

Perhaps the most remarkable feature of this rearrangement is the great speed of the reaction and the mildness of the reagents that can induce the change. The formation of carbon-carbon bonds under such mild conditions in essentially quantitative yields must hold great promise for the synthesis of complex organic structures. We are currently exploring such possibilities.

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### Preparation of Diamondoid Hydrocarbons by Rearrangement Employing a Chlorinated Platinum-Alumina Catalyst

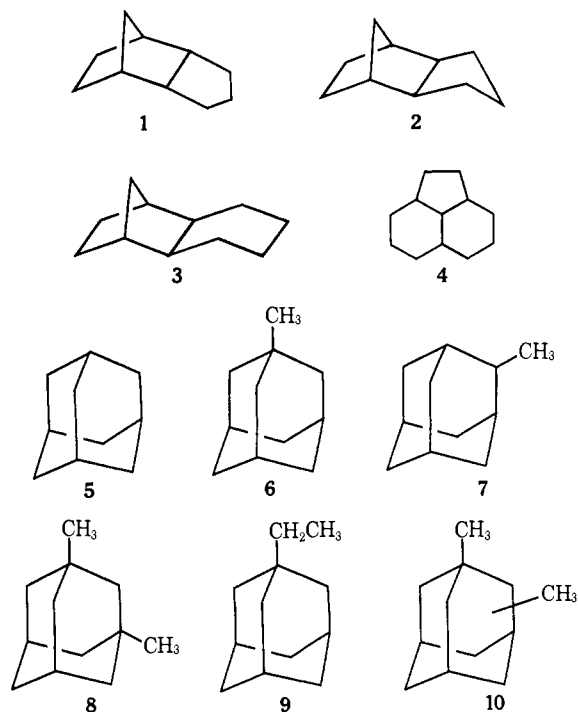
Sir:

The use of Lewis acids such as  $\text{AlCl}_3$  and  $\text{AlBr}_3$ , singly or in combination with alkyl halides and/or hydrogen halides (the so-called "sludge" method), as catalysts for the conversion of strained tricyclic hydrocarbons containing ten or more carbon atoms into adamantanes has been extensively investigated following the discovery in 1956 by Schleyer and Donaldson<sup>1</sup> of the first example of adamantane formation by rearrangement of *endo*-tetrahydrodicyclopentadiene (**1**) with  $\text{AlCl}_3$ .<sup>2,3</sup> The yields in this reaction are low (15–20%);<sup>4</sup> apparently  $\text{AlCl}_3$  is catalytically unselective inasmuch as fragmentation processes and other side reactions produce hundreds of by-products. Several attempts have been made to improve on this method: replacement of  $\text{AlCl}_3$  by  $\text{BF}_3\text{-HF}$  gives 30% yields of adamantane with the disadvantage, however, that a nonglass inert apparatus must be employed,<sup>5</sup> and yields of up to 40% have been realized with an  $\text{AlCl}_3\text{-HCl}$  system under 40 atm pressure of hydrogen.<sup>6</sup> The only gas-phase process recorded gives 6–13% yields of adamantane and at least 40 acyclic, alicyclic, and aromatic by-products from **1** on an aluminosilicate catalyst at 450–475°.<sup>7</sup>

Within the last few years several solid catalysts capable of isomerizing *n*-butane, *n*-pentane, and *n*-hexane to near their equilibrium isomer distributions at low temperatures have been described.<sup>8</sup> The essential

feature of the catalytic activity of these materials is the introduction of chlorine into platinum-alumina by reaction with various chlorinating agents such as carbon tetrachloride or thionyl chloride. We have examined the reactivity of one of these catalysts toward several hydrocarbons all of which are known to give adamantanes under conventional aluminum halide catalysis,<sup>2,9</sup> and we now disclose that there is a dramatic increase in selectivity for adamantane formation.

The catalyst was prepared from alumina and chloroplatinic acid (0.5% by weight in platinum) and was activated by sequential treatment with  $\text{H}_2$ ,  $\text{HCl}$ , and  $\text{SOCl}_2$ , according to the method of Giannetti and Sebulsky.<sup>8d</sup> The rearrangement procedure was simply a "hot-tube" process whereby a stream of the hydrocarbon vapor in dry  $\text{HCl}$  was passed through an electrically heated glass tube containing the catalyst while the products were collected in a cold trap. The adamantane precursors investigated were **1**, its *exo* isomer **2**, *exo*-2,3-tetramethylenenorbornane (**3**), and perhydroacenaphthene (**4**) (a mixture of four stereoisomers). The reaction details and the products, which were identified by direct comparison with authentic samples, are summarized in Table I.



It is immediately obvious that the catalyst exhibits a remarkable selectivity for adamantane formation in all four cases with by-product formation amounting to 1% or less, and with an essentially quantitative recovery of material. The rearrangement of **3** provided the most dramatic example; glpc analysis of the *crude* white crystalline product revealed that within the limits of detectability 1- and 2-methyladamantane were the sole products in quantitative yield. Similarly, in the  $\text{C}_{12}$  case the only products detected were the substituted adamantanes listed in Table I. Adamantane itself

(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) Cf. the review article by R. C. Fort, Jr., and P. von R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

(3) The use of  $\text{AlBr}_3$  "sludge" catalysts has been described by A. Schneider, R. W. Warren, and E. J. Janoski, *J. Org. Chem.*, **31**, 1617 (1966), and V. Z. Williams, Jr., P. von R. Schleyer, G. J. Gleicher, and L. B. Rodewald, *J. Amer. Chem. Soc.*, **88**, 3862 (1966).

(4) P. von R. Schleyer, M. M. Donaldson, R. D. Nicholas, and C. Cupas, *Org. Syn.*, **42**, 8 (1963).

(5) R. E. Ludwig, U. S. Patent 2,937,211 (1960); *Chem. Abstr.*, **54**, 19540c (1960).

(6) H. Koch and J. Franken, *Brennst.-Chem.*, **42**, 90 (1961); *Chem. Abstr.*, **55**, 21059i (1961).

(7) A. F. Plate, Z. K. Nikitina, and T. A. Burtseva, *Neftekhimiya*, **1**, 599 (1961); *Chem. Abstr.*, **57**, 4938a (1962).

(8) (a) A. G. Goble and P. A. Lawrence, *Prepr. Proc. Int. Congr. Catal.*, **3rd**, 1964, 320 (1965); (b) A. G. Goble, J. N. Haresnape, and T. C. O'May, Belgian Patent 634,142 (1964); *Chem. Abstr.*, **61**, 518h (1964); (c) M. D. Riordan and J. H. Estes, British Patent 1,021,587 (1966); *Chem. Abstr.*, **64**, 14088c (1966); (d) J. P. Giannetti and R. T.

Sebulsky, *Ind. Eng. Chem., Prod. Res. Develop.*, **8**, 356 (1969); (e) J. P. Giannetti, H. G. McIlvred, and R. T. Sebulsky, *Ind. Eng. Chem., Process Des. Develop.*, **9**, 473 (1970).

(9) A. Schneider, British Patent 1,068,518 (1967); *Chem. Abstr.*, **67**, 81859v (1967).

Table I

	Reactant		
	1 or 2	3	4
	Temp, °C		
	165	168	169
	Catalyst: reactant wt ratio		
	7.0-8.6:1	5.4:1	7.5:1
	%		
Adamantane (5)	60		
1-Methyladamantane (6)		98	
2-Methyladamantane (7)		2	
1,3-Dimethyladamantane (8)			86
1-Ethyladamantane (9) <sup>a</sup>			7
1,X-Dimethyladamantane (10) <sup>b</sup>			7
Material recovery	98-100	98-100	98-100
Starting material	39	None	None
By-products	~1	None	None

<sup>a</sup> An authentic sample was synthesized from 2-(1-adamanty)-acetic acid: K. Bott, *Angew. Chem., Int. Ed. Engl.*, **4**, 956 (1965); D. Grant, to be published. <sup>b</sup> This component was a mixture of 1,2-dimethyladamantane and *cis*- and *trans*-1,4-dimethyladamantane; cf. J. Vais, J. Burkhard, and S. Landa, *Z. Chem.*, **9**, 268 (1969); see also ref 3.

was obtained from either 1 or 2 or from mixtures of the two. Commencing with 1 there was initially a facile isomerization into 2 followed by adamantane formation. At the beginning of each run pure adamantane collected in the receiver, but as the reaction proceeded the catalyst suffered some deactivation; nevertheless, yields of up to 60% adamantane were realized with only ca. 1% by-product formation, so that the selectivity is almost as high as with the C<sub>11</sub> and C<sub>12</sub> cases. The problem of catalyst deactivation can be overcome by recycling the material, and the catalyst is easily reactivated by treatment first with a stream of oxygen at 500° and then by repeating the H<sub>2</sub>-HCl-SOCl<sub>2</sub> procedure.

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### Carbon-Sulfur Bond Distances and Sulfur Valence Angles in 5-Thiabicyclo[2.1.1]hexane and 7-Thiabicyclo[2.2.1]heptane as Determined by Gas Electron Diffraction

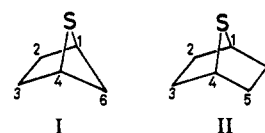
Sir:

In a recent study of the acetolysis of 2-*endo*-chloro-7-thiabicyclo[2.2.1]heptane,<sup>1</sup> a change from an S<sub>N</sub>1 mechanism to a mechanism of rate-determining solvent attack on the equilibrating sulfonium ion was observed. This drastic change in the rate-determining step may be closely related to the geometrical arrangement of the atoms in this molecule. A characteristic difference in the chemical shift observed for 5-thiabicyclo[2.1.1]-hexane<sup>2</sup> may also depend on its structure. However,

(1) I. Tabushi, Y. Tamaru, T. Sugimoto, and Z. Yoshida, unpublished results.

(2) I. Tabushi, Y. Tamaru, and Z. Yoshida, *Tetrahedron Lett.*, 2931 (1970).

little is known about the structures of thiapolycyclics. Accordingly, we have made an electron-diffraction study of 5-thiabicyclo[2.1.1]hexane (I) and 7-thiabicyclo[2.2.1]heptane (II). Now we wish to report the



significant differences observed in their C-S bond distances and C-S-C angles.

The samples, prepared by a method described elsewhere,<sup>3</sup> were vaporized<sup>4</sup> at 54 (I) and 104° (II) and diffraction photographs were taken<sup>5</sup> with 40-kV electrons at camera lengths of 11.3 and 24.9 cm. Molecular intensities ( $10 \leq q \leq 110$ ) obtained by a standard process<sup>6</sup> were analyzed.<sup>7</sup>

The structural parameters listed in Table I were determined first from the radial distribution curves and then by a least-squares analysis,<sup>6</sup> with the following assumptions.<sup>8</sup> (1) Molecules I and II have C<sub>s</sub> and

Table I. Geometrical Structures of I and II<sup>a</sup>

Parameter	I	II
$r_d(\text{C-S})^b$	1.8656 ± 0.004	1.837 ± 0.006
$r_d(\text{C-C})_{av}$	1.5530 ± 0.003	1.549 ± 0.003
$r_d(\text{C}_1-\text{C}_6)$	1.573 ± 0.01	
	- 0.02	
$r_d(\text{C-H})_{av}$	1.105 ± 0.008	1.108 ± 0.009
$\angle \text{C}_1-\text{S}-\text{C}_4$ , deg	69.7 ± 0.5	80.1 ± 0.8
$\theta[(\text{C}_1-\text{S}-\text{C}_4)-(\text{C}_1-\text{C}_2-\text{C}_3-\text{C}_4)]^c$ , deg	115.2 ± 3	122.4 ± 1
$\theta[(\text{C}_1-\text{C}_2-\text{C}_3-\text{C}_4)-(\text{C}_1-\text{C}_6-(\text{C}_5)-\text{C}_4)]^c$ , deg	118.5 ± 3	115.3 ± 2
$/(C-S)^d$	0.061 ± 0.01	0.062 ± 0.01

<sup>a</sup> Uncertainties represent estimated limits of error. <sup>b</sup> Thermal-average bond distances in ångströms. <sup>c</sup> Dihedral angles. <sup>d</sup> Root-mean-square vibrational amplitudes.

C<sub>2v</sub> symmetry, respectively. (2) The C<sub>1</sub>-C<sub>2</sub> and C<sub>2</sub>-C<sub>3</sub> distances are equal to each other and (for I) are shorter than the C<sub>1</sub>-C<sub>6</sub> distance<sup>9</sup> by 0.034 Å. (3) All the C-H distances are equal. (4) All the C-C<sub>1</sub>-H angles are equal. (5) All the H-C-H angles are equal. (6) The H-C<sub>i</sub>-H plane (*i* = 2 and 6 for I and 2 for II) is perpendicular to the C-C<sub>i</sub>-C plane, and the angles bisect each other. (7) The mean amplitudes of vibration (except for the bonded C-S amplitudes given in Table I) were estimated from those in norbornane<sup>9</sup> and used as constants. Uncertainties in the structural parameters originating from the above assumptions were estimated and included in the limits of error quoted in the table.

(3) I, ref 2; II, E. J. Corey, and E. Block, *J. Org. Chem.*, **31**, 1663 (1966).

(4) A. Yokozeki and K. Kuchitsu, *Bull. Chem. Soc. Jap.*, **44**, 72 (1971).

(5) Y. Murata, K. Kuchitsu, and M. Kimura, *Jap. J. Appl. Phys.*, **9**, 591 (1970).

(6) Y. Morino, K. Kuchitsu, and Y. Murata, *Acta Crystallogr.*, **18**, 549 (1965).

(7) A HITAC-5020E computer at the Computer Center of the University of Tokyo was used.

(8) A. Yokozeki and K. Kuchitsu, *Bull. Chem. Soc. Jap.*, **43**, 2017 (1970).

(9) Y. Morino, K. Kuchitsu, and A. Yokozeki, *ibid.*, **40**, 1552 (1967); A. Yokozeki and K. Kuchitsu, *ibid.*, in press.