

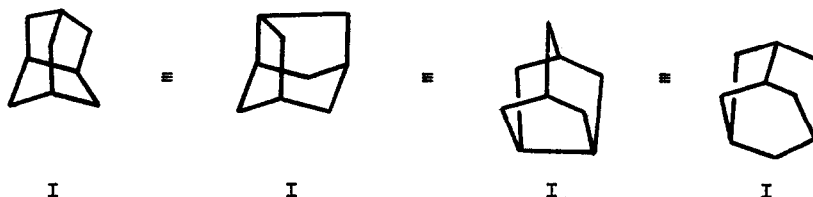
NORADAMANTANE BY ALUMINUM HALIDE CATALYZED REARRANGEMENT

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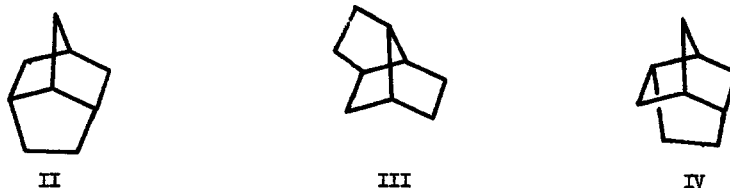
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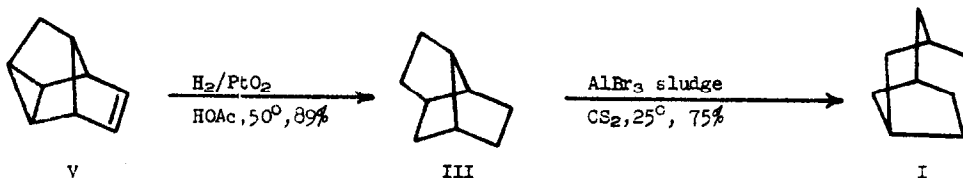
Lewis acid catalyzed rearrangements of the type which yield adamantane (1), alkyl adamantanes (2), and the adamantalogs, diamantane (Congressane) (3) and triamantane (4) are proving to be remarkably general and useful reactions (5). We report here that the lower adamantane homolog, noradamantane (tricyclo[3.3.1.0^{3,7}]nonane) (I), can also be obtained in excellent yield by the rearrangement route.



As starting material for the preparation of I, a tricyclic isomer was needed. Only four tricyclononanes (I-IV), without three or four-membered rings or improbably strained structures, are possible. Of these, brendane (II) and brexane (III) are known compounds (6), but IV (which might colloquially be called "twist-brendane") apparently has not been reported. Noradamantane alone among I-IV does not contain the rather highly strained bicyclo[2.2.1]-heptane part structure. Hence, I should be the most stable tricyclononane isomer. The other hydrocarbons, II-IV, are thus all good potential starting materials for the preparation of I by rearrangement.



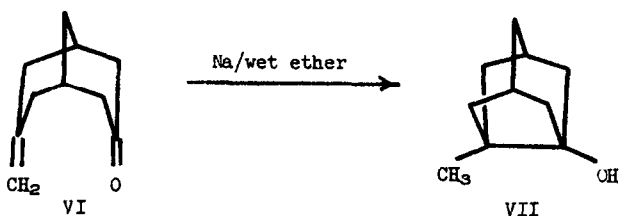
Since the published routes to brendane (II) and brexane (III) are rather cumbersome (6), we developed our own procedure. Tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (V), a readily available compound (7), could be hydrogenated at 50° in a Parr apparatus, using PtO₂ catalyst and acetic acid solvent. The product, obtained in 89% yield, was almost pure brexane (III) (6,8). The rearrangement of III to noradamantane (I) was especially easy. With the Williams AlBr₃ sludge catalyst (4) and CS₂ as the solvent, III was converted completely to I within 0.5 hour at room temperature. After this time starting material was all gone, and a yield of 75% of I could be isolated. At 0°, the isomerization was half complete within five minutes. At this stage of the reaction a small peak, possible II (or IV), appeared in the gas chromatogram. III cannot be converted to I directly, but must pass through structures such as II or IV as intermediates. The small peak had disappeared by the end of the reaction. At longer reaction times at room temperature traces of new materials could be detected by gas chromatography; these were probably bicyclic products of ring opening.



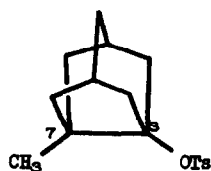
Noradamantane (I) melted in a sealed capillary at 203–204°, some 65° below the value for adamantane (1,5), but still remarkably high for a C₁₀H₁₄ hydrocarbon. The n.m.r. spectrum displayed three moderately broad peaks at 60 MHz: resonances at $\delta=2.10$ and 2.40 (area 2H each) due to the two types of bridgehead hydrogens, and a main absorption (10H) at $\delta=1.60$ due to the adamantane-like (9) methylene groups. The base peak in the mass spectrum was at $m/e = 80$. Other intense peaks were found at $m/e = 79, 81, 93$ and 122 (molecular ion). The infrared spectrum was quite simple, with bands at 2920, 2850, 1456, 1444w, 1320, 1300w and 1076 cm.⁻¹

Rearrangement reactions of this type do not constitute a structure proof, at least of

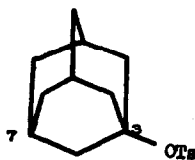
the conventional type. Our product was obviously not identical with brexane (III), its precursor. Brendane (II) could also be ruled out, for a comparison with spectra of authentic material was possible (6,8). This left only IV, for which a more complicated n.m.r. spectrum than actually observed would have been expected. Prior to our experiments, noradamantane (I) had been prepared by Vogt and Hoover (10) by a structurally unambiguous synthesis. Direct comparison of samples prepared in the two laboratories (n.m.r., mass spectra, gas chromatography, mixed m.p.) confirmed their identity.



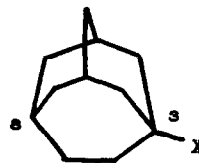
Derivatives of noradamantane have been reported only twice before in the literature, first by Meerwein (11), and more recently by Eakin, Martin and Parker (12). The latter group reduced VI to VII by the action of sodium in wet ether. Because of our interest in bridgehead reactivity (13,14), we converted VII to its tosylate (VIII), m.p. 73-75°, and measured the acetolysis rate constants: k_1 (100.0°) = 1.72×10^{-7} sec.⁻¹; k_1 (150.0°) = 3.50×10^{-5} sec.⁻¹. The activation constants were: $\Delta H^\ddagger = 32.6$ kcal/mole; $\Delta S^\ddagger = -2.6$ e.u. The acetolysis product of VIII was exclusively the acetate of VII. The calculated rate constant at 25°, 2.17×10^{-12} sec.⁻¹, was 3×10^8 slower than that of 1-adamantyl tosylate (IX) (5.86×10^{-4} sec.⁻¹ at 25°) (13). A reactivity difference of 10^{11} between VIII and corresponding 3-homoadamantyl derivatives (X) can be estimated (13). The following series illustrates the marked effect upon the solvolysis rate produced by the contraction of the C₃..C₇ (C₈ in X) bridge from two methylene groups (X), to one methylene (IX) to none (VIII).



VIII

Rel. rates 10^{-11} 

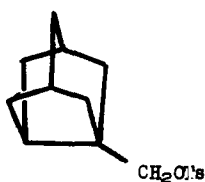
IX

Rel. rates 10^{-9} 

X

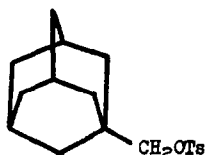
Rel. rates 1

A sample of 3-noradamantylcarbinyl tosylate (XI), m.p. 67-69° was kindly provided by Drs. Vogt and Hoover (10). The acetolysis rate constants and derived thermodynamic parameters were: k_1 (50.0°) = 1.14×10^{-5} sec.⁻¹; k_1 (75.0°) = 1.25×10^{-4} sec.⁻¹; ΔH^\ddagger = 20.7 kcal/mole; ΔS^\ddagger = 17.2 e.u. Most neopentyl-type tosylates react at practically the same rate as neopentyl tosylate itself (15). 1-Adamantylcarbinyl tosylate (XII) (15) is no exception to this rule, but XI reacted with remarkable rapidity. The rate constant calculated at 25°, 7.02×10^{-7} sec.⁻¹, was 17,000 times faster than that of neopentyl tosylate (15). The product appeared to be exclusively 1-adamantyl acetate. The fastest neopentyl-type arenesulfonate we have examined (15), 1-methylcyclobutylcarbinyl p-nitrobenzenesulfonate (XIII) -- a compound capable of releasing some 20 kcal. of ring strain energy when it rearranges to the 1-methylcyclopentyl cation -- reacted 24,600 times faster than neopentyl p-nitrobenzenesulfonate at 25° (16). Evidently relief of strain present in XI during the solvolysis process is quite efficient, and a very much enhanced reaction rate results. A full interpretation of these rate data will be presented in future publications.



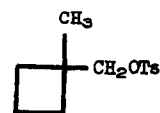
XI

Rel. rates,
HOAc, 25° 17,000
neopentyl-OTs = 1.0



XII

Rel. rates 3.9 (15)



XIII

Rel. rates 24,600 (16)

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