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FURTHER EXAMPLES OF THE ADAMANTANE REARRANGEMENT

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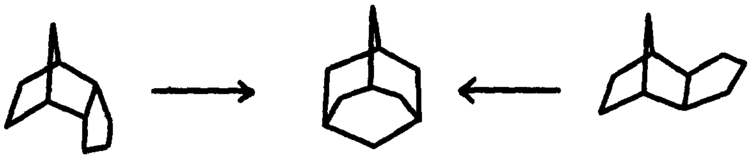
THE Lewis acid catalyzed conversion of the *endo* (I) and *exo* (II) isomers of trimethylenenorbornane (tetrahydrodicyclopentadiene) to adamantane (III)[1] represents one of the most profound rearrangements known in carbonium ion chemistry. The present investigation[2] was undertaken in the hope of obtaining insight into the mechanism of this complicated transformation. The results of the exploratory experiments reported below contribute little definitive information in this regard but they serve to demonstrate the generality of the adamantane rearrangement and to show that its extensions have preparative utility.



I III II

Besides the $C_{10}H_{16}$ isomers of adamantane, (I) and (II), we have investigated the action of $AlCl_3$ upon hydrocarbons (IV) and (V). Both formed many products as shown by gas chromatography, but no adamantane

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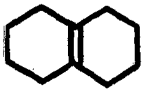
[1] P.von R. Schleyer, *J.Amer.Chem.Soc.* *79*, 3292 (1957); P.von R. Schleyer and M.M. Donaldson, *Ibid.* *82* 4645 (1960).

[2] R. D. Nicholas, Ph. D. Thesis, Princeton University (1960).

was produced from either starting material. Therefore, we have adopted the working hypothesis that saturated tricyclic compounds of ten or more carbon atoms were most likely to rearrange to isomers containing the adamantane skeleton.



IV

V

Six methyl substituted trimethylenenorbornanes (Table 1) were prepared by standard methods[2] from the corresponding ketones.[3] Each hydrocarbon was stirred with 1/4 to 1/3 of its weight of aluminum chloride or aluminum bromide under the conditions outlined in Table 1. Work-up gave fractions boiling in the range expected for $C_{11}H_{18}$ compounds. Comparison of the physical, spectroscopic and gas chromatographic properties of authentic samples of 1-methyladamantane (VI)[4] and of 2-methyladamantane (VII)[5] with those of the $C_{11}H_{18}$ reaction product revealed the compositions recorded in Table 1. Unlike the partial conversions of I and II to adamantane (III) under similar conditions, the isomerizations of the methyltrimethylenenorbornanes to methyladamantanes was complete. None of the starting materials remained in the products.

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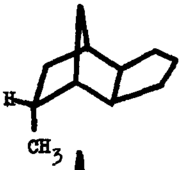
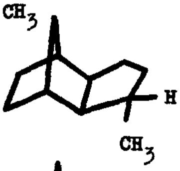
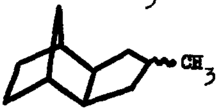
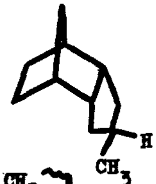
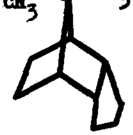
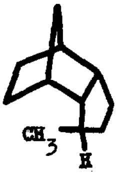
[3] J. Pirsch, Chem.Ber. 67, 1115 (1934); H. Bruson and T. W. Reiner, J.Amer.Chem.Soc. 67, 723 (1945); M. M. Donaldson, Ph. D. Thesis, Princeton University (1958); R. B. Woodward and T. J. Katz, Tetrahedron 5, 70 (1959).

[4] H. Stetter, M. Schwarz and A. Hirschhorn, Chem.Ber. 92, 1629 (1959).

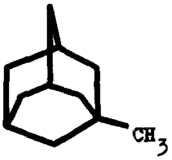
[5] P. von R. Schleyer and R. D. Nicholas, J.Amer.Chem.Soc. 83, 182 (1961).

TABLE 1

Composition of Methyladamantane Product From Isomerization of Methyltrimethylenenorbornanes

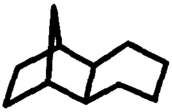
Starting material	Temp.	Time	% Yield $C_{11}H_{18}$	Composition % VI	% VII
	Room	Overnight	40	99.7	0.3
	Room	20 hr	77	92.3	7.7
	Room	Overnight	47[a]	87.3	12.7
	Room	3 Days	49[a]	84.5	15.5
	Reflux	4 hr	65	98.6	1.4
	Reflux	2 hr	-	Main	?

[a] Starting material was contaminated with olefin.



VI

VII



VIII

exo-Tetramethylenenorbornane (VIII) was prepared easily by hydrogenation of the butadiene-norbornadiene Diels-Alder adduct.[6] When mixed with 25% of its weight and stirred magnetically, there was an initial evolution of heat. Solid formed after a short while and the entire contents of the flask were solid the next morning. Sublimation gave a quantitative yield of substantially pure 1-methyladamantane (VI), m.p. 95.0-97.8°, shown to be free from isomers by gas chromatography (reported m.p. 103° [4]; our best value was 104.6-105.1°). The amazing facility of this transformation was further demonstrated by using cyclohexane as solvent and similar proportions of reagents; rearrangement of VIII to VI was complete in four hours under autogenous temperature. By way of contrast, no adamantane was formed from I or II with more vigorous conditions of temperature when a solvent was used.[1]

Isoprene and norbornadiene were the starting materials for the preparation of IX, the homolog of VIII. The Diels-Alder reaction gave 37% yield and the subsequent hydrogenation 83% of material, b.p. 101-103° at 15 mm, n_D^{20} 1.5049. IX was more stable than VIII to the action of $AlCl_3$; after two days at room temperature only a small change in composition was detected by gas chromatography. At 130° overnight, transformation was complete. A 74% yield of 1,3-dimethyladamantane (X) with identical infra-

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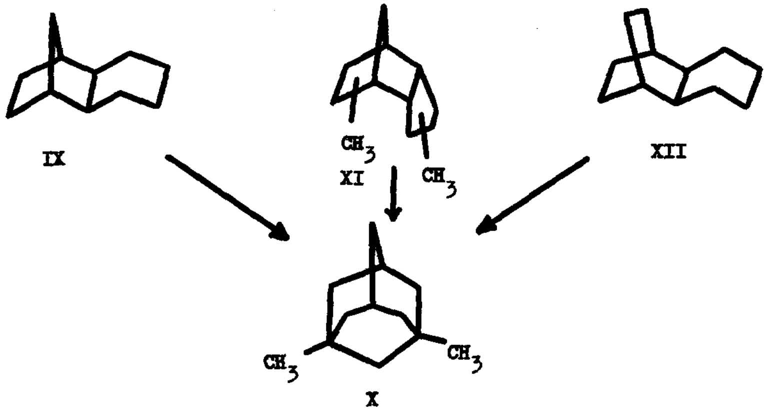
[6] K. Alder, J. Mönch and H. Wirtz, Liebigs Ann. 627, 47 (1959).

red spectrum to that reported[7] was obtained. The material was homogeneous.



Commercially available (Enjay Company) methylcyclopentadiene dimer, a mixture of isomers, was hydrogenated with difficulty. Stirring XI, the mixture of saturated hydrocarbons so obtained, with $AlCl_3$ on the steam bath overnight gave a 60% yield of $C_{12}H_{20}$ hydrocarbons. Analysis by gas chromatography indicated the presence of 39% X and two other unidentified components, 42% and 19%. Tetrahydrodicyclohexadiene (XII)[8] was heated with $AlCl_3$ on the steam bath. After four hours there was no further change in the product composition. Work-up gave 72% of crude material which contained 63% of X and two other unidentified components in amounts of 6% and 31%.

Further implications of these results will be discussed subsequently.

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[7] S. Landa and Z. Kamycek, Chem.Listy 52, 1150 (1958); Coll.Czech. Chem.Comm. 24, 1320 (1959).

[8] K. Alder and G. Stein, Chem.Ber. 67, 613 (1934).