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5-SUBSTITUTED BICYCLO[2.1.1]HEXENES (1)

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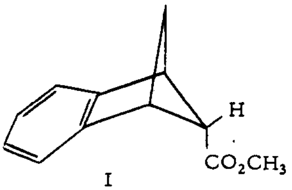
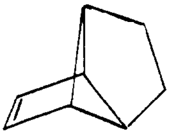
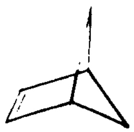
The remarkable difference in reactivity between *exo*- and *endo*-bicyclo[2.1.1]hexyl-5 tosylates (3) has led to an interest in examining the corresponding bicyclo[2.1.1]hexene derivatives. Difficulty has been reported in preparing the bicyclo[2.1.1]hexene ring system (4); however, recently, Tanida and Hata (5) have prepared methyl benzobicyclo[2.1.1]hexene-2-carboxylate (I), Meinwald and Kaplan (6) have prepared tricyclo[3.3.0.$0^{2,6}$]oct-3-ene (II), and Meinwald and Uno (7) have prepared the parent hydrocarbon III. The compounds do not appear to be useful for the preparation of the desired bicyclo[2.1.1]hexene derivatives. Therefore, we wish to report a convenient synthesis for 5-substituted bicyclo[2.1.1]hexenes.



I



II



III

The Diels-Alder reaction of *trans*-1,2-dichloroethylene with cyclopentadiene gave *trans*-5,6-dichloronorbornene (IV) (8). Epoxidation with peracetic acid afforded *exo*-2,3-epoxy-*trans*-5,6-norbornane (V) (9). Reduction with lithium aluminum hydride to the alcohol VI* followed by oxidation with chromic acid gave the ketone VII quantitatively. Selenium dioxide oxidation of VII produced the yellow diketone VIII which was converted to its mono-tosylhydrazone IX (10). Elution of IX over basic alumina produced the yellow crystaline

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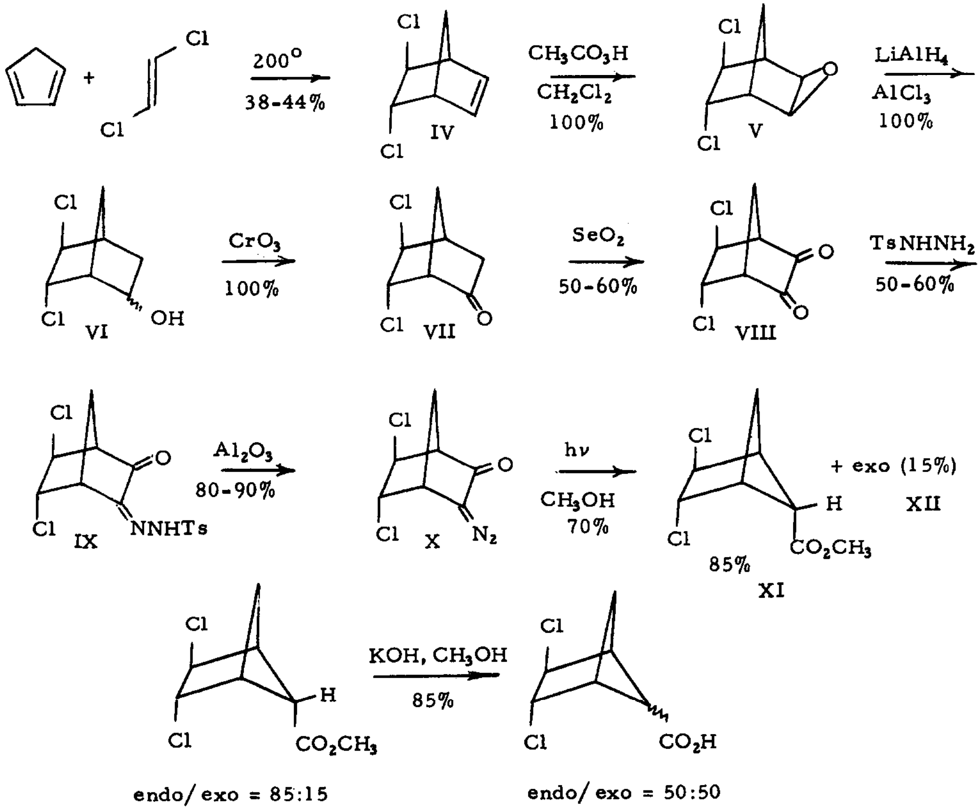
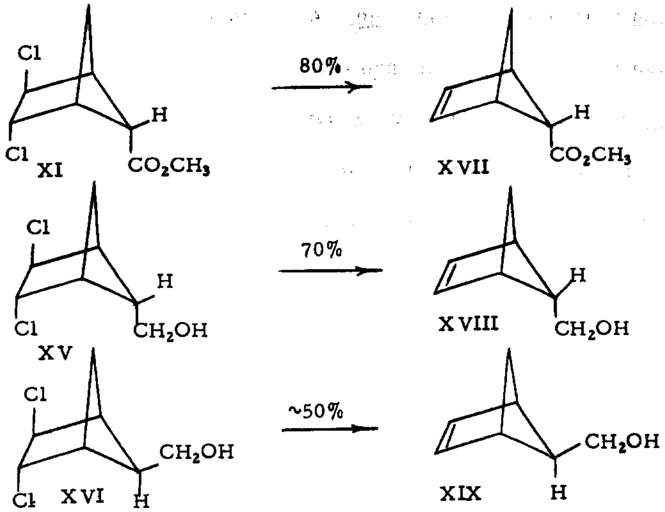
* The position of the hydroxyl group in VI or the keto group in VII with respect to the chlorines has not been established.

diazoketone X. Photolysis of the diazoketone in absolute methanol afforded a mixture of the epimeric endo- and exo-trans-2,3-dichlorobicyclo[2.1.1]hexane-5-carboxylic acid methyl esters (XI and XII respectively) in the ratio of 85:15. Saponification of the epimeric mixture in methanolic potassium hydroxide led to a 50:50 mixture of the epimeric acids XIII and XIV which could be separated by crystallization from carbon tetrachloride. Esterification of the exo acid with methanol via the acid chloride gave XII in quantitative yield. Reduction of XI and XII with lithium aluminum hydride produced the corresponding carbinols XV and XVI.



Elimination of halogen from XI, XV and XVI proved difficult, but magnesium amalgam was found to effect the reaction slowly in good yield. Thus, methyl bicyclo[2.1.1]hexene-endo-5-carboxylate (XVII), bicyclo[2.1.1]hexene-endo-5-methanol (XVIII), bicyclo[2.1.1]-hexene-exo-5-methanol (XIX) were successfully prepared.



In each case, the structure of the bicyclo[2.1.1]hexene derivative was demonstrated by hydrogenation to the known bicyclo[2.1.1]hexane derivative.*

The extension of these reactions to the epimeric bicyclo[2.1.1]hexene-5-ols and the study of the reactivity are now in progress and will be reported later.

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* In all cases the olefins were purified by preparative v.p.c. The NMR spectra of XVII, XVIII, and XIX showed a characteristic triplet (J = 2 cps.) at τ3.17, 3.38 and 3.06 respectively. Hydrogenation proceeded with the uptake of one equivalent of hydrogen in each case. The hydrogenation products had NMR and IR spectra identical to those of authentic samples (10).

References

1. This work was supported by the Public Health Service (GM 12800).
2. National Science Foundation Predoctoral Fellow, 1965-1968.
3. K. B. Wiberg and R. Fenoglio, Tetrahedron Letters, 1273 (1963).
4. J. Meinwald and J. K. Crandall, J. Am. Chem. Soc., 88, 1292 (1966).

5. H. Tanida and Y. Hata, ibid., **88**, 4289 (1966).

6. J. Meinwald and B. E. Kaplan, ibid., **89**, 2611 (1967).

7. J. Meinwald and F. Uno, ibid., **90**, 800 (1968).

8. L. Schmerling, J. R. Luvisi and R. W. Welsh, ibid., **78**, 2819 (1956).

9. V. Mark, U.S. Patent 2,771,470; November 20, 1956 .

10. K. B. Wiberg, B. R. Lowry and T. H. Colby, J. Am. Chem. Soc., **83**, 3998 (1961).