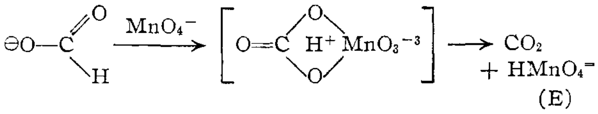
electrophilic nature of the permanganate oxygen and the electron donor character of the charged oxygen atom of the formate. This mechanism is in a sense analogous to the mechanism proposed by Denney[8] for the rearrangement of 9-decalyl hydroperoxide benzoate.

Since approximately one-half of the oxygen introduced into the formate came from the permanganate, mechanism E may be considered, in which one of the oxygens of the formate and one from the permanganate become equivalent in the intermediate. Cleavage of the intermediate would then lead to carbon dioxide in which one oxygen would have one-half the O^{18} content of the permanganate. An equivalent result would be obtained if the intermediate in mechanism C would permit an exchange of the MnO_3 group from one oxygen to the other. It unfortunately does not appear possible to obtain direct evidence concerning these possible mechanisms at the present time.



(E)

SEATTLE, WASHINGTON

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[8] D. B. Denney, THIS JOURNAL, **77**, 1706 (1955).

[CONTRIBUTION FROM THE ROLLIN H. STEVENS MEMORIAL LABORATORY OF THE DETROIT INSTITUTE OF CANCER RESEARCH]

The Rearrangement of Some Substituted Allyl Alcohols to their Isomeric Ketones[1]

BY ANDRE S. DREIDING AND JOHN A. HARTMAN[2]

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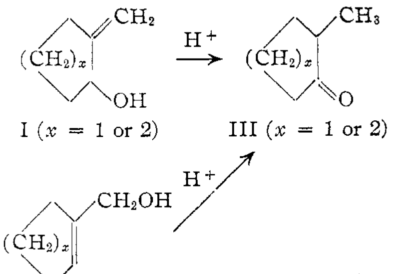
The allylic pair 2-methylenecyclohexanol and 1-cyclohexenemethanol rearrange to the isomeric 2-methylcyclohexanone in the presence of sulfuric acid. Similar results are obtained in the homologous five-membered ring series.

It has been shown that the enolic forms of some β-dicarbonyl compounds are reduced by an excess of lithium aluminum hydride to give one or a pair of substituted allyl alcohols, the number being dependent on the symmetry of β-dicarbonyl compound.[3]

A pair of allyl alcohols obtained by such a procedure is usually characterized by their susceptibility to the acid-catalyzed oxotropic rearrangement which results in the more stable isomer. However, complete conversion is often not realized in the absence of some stabilizing factor such as conjugation and, at elevated temperatures, etherification and/or dehydration may compete with rearrangement.[4]

The isolation of the 2-methylenecycloalkanols (I) (x = 1 and 2) and the 1-cycloalkenemethanols (II) (x = 1 and 2) has furnished two pairs of isomeric allyl alcohols which should be capable of undergoing at least a partial rearrangement on treatment with acid.[3] A projection of the work of Brown[5] on the stabilities of double bonds, *exo vs. endo*, in five- and six-membered rings has been attempted on these two pairs of alcohols in the absence of experimental evidence. It has been predicted that in the six-membered ring series the primary alcohol II (x = 2) should be more stable in a potential anionotropic system and, conversely, the secondary alcohol I (x = 1) should be favored in the five-membered ring series.[6]

We wish to report that in a given series both alcohols were unstable to acid and were converted to their isomeric 2-methylcycloalkanone (III).



I (x = 1 or 2) III (x = 1 or 2)

II (x = 1 or 2)

In early experiments, in the formation of I and II, the alcoholate complexes from the lithium aluminum hydride reductions were worked up with dilute sulfuric acid. The isolated products gave small yields of a semicarbazone. This was in contrast to a high yield of the 2,4-dinitrophenylhydrazone (DNPH) of III which formed immediately with a 5% solution of the reagent in 50% sulfuric acid at room temperature. The formation of a semicarbazone could not be observed when the lithium aluminum–alcohol complex was decomposed by the weakly alkaline Rochelle salt.[7] However, the alcohols (I and II) retained the property of precipitation with the acid 2,4-dinitrophenylhydrazine solution. The secondary alcohols (I) reacted more rapidly than the primary (II) and gave slightly higher yields, both giving the same DNPH of III.[8]

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[1] This work was supported by institutional grants from The American Cancer Society, Inc., The American Cancer Society, Southeastern Michigan Division and the Kresge Foundation.

[2] To whom inquiries should be addressed.

[3] A. S. Dreiding and J. A. Hartman, THIS JOURNAL, **75**, 939, 3723 (1953).

[4] E. A. Braude, *Quart. Rev.*, **4**, 404 (1950).

[5] H. C. Brown, J. H. Brewster and H. Schecter, THIS JOURNAL, **76**, 467 (1954).

[6] O. H. Wheeler, Abstracts of the 125th Meeting of the American Chemical Society, Kansas City, Mo., April 1954, p. 25-N. See also *Chem. and Ind.*, 900 (1954).

[7] R. E. Lutz and J. S. Gillespie, THIS JOURNAL, **72**, 2002 (1950). The reported reduction of dibenzoylethylene with lithium aluminum hydride and sulfuric acid hydrolysis gave 1,4-diphenyl-2-butene-1,4-diol and 1,4-diphenylbutan-1-ol-4-one. The latter was presumably derived from a stable enolate of a 1,4-reduction. Using Rochelle salt hydrolysis we obtained similar results. Acid treatment of the unsaturated diol gave a spectrum typical of a styrene chromophore (λ^{alc}_{max} 252 mμ) and not that of the hydroxy ketone (λ^{alc}_{max} 243 mμ).

[8] A partial oxidation of some substituted allyl alchols has been observed by a less strongly acidic solution of 2,4-dinitrophenylhydrazine, the products being the DNPH's of the unrearranged unsaturated conjugated carbonyl compound. See E. A. Braude, *et al.*, *J. Chem. Soc.*, 1762 (1951); and 2202 (1953).

While the treatment of I and II with 50% sulfuric acid is not comparable with the conditions of the usual oxotropic rearrangement, the conversion of I and II into III has been carried out at much lower acid concentrations at reflux temperatures.[9] Thus heating with 10% and even 1% sulfuric acid and then steam distilling the volatile material gives up to a 65% yield of III ($x = 2$) when isolated as its semicarbazone. An authentic sample of III ($x = 2$) could be recovered, as its semicarbazone, to the extent of 90% by this method. The following yields of the semicarbazone of III were obtained with the indicated reflux time, zero indicating the interval necessary to bring the mixture to boiling, and the dilute acid: I ($x = 2$): 59%, 0 time, 10% aqueous sulfuric; 65%, 1.5 hr., 10%; 59%, 4 hr., 10%; 23%, 0, 1%; 50%, 20 hr., 1%; I ($x = 1$): 50%, 0.5 hr., 10%; 46%, 24 hr., 10%; 43%, 0, 10%; 50%, 0, 1%; II ($x = 2$): 56%, 4 hr., 10%; 25%, 24 hr., 10%; 40%, 20 hr., 1%; II ($x = 1$): 41%, 0, 10%.[10] The yields by this method are not as good as the earlier mentioned procedure with the acid 2,4-dinitrophenylhydrazine solution and it is possible that at the higher temperatures side reactions become more important.

Discussion

This acid-catalyzed rearrangement has recently been described as characteristic of the alkaloid garryfoline[11] and the diterpene steviol,[12] both of which contain a 2-methylenecyclopentanol ring. A mechanism has been proposed to account for the steric requirements necessary, in the just mentioned cases, to effect this transformation.[11] An exhaustive literature search failed to uncover any simple analogous cases as was concurred earlier.[11a] A subsequent finding, which necessitated a revision at the time of proof reading, indicated that our observations were not without analogy and also may have been incomplete regarding the exclusiveness of the products. While we have been unable to convert allyl alcohol into propionaldehyde, methallyl alcohol was reported to have been converted into *iso*-butyraldehyde in 96% yield by refluxing with 12% sulfuric acid.[13] In a similar manner, the allylic pair 2-methyl-2-butene-1-ol and 2-methyl-1-butene-3-ol were both converted into a mixture containing predominantly the isomeric ketone and some isomeric aldehyde. This earlier work would suggest that our product might have contained some of the isomeric cycloalkanecarboxaldehyde even though the derivatives obtained were identical with those of the ketones (III).

Since all of these simple cases appear to be explainable on the basis of the addition of a proton to the double bond, preceded by an allylic rearrangement in the case of II, followed by a 1,2-shift of a hydride ion to give the conjugate acid of the ketone, it is of interest that we have been unable to effect this change in the cyclic allyl alcohols obtained by the lithium aluminum hydride reduction of the cyclic β-diketones.[3]

Acknowledgment.—One of the authors (J.A.H.) wishes to thank Professor Carl Djerassi for making his results available before publication and for discussions on the subject.

Experimental[14]

General Procedure.—The samples (0.2–0.3 g.) were heated with dilute sulfuric acid (25–50 cc.) by a Glas-Col mantle for various time intervals. After collecting about 25 cc. of distillate the condenser was rinsed with a little 95% ethanol and the distillate and washings treated with a nearly saturated solution prepared with 0.50 g. of semicarbazide hydrochloride and 0.55 g. of anhydrous sodium acetate. Upon mixing the latter with the distillate, the derivatives formed as easily filterable solids and after chilling and filtering the samples were desiccated over phosphorus pentoxide. The authenticity of the derivatives was checked by mixture melting point determinations with authentic samples, which were not depressed.

The Rearrangement of 2-Methylenecyclohexanol in the Presence of 2,4-Dinitrophenylhydrazine.—When 0.519 g. of I ($x = 2$) in 3 cc. of ethanol was added to 1.0 g. of 2,4-dinitrophenylhydrazine in 16 cc. of 50% sulfuric acid there was an immediate precipitation. After 24 hours at room temperature the derivative was separated by filtration. Warming the filtrate gave an additional small amount of solid which when combined and desiccated weighed 1.16 g. (86%), m.p. 104–124°. Two recrystallizations from ethanol–ethyl acetate gave the 2,4-dinitrophenylhydrazone of 2-methylcyclohexanone, m.p. 137.4–138°, not depressed by mixing with an authentic sample.

The Rearrangement of 1-Cyclohexenemethanol in the Presence of 2,4-Dinitrophenylhydrazine.—When 0.515 g. of II ($x = 2$) was treated in an identical manner the mixture took on a dark color with oiling. The oil solidified after a few minutes and was broken up with a rod and allowed to stand overnight. The crude derivative weighed 0.992 g. (74%), m.p. 90–112°, and after two recrystallizations as above gave the same derivative, m.p. 134.8–137°, and not depressed by admixture with the derivative obtained in the previous experiment.

The Rearrangement of 2-Methylenecyclopentanol in the Presence of 2,4-Dinitrophenylhydrazine.—A mixture of 0.110 g. of I ($x = 1$) in 1 cc. of ethanol was treated as above to give 0.230 g. (74%) of the 2,4-dinitrophenylhydrazone of III ($x = 1$), m.p. 130–136°. Two recrystallizations from ethanol gave dark orange needles, m.p. 156–158°; reported[3] m.p. 159°.

The Rearrangement of 1-Cyclopentenemethanol in the Presence of 2,4-Dinitrophenylhydrazine.—The crude derivative, obtained as above, from 0.110 g. of II ($x = 1$) was obtained in a 74% yield. However, three recrystallizations were required to raise the melting point to 158–159°.

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[9] For base and/or thermal catalyzed reactions of this type see F. W. Semmler, *Ber.*, **33**, 1455 (1900); W. Treibs and H. Schmidt, *ibid.*, **60**, 2340 (1927); H. Schmidt, *ibid.*, **77**, 171 (1944); **62**, 103 (1929).

[10] The melting points of the semicarbazones obtained were between 180–188° for III ($x = 2$) and between 172–182° for III ($x = 1$).

[11] C. Djerassi, C. R. Smith, A. E. Lippman, S. K. Figdor and J. Herran, THIS JOURNAL, **77**, 480, 6633 (1955); K. Wiesner and J. A. Edwards, *Experientia*, **11**, 255 (1955).

[12] E. Mosettig and W. R. Nes, *J. Org. Chem.*, **20**, 884 (1955).

[13] G. Hearne, M. Tamele and W. Converse, *Ind. Eng. Chem.*, **33**, 805 (1941).

[14] The melting points are not corrected.