 | 6 | 0.0 | 95 |
| 14 | 2-Methyl-3-hexanone | 3-Methyl-2-hexanone | 300 | 3 | 24.4 | 25 |
|  |  | 5-Methyl-3-hexanone | 300 | 3 | 1 | 25 |
| 15 | 3-Methyl-2-hexanone | 2-Methyl-3-hexanone | 300 | 1 | 23.7 | 50 |
| 16 | 5-Methyl-3-hexanone | 5-Methyl-2-hexanone | 300 | 10 | 4.1 | 90 |
|  |  | 2-Methyl-3-hexanone | 300 | 10 | *a* | 90 |
| 17 | 5-Methyl-2-hexanone | 5-Methyl-3-hexanone | 300 | 5 | 7.6 | 90 |
| 18 | 2,4-Dimethyl-3-pentanone | 3,4-Dimethyl-2-pentanone | 330 | 1 | 32 | 20 |

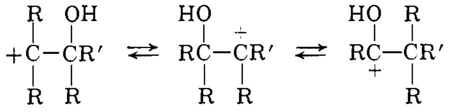
[a] A small amount of this compound was present in the starting material.

or stepwise alkyl–alkyl and/or alkyl–hydrogen interchange.[7,8]



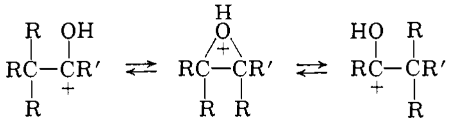
$$\mathrm{R\overset{R}{\underset{R}{C}}-\overset{OH}{\underset{+}{C}}R' \rightleftarrows {}^{+}\overset{R}{\underset{R}{C}}-\overset{OH}{\underset{R}{C}}R' \rightleftarrows R'\overset{R}{\underset{R}{C}}-\overset{OH}{\underset{+}{C}}R} \qquad (1)$$

Other mechanisms include the alkyl (or hydrogen) shift above. The first of these shifts may be followed by, or concerted with, OH migration.[9]

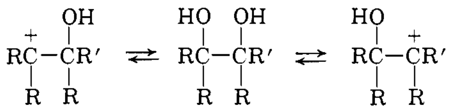


$$\mathrm{{}^{+}\overset{R}{\underset{R}{C}}-\overset{OH}{\underset{R}{C}}R' \rightleftarrows R\overset{HO}{\underset{R}{C}}-\overset{+}{\underset{R}{C}}R' \rightleftarrows R\overset{HO}{\underset{+}{C}}-\overset{R}{\underset{R}{C}}R'} \qquad (2)$$

It should be noted that the oxygen function is located on a different carbon in the product than in the reactant. This oxygen function rearrangement was demonstrated experimentally in 1958 in a benzopinacolone carbon-14 tracer experiment,[10] after Barton and Porter had shown[11] by a similar tracer experiment 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. Mechanism 3 involves oxygen function rearrangement by stepwise or concerted epoxide conjugate acid formation.[12] The oxygen function rearrangement may also take place by reversible pinacol formation.[13]



$$\mathrm{R\overset{R}{\underset{R}{C}}-\overset{OH}{\underset{+}{C}}R' \rightleftarrows R\underset{R}{C}\overset{\overset{H}{O^{+}}}{-}\underset{R}{C}R' \rightleftarrows R\overset{HO}{\underset{+}{C}}-\overset{R}{\underset{R}{C}}R'} \qquad (3)$$



$$\mathrm{R\overset{+}{\underset{R}{C}}-\overset{OH}{\underset{R}{C}}R' \rightleftarrows R\overset{HO}{\underset{R}{C}}-\overset{OH}{\underset{R}{C}}R' \rightleftarrows R\overset{HO}{\underset{R}{C}}-\overset{+}{\underset{R}{C}}R'} \qquad (4)$$

An additional pathway not considered in previous work would involve reversible alkyne formation (where there are two hydrogens on one of the carbons $\alpha$ to the carbonyl group).

$$\mathrm{RCOCH_2R' \rightleftarrows RC{\equiv}CR' \rightleftarrows RCH_2COR'} \qquad (5)$$

The results on the straight-chain ketones shown in Table I can be rationalized in terms of any of the above mechanisms. However, the stepwise version of mechanism 1, while the simplest formulation of all, would involve formation of a high-energy primary carbonium ion, and hence is probably not a very likely possibility.

The results obtained from experiments on branched-chain ketones are given in Table II. Runs 10 and 11 demonstrate that good rearrangement yields can be obtained with little decomposition when branched-chain ketones are subjected to the catalyst. Significant mechanistic information is provided by the data from runs 12 and 13. 2-Methyl-3-pentanone could give either 3-methyl-2-pentanone or 4-methyl-2-pentanone, or both, by either mechanism 1 or an oxygen function rearrangement mechanism, 2, 3, 4, or 5. Path A below (mechanism 1) proceeds through secondary carbonium ion intermediates to 3-methyl-2-pentanone. Path B below (mechanism 1) involves primary carbonium ion and leads to 4-methyl-2-pentanone. Oxygen function rearrangement mechanisms 2, 3, and 4 (illustrated by

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

[8] 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.

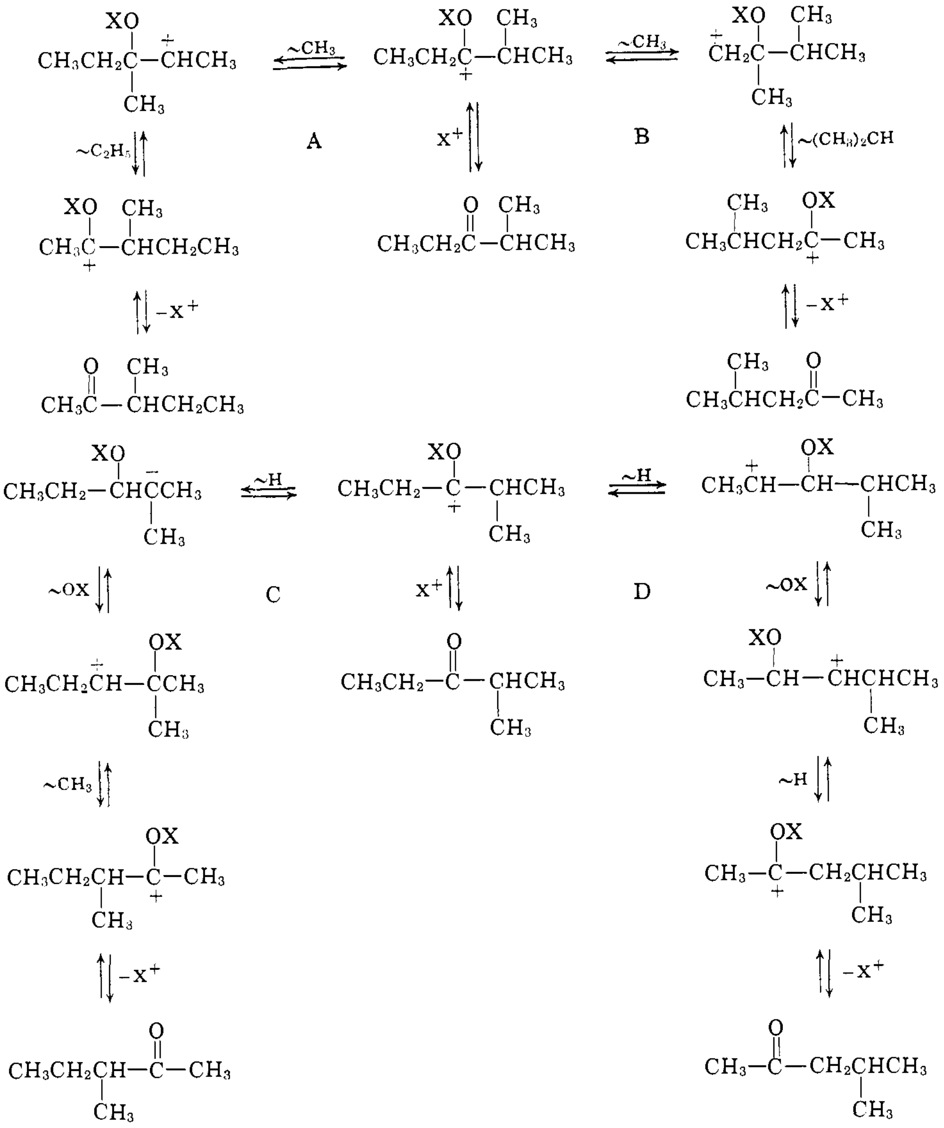
[9] S. Barton, F. Morton, and C. R. Porter, *Nature*, **169**, 373 (1952).

[10] A. Fry, W. L. Carrick, and C. T. Adams, *J. Am. Chem. Soc.*, **80**, 4743 (1958).

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

[12] H. D. Zook, W. E. Smith, and J. L. Green, *J. Am. Chem. Soc.*, **79**, 4436 (1957).

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



2) would also lead to the formation of the same two compounds.

Finally according to mechanism 5, 2-methyl-3-pentanone could form 4-methyl-2-pentanone through 4-methyl-2-pentyne, but not 3-methyl-2-pentanone.

The results from run 12 indicate that only 3-methyl-2-pentanone was formed from 2-methyl-3-pentanone. Since 4-methyl-2-pentanone was not formed, paths B and D and mechanism 5 must not operate in this case. The reaction probably proceeded either by path A or C (or the mechanism 3 or 4 equivalent of path C), or by a combination of these paths. On the basis of the relative stabilities of carbonium ions, one logically would have favored path A (secondary ions) over path B (primary ions) and path C (secondary and tertiary ions) over path D (secondary ions). However, if path C were operating, it would perhaps be surprising that no path D product at all would be formed. The high recovery of 4-methyl-2-pentanone in run 13 indicates its high stability to the reaction conditions and shows clearly that failure to detect it in run 12 was not due to its decomposition.

An attempt to produce 2-methyl-3-pentanone from 4-methyl-2-pentanone (run 13) was fruitless. Even though the reverse of path B appeared unlikely, it was considered that reaction according to mechanism 5 or the reverse of path D was a possibility. One possible explanation for the fact that no 2-methyl-3-pentanone was detected in run 13 is that it might have decomposed as soon as it formed. Support for this idea was obtained by a study of the gas chromatographic low retention time materials present in the products produced in runs 12 and 13. Each of the low retention time materials present in run 13 was present in run 12. Therefore, the possibility remains that a small amount of 2-methyl-3-pentanone was formed and was completely decomposed as soon as it formed. However, it should be pointed out that only a small amount of rearrangement could have occurred by mechanism 5 or the reverse of path D since there was a 95% recovery of the starting material.

Similar mechanistic information was obtained from runs 14–17. Consistent with rearrangement *via* the most stable carbonium ions, 2-methyl-3-hexanone forms mostly 3-methyl-2-hexanone. However, the fact that some 5-methyl-3-hexanone is formed in run 14 *requires* at least some reaction by an oxygen function rearrangement path (mechanism 2, 3, 4, or 5).

Runs 14 and 15 demonstrate the ease with which 2-methyl-3-hexanone and 3-methyl-2-hexanone can be interconverted. The much more difficult interconversion of 5-methyl-2-hexanone and 5-methyl-3-hexanone

**Table III.** Results Obtained by Passing Some Cyclic Ketones over Solid Supported Phosphoric Acid Catalyst

| Run | Starting material | Product | Temp, °C | No. of passes | Product in recovered material, % | Recovered material, % |
|---|---|---|---|---|---|---|
| 19 | 2,6-Dimethylcyclohexanone | Methyl 2-methylcyclopentyl ketone | 300 | 3 | Trace | 75 |
| | | *m*-Xylene | 300 | 3 | 58.5 | 75 |
| | | *o*-Xylene | 300 | 3 | 19.5 | 75 |
| 20 | *m*-Xylene | *o*-Xylene | 300 | 3 | 0.0 | 95 |
| 21 | 2-Methylcyclohexanone | Methyl cyclopentyl ketone | 230 | 1 | Trace | 90 |
| | | Toluene | 230 | 1 | 5 | 90 |
| 22 | Cyclohexanone | Benzene | 300 | 1 | 3 | 80 |

**Table IV.** Results of Isomerization of Aldehydes over Solid Supported Phosphoric Acid Catalyst

| Run | Starting aldehyde | Product | Temp, °C | No. of passes | Product in carbonyl fraction, % | Carbonyl material in recovered material, % |
|---|---|---|---|---|---|---|
| 23 | Trimethylacetaldehyde | Methyl isopropyl ketone | 300 | 1 | 100 | 91 |
| 24 | Isobutyraldehyde | Butanone | 300 | 3 | 100 | 49 |
| 25 | Propionaldehyde | Acetone | 300, 230 | 1 | 0 | Polymer, etc. |

(runs 16 and 17) is most readily accounted for by the fact that paths similar to A and C are not available to these compounds (because of no α branching). Also, the higher recovery of ketonic material in runs 16 and 17 compared to 14 and 15 shows that 5-methyl-2-hexanone and 5-methyl-3-hexanone are much more stable to the catalyst at 300° than their isomeric compounds 2-methyl-3-hexanone and 3-methyl-2-hexanone which have branching adjacent to the carbonyl group. This is similar to the results obtained from the compounds studied in runs 12 and 13.

Run 18 demonstrates that a compound which has branching on both sides of the carbonyl group rearranges when it is subjected to this catalyst. Undoubtedly higher recovery of ketonic material could be obtained by working at lower temperature.

The results obtained from experiments on a few cyclics are given in Table III. If the rearrangement of 2,6-dimethylcyclohexanone and of 2-methylcyclohexanone were to occur by the usual intramoleuclar mechanism, methyl 2-methylcyclopentyl ketone and methyl cyclopentyl ketone, respectively, would be expected as products. The results of runs 19 and 21 indicate that only traces of these two compounds are formed; the major reaction products, aromatic hydrocarbons, result from a dehydration and dehydrogenation process. Since no *o*-xylene was produced when *m*-xylene was passed over the catalyst (run 20), the reaction probably proceeds by rearrangement of α-hydrogen or α-methyl to the carbonyl carbon of the ketone conjugate acid, followed by loss of a β-proton to give a monoolefin, dehydration to a diene, and dehydrogenation to *m*- or *o*-xylene.

Some results from the treatment of aldehydes with the catalyst are given in Table IV. Trimethylacetaldehyde is converted almost quantitatively into 3-methyl-2-butanone (a conversion accomplished by numerous acidic media), and isobutyraldehyde is converted to butanone (a previouly unreported rearrangement so far as we can determine). Only polymeric material, no acetone, could be obtained from propionaldehyde.

A series of competitive experiments demonstrates that branched-chain ketones rearrange more readily than straight-chain ketones, as expected from relative carbonium ion stabilities. At 250° after two passes over the catalyst, no rearrangement of 3-pentanone to 2-pentanone or 3-hexanone to 2-hexanone could be detected, but 2-methyl-3-pentanone rearranged to 3-methyl-2-pentanone to the extent of 3.3%, and 2,4-dimethyl-3-pentanone rearranged to 3,4-dimethyl-2-pentanone to the extent of 3.6%. At 310°, 3-pentanone did rearrange to 2-pentanone, but the extent of the reaction, 11.8%, was only about half of the 20.4% of 3-methyl-2-pentanone obtained from 2-methyl-3-pentanone at the same temperature. When a mixture of 3-pentanone, 3-hexanone, 2-methyl-3-pentanone, and 2,4-dimethyl-3-pentanone was passed over the catalyst five times at 300°, no rearrangement products of the straight-chain ketones could be detected. Large amounts of the expected branched-chain isomers, 3-methyl-2-pentanone and 3,4-dimethyl-2-pentanone, were obtained, again indicating the greater ease of rearrangement of branched- than straight-chain compounds. The branched-chain compounds also decompose more readily than the straight-chain compounds, as shown by the low recovery of the former compared to the latter.[14]

Reversible alkyne formation, mechanism 5, cannot be the only mechanism for these ketone rearrangements, since compounds with branching on both carbons α to the carbonyl group (and compounds like benzopinacolone[10]) rearrange readily. However, it is well known

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(14) One of the decomposition products from 3-pentanone was identified as 2-pentene. No 2-pentanone or 3-pentanone was obtained when a mixture of 2-pentene and water was passed over the catalyst.

that alkynes can be converted to ketones by treatment with acids in the presence of a catalyst, and Schaad and Ipatieff have shown[15] that alkynes are converted to ketones by a solid supported phosphoric acid catalyst.[16] They reported that 1- and 2-pentyne were converted to 2-pentanone.[17]

When a mixture of 2-pentyne and water was passed over the catalyst at 300°, 40.5% of the recovered material was 3-pentanone and 43.2% was 2-pentanone after one pass. Only a trace of the alkyne was left after the first pass over the catalyst, and none at all could be detected after the second pass. A similar experiment on 1-pentyne gave 12.6% 3-pentanone and 72.3% 2-pentanone.

The fact that no pentynes could be detected after the first pass in the above experiments and that no pentynes could ever be detected when ketones were the starting materials provides evidence, albeit not conclusive, against the operation of mechanism 5 in those cases where an alkyne could be formed.

Additional evidence, still not conclusive for all cases, against mechanism 5 is provided by experiments with 4-methyl-2-pentyne. A mixture of the alkyne and water was passed over the catalyst five times at 300°. The results of the gas chromatographic analysis of the products are presented in Table V. Clearly, 4-methyl-2-pentanone is the major reaction product, together with smaller amounts of 2-methyl-3-pentanone and 3-methyl-2-pentanone. The 4-methyl-2-pentanone and 2-methyl-3-pentanone are the products expected from direct hydration of the alkyne. 2-Methyl-3-pentanone has been shown (Table II) to rearrange to 3-methyl-2-pentanone, *but not to 4-methyl-2-pentanone.* The present data show that if 2-methyl-3-pentanone were to dehydrate to form 4-methyl-2-pentyne, 4-methyl-2-pentanone would be the major product.

**Table V.** Gas Chromatographic Analyses of the Products Formed in the 4-Methyl-2-pentyne Experiment

| No. of passes | Starting material, % | 4-Methyl-2-pentanone, % | 2-Methyl-3-pentanone, % | 3-Methyl-2-pentanone, % | Impurities, % |
|---|---|---|---|---|---|
| 0 | 98.1 | 0.0 | 0.0 | 0.0 | 1.9 |
| 1 | 13.0 | 40.4 | 16.6 | 7.4 | 22.6 |
| 3 | Trace | 46.8 | 13.7 | 8.9 | 30.6 |
| 5 | Trace | 47.0 | 12.5 | 8.8 | 31.7 |

It is more difficult to eliminate any of the other suggested mechanisms, and it seems very likely that compounds with different structures will react by different mechanisms. For highly branched chain ketones, mechanism 1 must be favored in view of the tracer results of Barton and Porter.[11] However, for straight-chain ketones, at least the stepwise version of that mechanism would require an intermediate primary carbonium ion, whereas all of the oxygen function rearrangement mechanisms would proceed through secondary carbonium ions. Although a different catalyst system (sulfuric acid) was used, Bhatia's[18] study of the effect of water activity (at high acid concentrations) on the rate of oxygen function rearrangement in pinacolone seems to eliminate mechanism 4, reversible pinacol formation, for that case at least. For the hydroxyl migration path, mechanism 2, the transition state must look very much like an epoxide conjugate acid, mechanism 3, and we have been able to think of no experiment which will provide a definitive choice between the two.

## Experimental Section

**Preparation of Solid Supported Phosphoric Acid Catalyst.**[16] Chromosorb W (75 g, 60–80 mesh) was mixed with 340 g of 85% phosphoric acid, and a uniform paste was made. The paste was compressed into a porcelain evaporating dish and baked for 36 hr at 120° in an open air oven, forming a solid cake. The catalyst was removed from the oven and forced through an 8-mesh screen in order to break it up into small pieces. The catalyst was then stored in an amber bottle. In some experiments 60–80 mesh Firebrick was substituted for Chromosorb W, giving a catalyst of equal activity. Celite, alumina, and several commercially available silica–alumina supports for the phosphoric acid were also tried, and although rearrangement was obtained in most cases, these preparations generally had poorer physical handling properties, lower rearrangement activity, or both. Approximately the same rearrangement activity was obtained using a variation in the proportion of phosphoric acid to support of four to nine parts by weight.

In the preliminary search for a catalyst system which would provide high rearrangement activity and low formation of polymeric or low molecular weight decomposition products, commerical concentrated sulfuric, perchloric, phosphoric, hydrofluoric, hydrochloric, hydrobromic, hydriodic, monofluorophosphoric, and difluorophosphoric acids were investigated. Although some rearrangement was observed in most cases, extensive polymerization and decomposition always occurred.

**General Procedure for Ketone Rearrangements on Solid Supported Phosphoric Acid Catalyst.** About 50 g of solid supported phosphoric acid catalyst was packed into a 75 × 1.8 cm Pyrex tubing column. The catalyst bed was supported by indentations in the glass about 12 cm from the bottom of the column. The bottom of the column was fitted with an ice-water condenser, which discharged into a two-necked flask. The side neck of the receiver was positioned so that the sample could easily be removed for recycling with a 4-in. syringe needle. The top of the column was fitted with a T tube closed at the top by a rubber septum. The side arm of the T tube was connected to a nitrogen source, and during a run a nitrogen flow rate of 5–10 cc/min was maintained. The sample, contained in a syringe, was injected through the rubber septum onto the heated catalyst bed. The injection rate was controlled by driving the syringe plunger by means of a 28-threads/in. drive column connected to a 2-rpm, 25-w, synchronous motor. Variation in the injection rate was obtained by varying the size of the syringe. (It could also be accomplished by changing the number of threads per inch on the drive column, or by using a motor with a different speed.) Using a 20-ml syringe, the injection rate was 20 ml/hr; with a 50-ml syringe it was 65 ml/hr. The packed part of the column was heated by two 2-ft semicircular refractories enclosed in a magnesia-insulated sheet metal furnace. The temperature was regulated by a variable transformer and measured by a 360° thermometer placed alongside the column. Before use, the packed column was heated to the desired reaction temperature for several hours with no sample or nitrogen passing through it. During this heating period a considerable amount of water was driven from the catalyst.

In a typical experiment, 10 ml of a ketone contained in a 20-ml syringe was injected onto the catalyst bed at 300° over a 0.5-hr period. The rearranged ketone, volatile decomposition and condensation products, and in some cases a small amount of water were condensed by the ice-water condenser and collected in the receiver. The material in the receiver was removed with the syringe and recycled as often as needed. Eventually the column packing became black due to the accumulation of decomposition materials. After a number of passes over the catalyst, the recovered material

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(15) R. E. Schaad and V. N. Ipatieff, *J. Am. Chem. Soc.*, **62**, 178 (1940).

(16) V. N. Ipatieff, U. S. Patent 1,993,513 (March 5, 1935).

(17) In view of our results, it is probable that they had a mixture of 2- and 3-pentanone. The physical properties of the two are almost identical.

(18) K. Bhatia, Ph.D. Dissertation, University of Arkansas, Fayetteville, Ark., 1965.

contained a considerable amount of gas chromatographic low retention time material (10–30 peaks). These materials apparently interfered with the rearrangement, since successive catalyst passes gave less and less rearrangement, even though the ratio of ketones was far from the equilibrium value and fresh ketone passed over the catalyst rearranged readily.

Using the above procedure, a number of ketones and related compounds were studied to determine the scope and mechanisms of the rearrangement reactions. The results are given in Tables I–V. In these scope experiments, no attempts were made to determine optimum temperatures or flow rates.

**Analytical Procedures.** After the required number of passes over the catalyst, the recovered material was removed from the receiver, dried, and without further purification analyzed by gas chromatography. The gas chromatographs used in this study were Model A-90-C, A-700 Autoprep, and 600-C Hy-Fi Wilkens Instrument and Research, Inc., instruments. Some 26 different chromatographic columns were employed, utilizing a wide variety of sizes, lengths, liquid phases, and solid supports.

When a reaction product was analyzed on the gas chromatographic column, the retention time of each separated component was obtained. Then, while the column remained under the same conditions, a standard mixture containing the starting ketone and the expected rearranged products was analyzed for the retention times of its components. If the retention time of any peak in the reaction product was about the same as that of any of the standard compounds, a standard mixture which contained approximately the same concentrations as those of the reaction product was prepared and it and the reaction product were analyzed on several columns of different polarity. A change in the polarity of the column substrate often resulted in greatly changed retention times and, in some cases, inversion of the order in which compounds eluted. The use of several columns of different polarity ensures the correct identity of the compound under study. By a study of relative areas of eluted peaks on one column in comparison with another column one was ensured of studying the same compound (peak) under study on the other column. In some cases, small amounts of known compounds were added to the reaction product to determine whether a particular peak's relative area increased in comparison to the other peaks or whether two peaks would form. If two peaks formed, the peak under study was not identical with the known compound.

The percentage compositions given in the tables were calculated from the integrated areas of the gas chromatographic peaks without correction for variation of sensitivity with compound structure. For the closely related compounds involved in this study, this procedure gives results accurate to 1% or better, as shown by analysis of known mixtures. The per cent of ketonic material in the recovered material is perhaps not quite so accurate since compounds of different types are being compared.

In a number of cases, the rearranged ketone was isolated by preparative chromatography. For these isolated samples, the gas chromatographic retention times on several columns, the nuclear magnetic resonance and infrared spectra, and the properties of derivatives were found to be identical with those of authentic samples.[19]

**Reactions of Alkynes with Solid Supported Phosphoric Acid Catalyst.** To test for the possible intermediacy of alkynes in the observed ketone rearrangements, 1-pentyne, 2-pentyne, and 4-methyl-2-pentyne were passed over the catalyst. Samples (15 ml) of the alkynes were used, and during the injection, a 5-ml sample of water was gradually injected from a separate syringe. The results of the 1- and 2-pentyne experiments are given in the text above, and those for 4-methyl-2-pentyne are given in Table V.

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(19) Further details of the separations and analyses are given in the Ph.D. dissertation of W. H. C., University of Arkansas, Fayetteville, Ark., 1966.

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# Reactions of Ketones and Related Compounds with Solid Supported Phosphoric Acid Catalyst. II. A Carbon-14 Tracer Study of the Mechanism of the Rearrangement of 3-Pentanone to 2-Pentanone[1a]

**Arthur Fry and Walter H. Corkern**[1b]

*Contribution from the Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701.*

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**Abstract:** Extensive rearrangement of 3-pentanone to 2-pentanone is accomplished by repeated passage over solid supported phosphoric acid catalyst at 340–360°. 3-Pentanone-3-$^{14}C$ rearranged almost exclusively to 2-pentanone-3-$^{14}C$ rather than 2-pentanone-2-$^{14}C$, indicating that an oxygen function rearrangement mechanism must be operative.

Acid-catalyzed rearrangements of straight-chain aliphatic ketones to isomeric ketones were unknown prior to the 1960 report[2] of the rearrangement of 3-pentanone to 2-pentanone in perchloric acid solution. For appreciable rearrangement to take place, sufficiently drastic conditions had to be used (*e.g.*, 72% perchloric acid, 100°, 12 hr) so that the recovered pentanone fraction amounted to only a few per cent of the starting material.[3] However, using a solid supported phosphoric acid catalyst, and starting with either 2- or 3-pentanone, good recoveries of extensively rearranged ketone are obtained.[4] This discovery made practical a detailed carbon-14 tracer study of the mechanism of the rearrangement.

The various mechanisms suggested for acid-catalyzed ketone rearrangements[4] fall into two classes, those which involve transfer of the oxygen function from one carbon to another, and those which do not. It is pos-

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(1) (a) Supported by U. S. Atomic Energy Commission Contract AT-(40-1)-3234; taken from the Ph.D. dissertation of W. H. C. and presented at the American Chemical Society Midwest Regional Meeting, Lawrence, Kan., Oct 27, 1966. (b) Monsanto Fellow, 1963–1964.

(2) A. Fry, M. Eberhardt, and I. Ookuni, *J. Org. Chem.*, 25, 1252 (1960) (the extent of the rearrangement was later shown[3] to be considerably less than originally reported).

(3) A. Fry, I. Ookuni, G. J. Karabatsos, J. D. Graham, and F. Vane, *ibid.*, 27, 1914 (1962).

(4) Paper I of this series: W. H. Corkern and A. Fry, *J. Am. Chem. Soc.*, 89, 5888 (1967).