

and Research Corporation. The author thanks the School of Chemistry and the Research Corporation for providing matching funds for the purchase of Raman equipment. The Raman spectra in Figure 1 were ob-

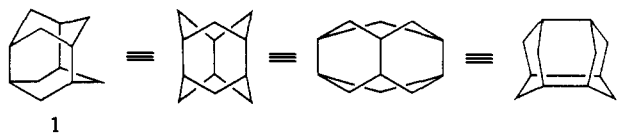
tained by Mr. C. S. Liu in Professor D. C. O'Shea's light scattering laboratory. The author is indebted to Dr. M. P. Thompson and Professor D. Puett for the highly purified samples of  $\alpha$ -lactalbumin.

## Communications to the Editor

### Iceane

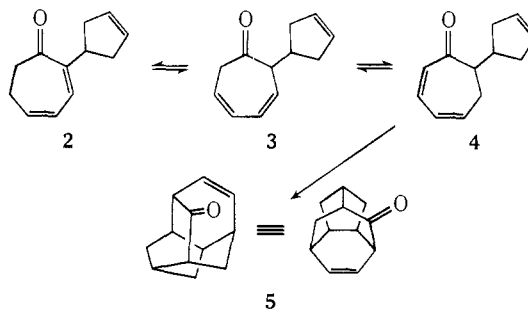
Sir:

The synthesis of strained bridged polycyclic hydrocarbons of high symmetry and unusual structure continues to be a challenging objective to organic chemists.<sup>1,2</sup> Tetracyclo[5.3.1.1<sup>2,6</sup>.0<sup>4,9</sup>]dodecane (**1**)<sup>2</sup> is par-



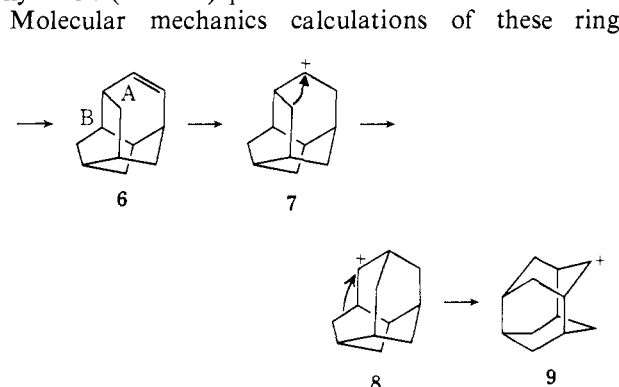
ticularly interesting in this regard. This highly symmetrical (point group  $D_{3h}$ ) rigid molecule has a carbon skeleton consisting of two chair cyclohexanes connected to each other by three axial bonds, and thus the periphery of this molecule is composed of three boat cyclohexanes. The trivial name "iceane" has been proposed<sup>3</sup> for **1** since this molecule is geometrically the hydrocarbon analog of crystalline water (Figure 1).<sup>4</sup> We wish to report the synthesis of iceane (**1**).

The facile construction of a  $C_{12}$  tetracyclic easily convertible to **1** was promised by the intramolecular  $\pi_s^4 + \pi_s^2$  cyclization of the appropriate alkenyl dihydrodropone.<sup>5</sup> Reaction of  $\Delta^3$ -cyclopentenylmagnesium bromide<sup>6</sup> with tropone<sup>7</sup> at 0° gave a mixture of 2-( $\Delta^3$ -cyclopentenyl)dihydrodropones, **2-4** (38%, bp 103–105° (1–3 mm)). Unlike our previously studied cases,<sup>5</sup> the symmetrical nature of the olefin and the geometric constraints imposed by the cyclopentene ring obviates the formation of tetracyclic cycloaddition products from dihydrodropones **2** and **3**. Pyrolysis of the dihydrodropones at 200–205° (heptane containing 5% *N,N*-dimethylaniline 24 hr) gave a single product, tetracyclo[5.3.2.0.2,4,0<sup>4,9</sup>]dodec-11-en-8-one (**5**) (mp 214.0–216.0°,  $\nu_{max}^{CCl_4}$  1719.3  $cm^{-1}$ ), in 21% yield.<sup>8,9</sup> Conversion of **5**

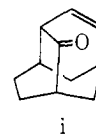


to its semicarbozone (mp 208.0–210.0°) followed by treatment with potassium hydroxide<sup>10</sup> gave olefin **6** (88%, mp 191.5–194.0°). The cmr spectrum of **6** (Figure 2A) exhibited seven lines which was consistent with its symmetrical structure.

Conceptually, two Wagner–Meerwein rearrangements separate the carbonium ion **7** from iceane. For example, migration of bond A results in the contraction of seven-member ring to produce **8** while a further 1,2-alkyl shift (bond B) produces the iceane skeleton **9**.<sup>11</sup>

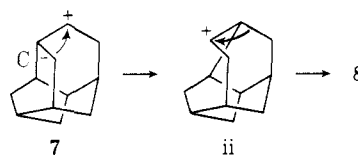


metrical triplets centered at  $\tau$  3.72 and 4.03, while an unobscured triplet, assignable to the allylic bridgehead proton adjacent to the carbonyl, appeared at  $\tau$  7.12.



(10) D. Todd, *Org. React.*, **4**, 378 (1948).

(11) Alternately, migration of bond C would produce (ii). A further 1,2-alkyl shift, as indicated, would produce the identical ion **8**.



(1) (a) G. Schroeder, *Angew. Chem., Int. Ed. Engl.*, **2**, 481 (1963); (b) P. E. Eaton and T. W. Cole, *J. Amer. Chem. Soc.*, **86**, 962, 3157 (1964); (c) P. v. R. Schleyer and M. M. Donaldson, *ibid.*, **82**, 4645 (1960); (d) C. A. Cupas, P. v. R. Schleyer, and D. J. Trecker, *ibid.*, **87**, 917 (1965).

(2) See also end paper, J. B. Hendrickson, D. J. Cram, and G. S. Hammond, "Organic Chemistry," 3rd ed, McGraw-Hill, New York, N. Y., 1970.

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

(4) A hexagonal diamond having the ice structure has also been described. "Iceane" is the first member of this family: F. P. Bundy and J. S. Kaper, *J. Chem. Phys.*, **46**, 3437 (1967).

(5) C. A. Cupas, W. Schumann, and W. E. Heyd, *J. Amer. Chem. Soc.*, **92**, 3237 (1970); (b) C. A. Cupas, W. E. Heyd, and M. S. Kong, *ibid.*, **93**, 4623 (1971); (c) L. Hodakowski and C. A. Cupas, *Tetrahedron Lett.*, 1009 (1973).

(6) P. D. Bartlett and M. R. Rice, *J. Org. Chem.*, **28**, 3351 (1963).

(7) P. Radlick, *J. Org. Chem.*, **29**, 960 (1964).

(8) Satisfactory elemental analyses were obtained for all new compounds.

(9) The proton nmr spectrum of **5** showed the same features characteristic of that of 2-homopropoadamantone (i) exhibiting two sym-

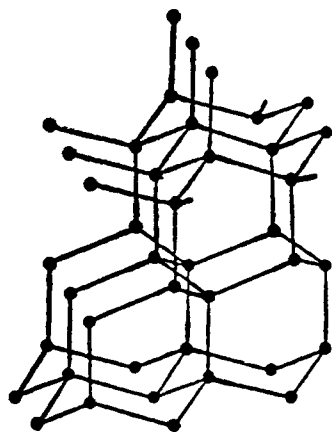
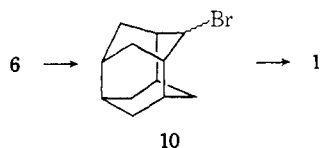


Figure 1. Assumed structure for the ice-Ih crystal.<sup>4</sup>

systems, by Schleyer and Engler,<sup>12a</sup> 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.<sup>12b</sup>

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.<sup>13</sup> This gave iceane, mp 327.0–328.5°.<sup>14</sup> 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  $\delta$  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.<sup>15</sup>

(12) (a) Private communication, P. v. R. Schleyer and E. Engler, Princeton University. See also E. M. Engler, J. D. Andose, 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).

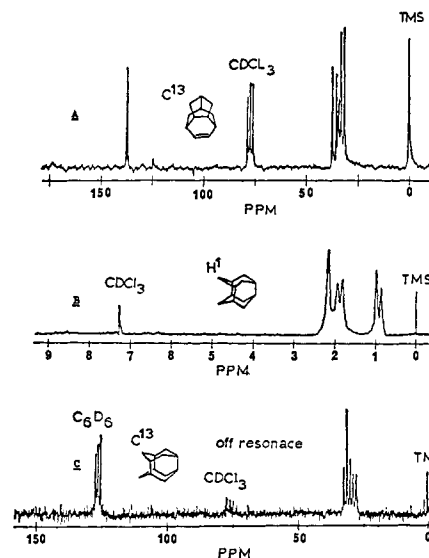
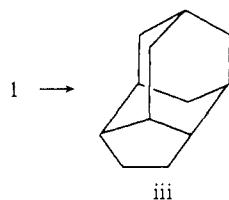


Figure 2. (A) 25.16-MHz spectrum of **6**; (B) 100-MHz spectrum of iceane (**1**); (C) 25.16-MHz spectrum (off-resonance of iceane (**1**)).

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

Sir:

An astonishingly large number of tetracyclic  $C_{12}H_{18}$  isomers are possible.<sup>1</sup> Of these, two have special appeal. II, "iceane,"<sup>2</sup> is the first member of an isomeric, hexagonal diamond<sup>3</sup> family with the Wurzite or ice structure.<sup>4</sup> I, 2,4-ethanoadamantane (tetracyclo[6.3.1.0<sup>2,6</sup>.0<sup>5,10</sup>]dodecane), like adamantane, was first discovered by Landa as a constituent from petroleum from Hodonin.<sup>5</sup> 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.<sup>6</sup>

In fact, treatment of tetracyclo[6.4.0.0<sup>4,12</sup>.0<sup>5,9</sup>]dodecane (III)<sup>7</sup> with  $AlBr_3$  or with  $AlBr_3$ -sludge catalyst in  $CS_2$  at 0 or 25° gave ethanoadamantane (I)<sup>8</sup> 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. Hanneman, H. M. Strong, 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. Hanuš, *Angew. Chem.*, **78**, 1060 (1966); (b) Z. Weidenhaber and S. Hála, *Sb. Vys. Sk. Chem.-Technol. Prague, Technol. Palt.*, **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.