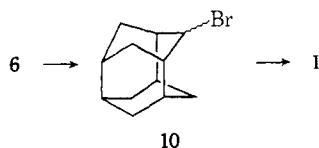


Figure 1. Assumed structure for the ice-1h crystal.⁴

systems, by Schleyer and Engler,^{12a} indicated that the saturated hydrocarbon derived from **6** was approximately 8.7 kcal/mol less stable than iceane itself, and thus our desired rearrangements were thermodynamically favorable.^{12b}

Treatment of **6** for 8 hr at 120° with 30% HBr–HOAc gave **10** (72% yield) which was reduced, without further



purification, with lithium aluminum hydride.¹³ This gave iceane, mp 327.0–328.5°.¹⁴ The pmr spectrum of iceane (Figure 2B) exhibited a singlet at 2.16 ppm for the bridgehead hydrogens and an AB quartet for the methylene hydrogens centered at 1.40 ppm with $J_{AB} = 12$ Hz. In addition, the cmr spectrum was dramatic in that it showed but two singlets δ 31.80 and 28.86 ppm which split into a triplet and a doublet in the off-resonance cmr spectrum (Figure 2C). The mass spectrum of iceane was noteworthy in that only two other lines, other than the base peak (m/e 162.2 amu), had relative intensities of greater than 20% (m/e 79 [23%] and 39 [34%] amu).

The chemistry of iceane (**1**) is under active investigation.¹⁵

(12) (a) Private communication, P. v. R. Schleyer and E. Engler, Princeton University. See also E. M. Engler, J. D. Audose, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 8005 (1973); using Allinger's force field, the difference is virtually the same, 8.9 kcal/mol. (b) N. L. Allinger, M. Tribble, M. A. Miller, and D. W. Wertz, *ibid.*, **93**, 1637 (1971).

(13) C. W. Jefford, D. Kirkpatrick, and F. Delay, *J. Amer. Chem. Soc.*, **94**, 8905 (1972).

(14) Melting points for all compounds were obtained using sealed capillaries.

(15) The calculations by Schleyer and Engler also indicate that ethanoadamantane (iii) is the most stable tetracyclic C_{12} system. We have also confirmed this prediction. Reaction of iceane (**1**) with an $AlCl_3$ sludge catalyst gave ethanoadamantane (iii).

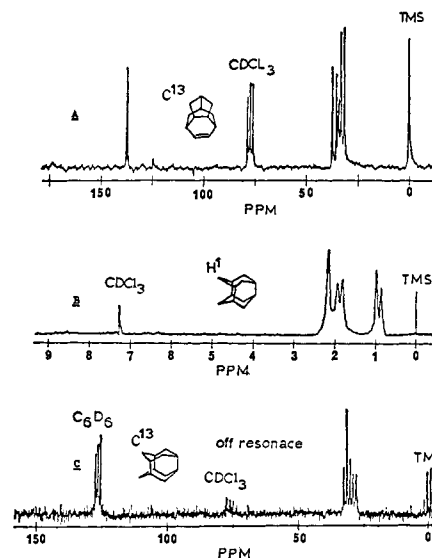
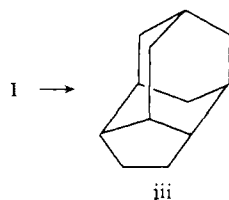


Figure 2. (A) 25.16-MHz spectrum of **6**; (B) 100-MHz spectrum of iceane (**1**); (C) 25.16-MHz spectrum (off-resonance of iceane (**1**)).

Acknowledgment. We are grateful to the Research Corporation for support of this work.

Chris A. Cupas,* Leonard Hodakowski

Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

Received January 31, 1974

Ethanoadamantane. The Most Stable $C_{12}H_{18}$ Isomer

Sir:

An astonishingly large number of tetracyclic $C_{12}H_{18}$ isomers are possible.¹ Of these, two have special appeal. II, "iceane,"² is the first member of an isomeric, hexagonal diamond³ family with the Wurzite or ice structure.⁴ I, 2,4-ethanoadamantane (tetracyclo[6.3-1.0^{2,6}.0^{5,10}]dodecane), like adamantane, was first discovered by Landa as a constituent from petroleum from Hodonin.⁵ As such diamondoid molecules probably arise in petroleum by rearrangement, this posed the possibility that I (and possibly II as well) might be prepared by Lewis acid-catalyzed isomerization, provided no other tetracyclic $C_{12}H_{18}$ isomers are more stable.⁶

In fact, treatment of tetracyclo[6.4.0.0^{4,12}.0^{5,9}]dodecane (III)⁷ with $AlBr_3$ or with $AlBr_3$ -sludge catalyst in CS_2 at 0 or 25° gave ethanoadamantane (I)⁸ in 40–70% yields. Reaction times were as short as 30–60 min; with $AlBr_3$, 90% of the product was I (glc). A careful study of this rearrangement by glc as a function of time

(1) A computer program written by Professor W. T. Wipke reveals that 5291 tetracyclic ring systems with 12 skeletal carbon atoms are possible (private communication).

(2) L. F. Fieser, *J. Chem. Educ.*, **42**, 408 (1965).

(3) F. P. Bundy and J. S. Kasper, *J. Chem. Phys.*, **46**, 3437 (1967); R. E. Hauneman, H. M. Stroug, and F. P. Bundy, *Science*, **155**, 995 (1967).

(4) C. A. Cupas and L. Hodakowski, *J. Amer. Chem. Soc.*, **96**, 4668 (1974), accompanying communication.

(5) (a) S. Hála, S. Landa, and V. Hájus, *Angew. Chem.*, **78**, 1060 (1966); (b) Z. Weidenhaber and S. Hála, *Sb. Vys. Sk. Chem.-Technol. Prague, Technol. Palit*, **D22**, 5 (1971).

(6) (a) R. C. Bingham and P. v. R. Schleyer, *Fortschr. Chem. Forsch.*, **18**, 1 (1971); (b) E. M. Engler and P. v. R. Schleyer, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci., Org. Chem., Ser. I*, **5**, 239 (1973).

(7) (a) I. A. Akhtar, G. I. Fray, and J. M. Yarrow, *J. Chem. Soc.*, 812 (1968); (b) One of us (G. J. K.) developed this synthesis independently.

(8) Satisfactory elemental analysis was obtained for this compound.

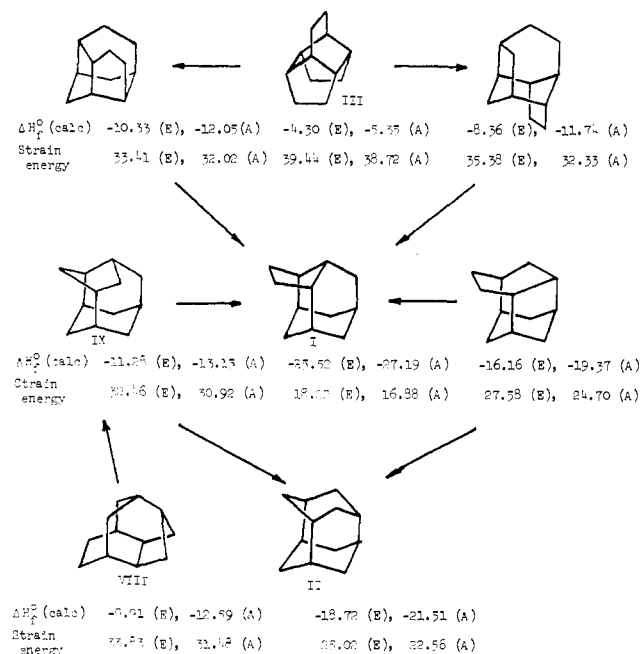
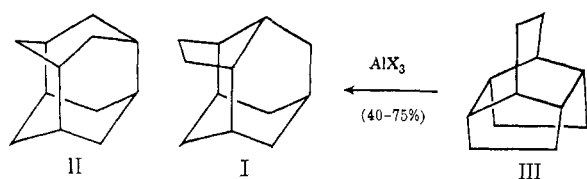


Figure 1. Rearrangement pathways of tetracyclic $C_{12}H_{18}$ hydrocarbons. Heats of formation and strain energies (in kcal/mol) were calculated using Engler (E) and Allinger (A) force fields.²⁴ Arrows indicate the direction of exothermic isomerization.



failed to provide any evidence for the formation of iceane (II). Disproportionation to give 1-ethyladamantane, 2-ethyladamantane, 1,3-dimethyladamantane, and other dimethyladamantanes⁹ was the major side reaction and took place to a greater extent with the sludge catalyst. Under more vigorous conditions, I itself disproportionates to the same products.

Rearrangement product I (mp 174–176°)¹⁰ was identical (ir, nmr, and mass spectrum) with the $C_{12}H_{18}$ hydrocarbon isolated from petroleum and assigned this structure by Hála, Landa, and Hanuš.⁵ The structure was proven by an independent synthesis, starting from 2-adamantanecarboxylic acid.¹¹ Treatment of the corresponding acid chloride¹² (bp 76–77° (0.3 mm), 138–140° (13 mm)) with an excess of diazomethane (dried over sodium)^{13,14} gave diazo ketone IV. Decomposition of IV in boiling toluene, with anhydrous copper sulfate (5.2 mmol per mmol of IV) as catalyst^{14b,15} and using a high dilution apparatus,¹⁶ gave a 55% yield of

(9) Cf. A. Schneider, R. W. Warren, and E. J. Janoski, *Trans. N. Y. Acad. Sci.*, **30** (2), 3 (1967); E. I. Bagrii, T. N. Dolgoplova, and P. I. Sainin, *Neftekhimiya*, **9**, 666 (1969).

(10) The melting point of II is very sensitive to its degree of purity; Landa⁶ reports mp 153–158° for 95% pure material.

(11) D. Fărcașiu, *Synthesis*, 615 (1972).

(12) S. Reiffers, quoted by J. Strating, J. Scharf, and H. Wynberg, *Recl. Trav. Chim. Pays-Bas*, **89**, 23 (1970).

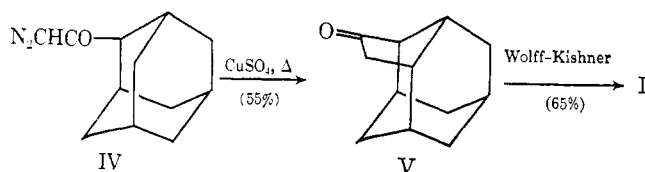
(13) F. Arndt, "Organic Synthesis," Collect. Vol. 2, Wiley, New York, N. Y., 1943, p 165.

(14) (a) F. Arndt, B. Eistert, and W. Partale, *Ber.*, **60**, 1364 (1927); (b) J. K. Chakrabarti, S. S. Szinai, and A. Todd, *J. Chem. Soc. C*, 1303 (1970).

(15) E. Wenkert, B. L. Mylari, and L. L. Davis, *J. Amer. Chem. Soc.*, **90**, 3870 (1968).

(16) D. Fărcașiu, *Org. Prep. Proced.*, **5**, 113 (1973).

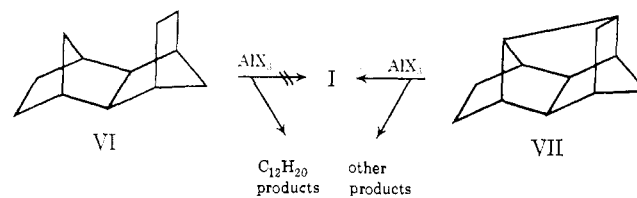
tetracyclo[6.3.1.0^{2,6}.0^{3,10}]dodecan-3-one (V)⁸ (ir (in



CCl_4) 1743, 1054 cm^{-1} ; nmr in CCl_4 characteristic pattern at δ 1.25–2.7 ppm, with a strong broad peak at 1.86 and two sharp peaks at 2.12 and 2.19 ppm; mass spectrum M^+ 176). I, obtained from V by modified Wolff–Kishner reduction,¹⁷ was identical with the product obtained by rearrangement.

Interestingly, VI,¹⁸ the first $C_{12}H_{18}$ precursor examined, failed to give any isomerization product at all.¹⁹ Instead, with $AlBr_3$ or with $AlBr_3$ -sludge only $C_{12}H_{20}$ alkyladamantane disproportionation products resulted.¹⁹ Under the gas phase conditions using a platinum–alumina catalyst which have been shown by McKervey to minimize or eliminate disproportionation,²⁰ only unchanged starting material was recovered. These same conditions²⁰ converted III in 75% isolated yield to I of over 90% purity.

Our first preparation of I by rearrangement⁶ utilized VII (pentacyclo[6.4.0.0^{2,10}.0^{3,7}.0^{5,9}]dodecane)²¹ as the



starting material. This result depended on disproportionation. Another tetracyclic product and two pentacyclic isomers were produced in this reaction but no tricyclic material.²² Ethanodiamantanes have also been synthesized by isomerization and by disproportionation–rearrangement.²³

Empirical force field (strain) calculations²⁴ provide convincing rationalizations of all of these results. Because of the prohibitively large number of tetracyclic $C_{12}H_{18}$ ring systems¹ and the complexity of the isomerization graph, our examination was restricted to the most probable rearrangement routes (Figure 1).^{6a,17,25}

Heats of formation, also given in Figure 1, were calculated using two different force fields, "Engler" (E)^{24a}

(17) H. W. Whitlock, Jr., and M. W. Siefken, *J. Amer. Chem. Soc.*, **90**, 4929 (1968).

(18) (a) K. Alder and F. Rickert, *Ann.*, **543**, 1 (1939); (b) J. K. Stille and D. A. Frey, *J. Amer. Chem. Soc.*, **81**, 4273 (1959); E. R. Hanna, K. T. Finley, W. H. Saunders, Jr., and V. Boekelheide, *ibid.*, **82**, 6342 (1960).

(19) The same result was obtained independently by Professor S. Landa (private communication).

(20) D. E. Johnson, M. A. McKervey, and J. J. Rooney, *J. Amer. Chem. Soc.*, **93**, 2798 (1971).

(21) H.-D. Scharf, *Tetrahedron*, **23**, 3057 (1967). We thank Dr. Scharf for a gift of VII.

(22) A detailed study of this reaction will be published subsequently.

(23) S. T. Rao, M. Sundaralingam, E. Osawa, E. Wiskott, and P. v. R. Schleyer, *Chem. Commun.*, 861 (1970); S. T. Rao and M. Sundaralingam, *Acta Crystallogr., Sect. B*, **28**, 694 (1972).

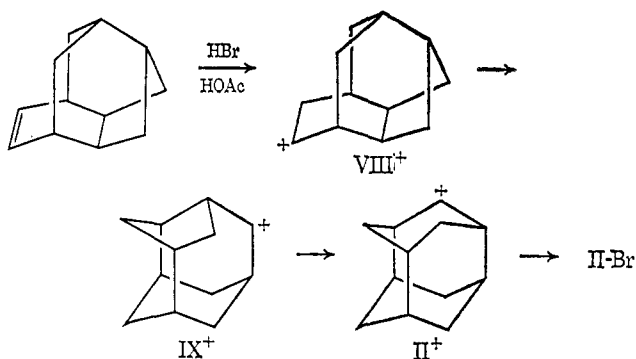
(24) (a) E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 8005 (1973); (b) N. L. Allinger, M. T. Tribble, M. A. Miller, and D. W. Wertz, *ibid.*, **93**, 1637 (1971).

(25) (a) A. T. Balaban, D. Fărcașiu, and R. Banica, *Rev. Roum. Chim.*, **11**, 1205 (1966); (b) E. M. Engler, M. Fărcașiu, A. Sevin, J. M. Cense, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 5769 (1973).

and "Allinger" (A).^{24b} Ethanoadamantane (I) is by far the most stable C₁₂H₁₈ isomer, being *ca.* 21–22 kcal/mol more stable than III and 6–7 kcal/mol more stable than iceane (II). This latter large difference, enhanced by the less favorable entropy of II, explains why no iceane is observed on AlBr₃ rearrangement. In fact, II rearranges to I under these conditions.⁴

Two principal routes, both involving only two 1,2-alkyl shifts, provide facile rearrangement pathways for conversion of III into I (Figure 1). The same is true for the isomerization of II into I. The carbocations involved, also favorable in energy, can be generated reversibly by hydride abstraction under the AlBr₃ conditions used. The dihedral angles involving the migrating bonds and the adjacent vacant carbocation orbitals are also favorable.^{25b}

However, as Figure 1 implies, iceane (II) is a local minimum on the C₁₂H₁₈ energy surface. The realization of this fact provided incentive for the development of the Cupas-Hodakowski synthesis of II.⁴ Their conditions only permit sequential cationic 1,2-shifts; intermediate cation IX⁺ can rearrange to the iceane but not



to the ethanoadamantane skeleton. Judging from the energies of the parent hydrocarbons, VIII, IX, and II, strain should be relieved in each step, VIII⁺ → IX⁺ and IX⁺ → II⁺.

Examination of the C₁₂H₁₈ graph also rationalizes the behavior of VI and VII on treatment with AlBr₃. No pathway is available for the conversion of VI to I which does not involve a prohibitively high energy intermediate. On the other hand, much of the strain energy (~45 kcal/mol) of pentacyclic VII can be relieved by bond rupture and disproportionation; X and XI are likely products, but VI is less favorable (Table I). X

Table I

	XI	VII	X	XII
ΔH_f° (calcd), kcal/mol	-16.49 (E)	+6.69 (E)	-13.73 (E)	-17.17 (E)
	-11.84 (A)	+7.42 (A)	-11.76 (A)	-17.31 (A)
Strain, kcal/mol	27.25 (E)	44.49 (E)	30.01 (E)	26.57 (E)
	32.23 (A)	45.42 (A)	32.33 (A)	26.76 (A)

is most easily convertible to I by two energetically favorable steps, X → XII and XII → I.

Acknowledgments. This work was supported by the National Institutes of Health (AI-07766 and GM-19134),

The National Science Foundation (GP-29078X), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Hoffmann-La Roche, Inc., Nutley, N. J. Computer time was supplied by Princeton University. Access to the Princeton Computer Graphics Laboratory, supported by the National Institutes of Health, facilitated the calculations. We thank Professor C. Cupas for stimulating discussions.

Dan Fărcașiu, Erik Wiskott, Eiji Ōsawa
Wilfried Thielecke, Edward M. Engler
Joel Slutsky, Paul v. R. Schleyer*

Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Gerald J. Kent

Department of Chemistry, Rider College
Trenton, New Jersey 08648

Received March 14, 1974

Domino Diels–Alder Reactions. I. Applications to the Rapid Construction of Polyfused Cyclopentanoid Systems

Sir:

Among several reasons for interest in a synthetic process which can achieve the multiple fusion of cyclopentane rings conveniently and in good yield is the speculation that such a method might serve as the ultimate tool for the efficient preparation of dodecahedrane. Although there are scattered reports of various ingenious techniques for the construction of representative polycyclopentanoid structures, the methodology is frequently intricate, and the overall yields are usually low.^{1–7} One might hope to achieve appropriate carbon–carbon bond formation rapidly and to enjoy the latitude of functional group incorporation, thereby providing an opportunity for further structural elaboration if desired. The present work describes a solution to this problem for the tetracyclic case based upon a multiple cycloaddition pathway, herein designated as the domino Diels–Alder reaction.

Conceptually, the generalized domino Diels–Alder reaction involves initial *intermolecular* ($\pi_4 + \pi_2$) cycloaddition of a dienophile to a 1,3-diene moiety, subsequent involvement of the newly formed olefinic center (or the residual double bond in the dienophile if originally acetylenic) in *intramolecular* ($\pi_4 + \pi_2$) bonding, and continuation of this sequence if structurally permissible. The key steps, illustrated for a reaction of order [2], are exemplified by the conversion of 1 to 3.⁸

(1) R. B. Woodward, T. Fukunaga, and R. C. Kelly, *J. Amer. Chem. Soc.*, **86**, 3162 (1964).

(2) I. T. Jacobson, *Acta Chem. Scand.*, **21**, 2235 (1967); L. A. Paquette, G. V. Meehan, and S. J. Marshall, *J. Amer. Chem. Soc.*, **91**, 6779 (1969).

(3) R. Russo, Y. Lambert, and P. Deslongchamps, *Can. J. Chem.*, **49**, 531 (1971); C. Mercier, P. Soucy, W. Rosen, and P. Deslongchamps, *Syn. Commun.*, **3**, 161 (1973).

(4) R. Srinivasan, *J. Amer. Chem. Soc.*, **92**, 7542 (1970); **94**, 8117 (1972).

(5) A. de Meijere, D. Kaufmann, and O. Schallner, *Angew. Chem., Int. Ed. Engl.*, **10**, 417 (1971); *Tetrahedron Lett.*, 553 (1973).

(6) P. E. Eaton and R. H. Mueller, *J. Amer. Chem. Soc.*, **94**, 1014 (1972).

(7) J. M. Edwards, I. H. Qureshi, U. Weiss, T. Akiyama, and J. V. Silverton, *J. Org. Chem.*, **38**, 2919 (1973).

(8) Higher order processes are, of course, conceivable. As early examples of order [2] behavior, we cite the reactions triggered by singlet