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STRAINED RING SYSTEMS. VI.[1a] A FACILE REARRANGEMENT OF ENDO-BICYCLO[2.2.0]HEX-2-YL ACETATE

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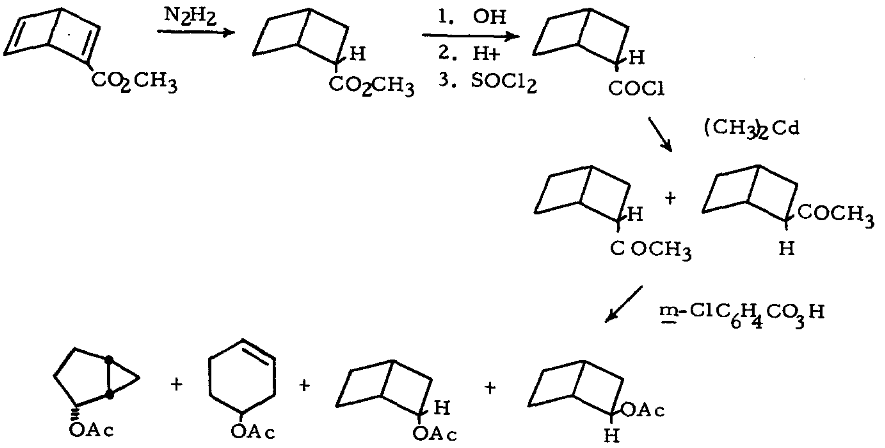
In developing alternate synthetic approaches to endo-bicyclo[2.2.0]hex-2-yl derivatives we have observed a facile rearrangement of the endo-acetate 1. The procedures are outlined below and begin with the elegant synthesis of "Dewar methyl benzoate" described by Pettit and co-workers.[2]



4 3 1 2

The endo-acid and acid chloride were found to be unrearranged but dimethylcadmium treatment produced a mixture of methyl ketones as evidenced by a pair of methyl singlets in the nmr spectrum at τ 8.02 and 8.13 in an approximate ratio of 71:29 favoring the endo-ketone.[3,4]

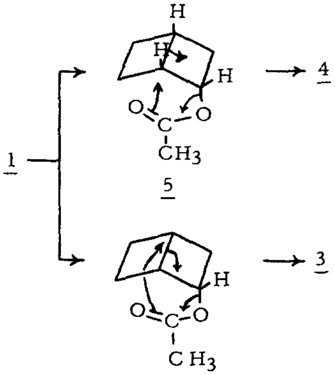
Baeyer-Villiger oxidation of this ketone mixture with m-chloroperbenzoic acid gave a mixture of acetates containing 1 (42%), 2 (35%), 3 (6%), and 4 (17%). G.c. analysis showed two peaks, the first containing 1 and 2, and the second made up of 3 and 4. The first g.c. fraction with 1 and 2 in a ratio of 54:46 was stored in carbon tetrachloride for 21 days at -26°. After this time partial rearrangement had occurred to give a mixture composed of 22% of 1, 46% of 2, 7% of 3, and 25% of 4. After being stored an additional 25 days in methylene chloride the product distribution had changed further to 14% of 1, 46% of 2, 9% of

3, and 31% of 4.[5]

It was determined that 3, 4, and the *trans* isomer of 4 were stable to the Baeyer-Villiger conditions. Acetate 2 had previously been shown to be stable to acetolysis[6] and its stability in the present case was assumed. Therefore, it is most reasonable to presume that products 3 and 4 are arising by rearrangement of 1.

Acid catalyzed addition reactions to bicyclo[3.1.0]hex-2-ene are reported to yield mixtures of *cis* and *trans* isomers of 2-substituted derivatives with the *trans* isomer predominating from apparent kinetic control.[7] Reduction by the Meerwein-Ponndorf method of bicyclo[3.1.0]hexan-2-one yields a mixture of *cis*- and *trans*-bicyclo[3.1.0]hexan-2-ol with the latter isomer predominating.[8] The *cis*-alcohol has been shown to be the thermodynamically favored isomer.[9]

Since in the present rearrangement only *cis*-bicyclo[3.1.0]hex-2-yl acetate (4) is produced (along with 3), we believe this must involve a concerted rearrangement as depicted in 5. Such a process would probably be the most favorable in such nonpolar solvents as carbon tetrachloride. We also favor a concerted mechanism in the formation of 3 but this is more tenuous. The lower amount of 3 is rationalized by the increased steric interference to such a 1,3-migration across the underside of the strained ring system. Suitable experiments designed to test these concerted processes are underway.



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1. a. For paper V in this series see R. N. McDonald and C. E. Reineke, *J. Org. Chem*, **32**, 1888 (1967); b. This represents a portion of the thesis presented by G. E. Davis to the Graduate School of Kansas State University for the requirements of the M. S. degree.
2. L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 3253 (1965).
3. The positional assignment of these nmr singlets comes from a synthesis of the *exo*-ketone by a different route.
4. Dimethylcadmium has been known to cause isomerizations in other strained ring systems, e. g. see K. B. Wiberg and B. A. Hess, *J. Org. Chem.*, **31**, 2250 (1966).
5. These percentages were determined by nmr and g. c. integrations. Compounds *3* and *4* were identified by comparison of the g. c. retention times and nmr spectra with those of authentic samples. No evidence for the presence of the *trans* isomer of *4* was found.
6. R. N. McDonald and C. E. Reineke, *J. Org. Chem.*, **32**, 1878 (1967).
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