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THE ACID-CATALYZED REARRANGEMENT OF ONE BICYCLO[2.2.2]OCTADIENONE TO ANOTHER

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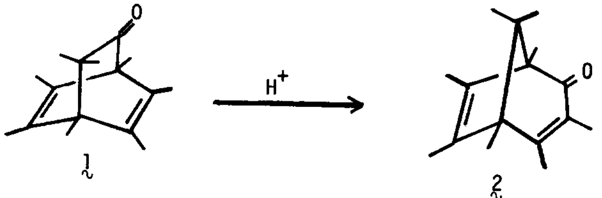
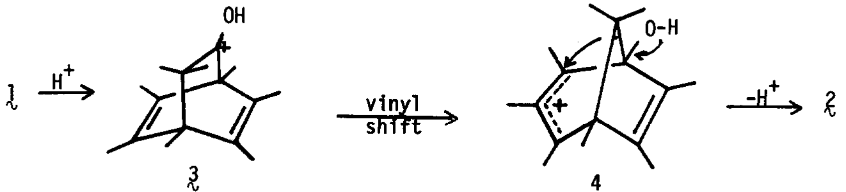
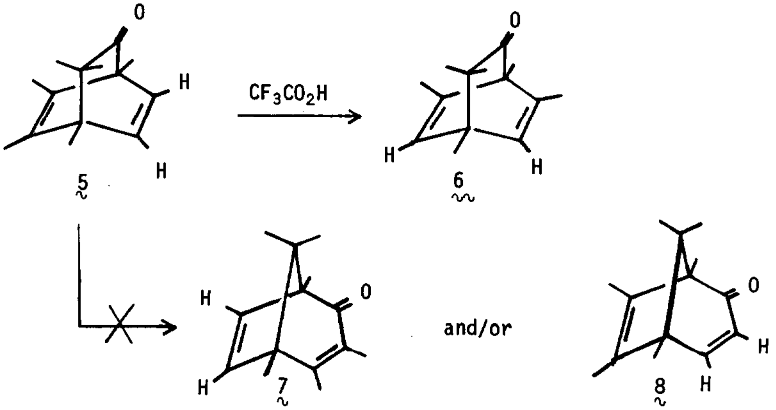
The rearrangement[1] of octamethylbicyclo[2.2.2]octa-2,5-dien-7-one (1) to the [3.2.1] ketone 2[2] can under the right conditions[3] be virtually quantitative.[4] The overall reaction



involves (a) a 1,2-vinyl shift to the protonated carbonyl group (3 → 4), and (b) a 1,2-bridge shift and proton loss (4 → 2).[5,6]

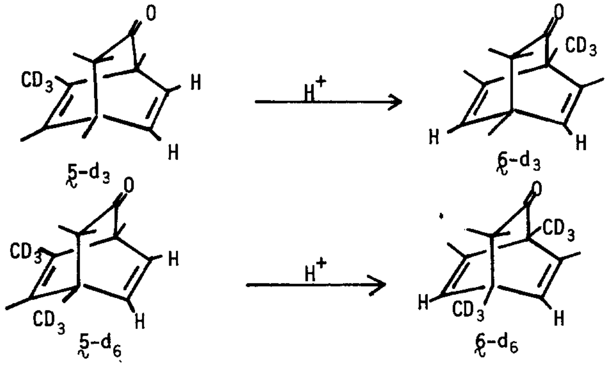


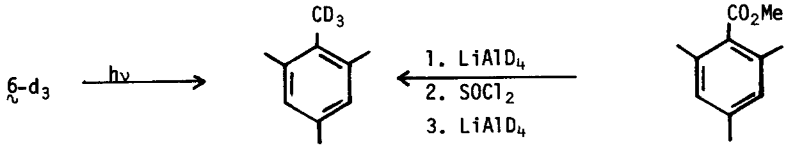
We report here that when the methyl substituents on one of the carbon-carbon double bonds in 1 are replaced by hydrogens, the acid-catalyzed rearrangement leads to a different type of product. Treatment of 5[7] with trifluoroacetic acid (neat, 10-30°, 0.5-2 hr) gave the isomeric



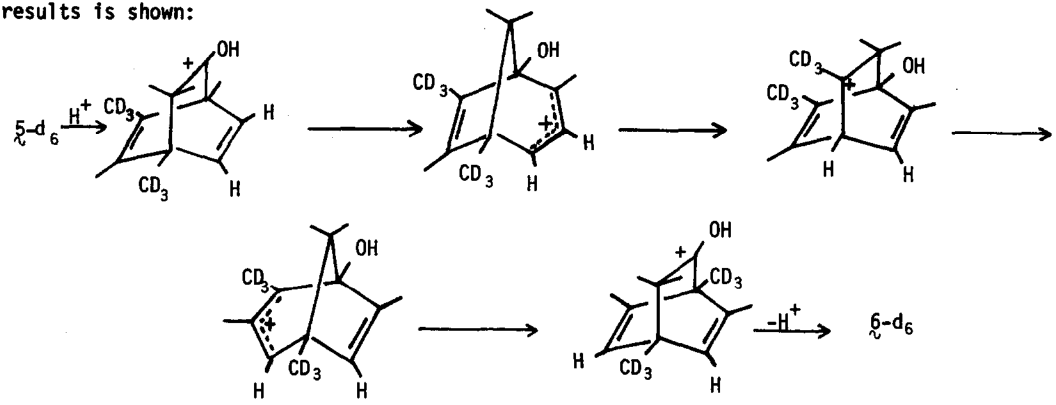
[2.2.2] ketone 6 instead of the expected [3.2.1] ketones 7 and/or 8.[9]

The structure of 6 follows from its spectral properties and chemical conversions. The $\nu_{C=O}$ 1705 cm^{-1} is identical with that of 5. The pmr spectrum showed two identical allylic methyl groups (δ1.71, d, J=1.4 Hz) coupled with two identical vinyl protons (δ5.69, q, J=1.4 Hz), a sharp singlet for the equivalent gem-dimethyl protons (δ0.90) and singlets at δ1.26 and 1.31 for the bridgehead methyls at C-1 and C-4 respectively. Irradiation of 6 (ether, Pyrex)[8] gave a quantitative yield of isodurene (1,2,3,5-tetramethylbenzene) and dimethylketene, proving that the two vinyl protons were no longer adjacent. The only structure consistent with these data is 6 or its isomer in which the relative position of the methyl group and proton on each carbon-carbon double bond is interchanged. Europium shift data distinguish between these possibilities in favor of 6, and this result is supported by the following mechanistically instructive labeling experiments.[10] Location of the label in 6-d$_3$ was confirmed by photolysis to give isodurene-2-CD$_3$ which was synthesized independently.[11] The absence of both bridgehead methyl signals (δ1.26, 1.31) in the pmr spectrum of 6-d$_6$ proves the label location in that product.





A possible mechanism for the formation of 6 from 5 consistent with the observed labeling results is shown:[5]



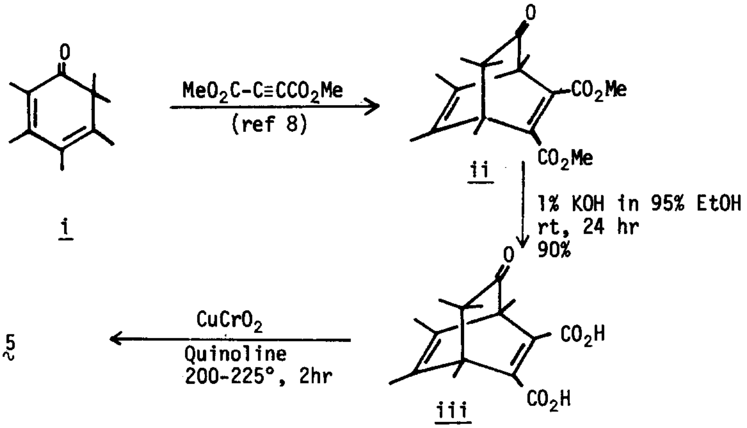
Migration of the methyl-substituted vinyl bridge is preferred to that of the unsubstituted bridge. Similar circumambulatory rearrangements involving the interconversion of [2.2.2] and [3.2.1] ions have been described earlier.[6] However, the reasons why ions of the [3.2.1] type in the above scheme do not collapse to products analogous to 2 is not yet known. Clearly methyl groups (and OH groups) in particular locations profoundly affect the outcome of these multistep carbonium ion rearrangements.

Acknowledgement. We are indebted to the National Science Foundation for their generous financial support.

REFERENCES

1. For a brief review of acid-catalyzed rearrangements of β,γ-unsaturated ketones see R. L. Cargill, T. E. Jackson, N. P. Peet and D. M. Pond, Accounts Chem. Res., 7, 106 (1974).
2. H. Hart and G. M. Love, J. Amer. Chem. Soc., 93, 6264 (1971).
3. H. Hart and M. Kuzuya, J. Amer. Chem. Soc., in press.
4. For closely related rearrangements, see H. Hart and G. M. Love, Tetrahedron Lett., 2267 (1971); H. Hart and G. M. Love, J. Amer. Chem. Soc., 93, 6266 (1971).
5. For convenience and clarity, all ions in this paper are represented by classical structures, though in many the charge is undoubtedly delocalized in obvious and well-known ways.
6. Further rearrangements in these systems may be possible, prior to collapse to 2. See, for example, ref. 2 and H. Hart and M. Kuzuya, ibid., 95, 4096 (1973); M. Kuzuya and H. Hart, Tetrahedron Lett., 3887 (1973).

7. Compound **5** was synthesized as follows:



The pmr spectrum (CCl$_4$) of **5**: δ0.87, 0.90 (3H each, s, gem-dimethyl), 1.32, 1.35 (3H each, s, bridgehead methyls at C-1 and C-4 respectively), 1.65, 1.72 (3H each, m, methyls at C-2 and C-3 respectively), 5.85, 5.90 (1H each, d, J=7Hz, vinyl protons at C-6 and C-5 respectively); Eu-shift reagent was used to distinguish between protons with similar chemical shifts. Ir $\nu_{C=O}$ 1705 cm^{-1}. Irradiation of **5** (ether, Pyrex)[8] gave a nearly quantitative yield of prehnitene (1,2,3,4-tetramethylbenzene), thus proving its structure.

8. R. K. Murray, Jr., and H. Hart, Tetrahedron Lett., 4995 (1968).

9. Compound **6** appears to be the first product formed under these reaction conditions. Further exposure of **6** to acid gives two additional products (neither of which is **7** or **8**). The relative yields of these products depend on reaction conditions; their structures and interconversion are still under investigation, and details will be reported in a full paper.

10. Compounds **5**-d$_3$ and **5**-d$_6$ were synthesized according to the scheme in footnote 7 but from i with CD$_3$ in place of CH$_3$ at C-3, and at both C-3 and C-5 respectively [H. Hart, P. M. Collins and A. J. Waring, J. Amer. Chem. Soc., **88**, 1005 (1966)]. The pmr spectra of the resulting ii, iii, and **5** were consistent with expectation.

11. J. Janssen, Ph.D. Thesis, Michigan State University, 1967.