Hegedüs[7] has made it possible to synthesize various 3-aralkyl-4-hydroxycoumarins not realizable heretofore by the conventional methods.[10,11] The primary advantage of the method reported herein resides in the fact that the aralkyl halides are either commercially available or can be made readily in the laboratory by conventional methods. The alkylation of 4-hydroxycoumarin is direct without passing through intermediates, the yields are generally very good and purification of the products obtained offers no difficulties.

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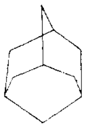
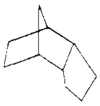
A SIMPLE PREPARATION OF ADAMANTANE

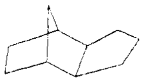
Sir:

Because of the analogy with the structure of the diamond, the highly symmetrical molecule, adamantane (tricyclo[3.3.1.1^{3,7}]decane) (I), has occasioned interest for many years.[1] The total synthesis of this hydrocarbon, first isolated from petroleum naphtha[2] in minute yields,[3] has been accomplished several times, utilizing a number of modifications of the same general approach.[1,4] The over-all yields of even the best of these methods, involving a moderately large number of steps, did not exceed a few per cent.; therefore, investigations of the chemistry of this compound have been hindered to a large extent by its unavailability. We wish to report a facile two-step preparation of adamantane from the very readily available compound, dicyclopentadiene (II).

endo-Trimethylenenorbornane[5] (tetrahydrodicyclopentadiene, III), which can be prepared from II in essentially quantitative yield by hydrogenation,[6] was refluxed with 10 per cent. of its weight of $AlBr_3$ or $AlCl_3$ overnight.[7] At the end of this time the products were distilled directly from the reaction pot, with no attempt at fractionation. The precipitation of adamantane was completed by cooling the distillate to Dry-Ice temperature; a yield of about 10 per cent. of crude I could be obtained by filtration through a coarse filter. Additional I could be obtained by subjecting the filtrate to fractional distillation through an efficient column. The forecuts, b.p. to 185°, contained a large number of components. The main fraction, b.p. 185.0°, n^{20}_D 1.4871, consisted of *exo*-trimethylenenorbornane (IV),[8] the expected product of the reaction.[9] The yield of this material, about 50 per cent., could be improved considerably by conducting the isomerization at lower temperatures. From the higher boiling cuts, b.p. to 195°, approximately 5 per cent. additional crude I was recovered. After washing with ethanol, fractional sublimation of the combined samples of I gave a 12–13 per cent. yield of pure adamantane, m.p. 269.6–270.8° (sealed tube). Reported m.p. 268.5–270°.[1] *Anal.* Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.31; H, 11.99. The infrared spectrum[10] and mass spectral pattern[11] of the rearrangement product further established its identity as adamantane.







Since, as would be anticipated, IV, under the same conditions, gave a similar yield of I, it may be possible to improve the yield of I considerably The driving force for the rearrangement is undoubtedly the result of the fact that I, in contrast to III and IV, possesses an arrangement of atoms uniquely free from angular and conformational strain. Conceptually, it is possible to visualize several routes for the conversion of III or IV into I. The simplest of these necessitates only three steps involving carbon-to-carbon rearrangements. The possible mechanisms of these unusual transformations will be commented on in greater detail later.

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[1] *Cf.* an excellent review, H. Stetter, *Angew. Chem.*, **66**, 217 (1954). More recent references will be found below.[3,4,10]

[2] S. Landa and V. Macháček, *Coll. Czech. Chem. Comm.*, **5**, 1 (1933).

[3] S. Landa, Š. Kriebel and E. Knobloch, *Chem. Listy*, **48**, 61 (1954) (*C. A.*, **49**, 1598 (1955)).

[4] V. Prelog and R. Seiwerth, *Ber.*, **74**, 1644, 1769 (1941); H. Stetter, O.-E. Bänder and W. Neumann, *ibid.*, **89**, 1922 (1956).

[5] The nomenclature used here will be that suggested previously (P. R. Schleyer and M. M. Donaldson, THIS JOURNAL, **78**, 5702 (1956)).

[6] For references, *cf.* E. Josephy and F. Radt, Eds., "Elsevier's Encyclopaedia of Organic Chemistry," Vol. 13, Elsevier Publishing Co., Inc., New York, N. Y., 1946, p. 1022.

[7] For a recent review of the action of Lewis acids upon alkanes, *cf.* H. Pines and J. Mavity in B. T. Brooks, *et al.*, Eds., "The Chemistry of Petroleum Hydrocarbons," Vol. III, Reinhold Publishing Corp., New York, N. Y., 1955, Chap. 39, pp. 9–58.

[8] H. Bruson and T. W. Riener, THIS JOURNAL, **67**, 723 (1945); *cf.* P. D. Bartlett and A. Schneider, *ibid.*, **68**, 6 (1946).

[9] M. M. Donaldson, unpublished results from this laboratory. *Cf.* J. F. Eykman, *Chem. Weekblad*, **1**, 7 (1903); **3**, 687 (1906).

[10] R. Mecke and H. Spiesecke, *Ber.*, **88**, 1997 (1955). The author is indebted to Dr. R. A. Dean, The British Petroleum Co., Ltd., for a copy of the spectrum of synthetic adamantane.

[11] Catalog of Mass Spectral Data, A.P.I. Research Project 44 Carnegie Institute of Technology, Pittsburgh, Pennsylvania, No. 939

SELENIUM AS AN INTEGRAL PART OF FACTOR 3 AGAINST DIETARY NECROTIC LIVER DEGENERATION

Sir:

Factor 3 is a dietary agent which prevents liver necrosis in the rat.[1] Concentrates of Factor 3 also protect against multiple necrotic degeneration (heart, liver, kidney and muscle necrosis) in the mouse,[2] as well as against exudative diathesis in the chick.[3] These fatal diseases result from a multiple deficiency. They are produced by diets which are low in cystine and simultaneously defi-

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[1] K. Schwarz, *Proc. Soc. Exp. Biol. and Med.*, **78**, 852 (1951).

[2] W. B. DeWitt and K. Schwarz, *Experientia*, in press.

[3] M. L. Scott, J. G. Bieri, G. M. Briggs and K. Schwarz, to be published.