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THE MECHANISM OF PYROLYSIS OF POLYCYCLOALKYL SULFONATES

THE HOMO-RETROENE REACTION IN THE NORADAMANTANE, ADAMANTANE AND DIAMANTANE SERIES

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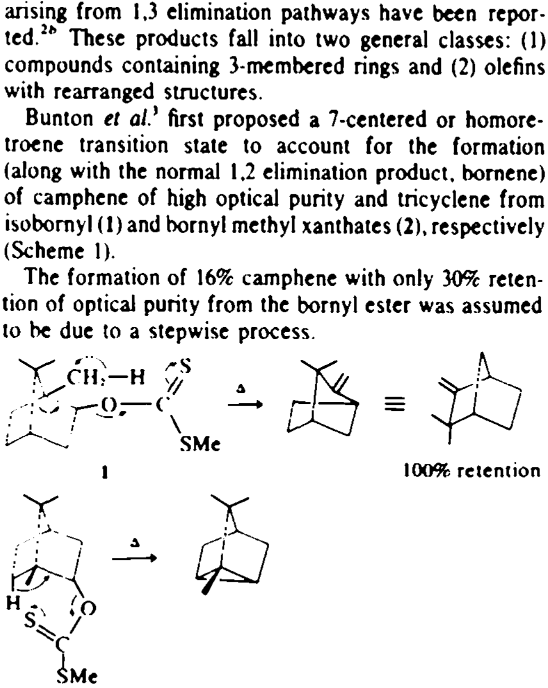
Abstract—The minor product, 4-protoadamantene (**5**), from the gas phase pyrolysis of 2-adamantyl mesylate (**3**) was shown by labelling experiments not to arise from the major product, 2,4-dehydroadamantane (**4**), but rather by a concerted process (homo-retroene reaction). In the formation of **4**, 1,3-elimination is favored by at least a 92:8 margin over a competitive route involving α-elimination to a carbene and then C–H insertion. Equatorial and axial 2-noradamantyl mesylates pyrolyze to give predominantly 4-brendene (**11**) and triaxane (**12**), respectively, as required by concerted 1,3-eliminations, and not by an ion pair mechanism. The cross-over product appears in each case to result from the epimerization of the starting material by a wall-catalyzed process. In agreement with the results of the noradamantyl substrates, pyrolysis of 3-diamantyl mesylate (**16**) gave results which suggest that product stability helps to determine the course of the reaction. The products with the least amount of strain were obtained, namely 3,5-dehydrodiamantane (**17**) and pentacyclo[8.3.1.$0^{2,8}$.$0^{4,11}$.$0^{7,12}$]tetradec-5-ene (**19**, protodiamantene). The ease of separation of the cyclopropanic and olefinic products makes these reactions synthetically useful.

Thermolytic 1,2 ester eliminations proceeding through 6-centered transition states (retroene reactions) are well known and widely applied in synthetic organic chemistry.[2] Occasionally, "abnormal" products apparently arising from 1,3 elimination pathways have been reported.[2b] These products fall into two general classes: (1) compounds containing 3-membered rings and (2) olefins with rearranged structures.

Bunton *et al.*[3] first proposed a 7-centered or homoretroene transition state to account for the formation (along with the normal 1,2 elimination product, bornene) of camphene of high optical purity and tricyclene from isobornyl (**1**) and bornyl methyl xanthates (**2**), respectively (Scheme 1).

The formation of 16% camphene with only 30% retention of optical purity from the bornyl ester was assumed to be due to a stepwise process.



1

100% retention

2

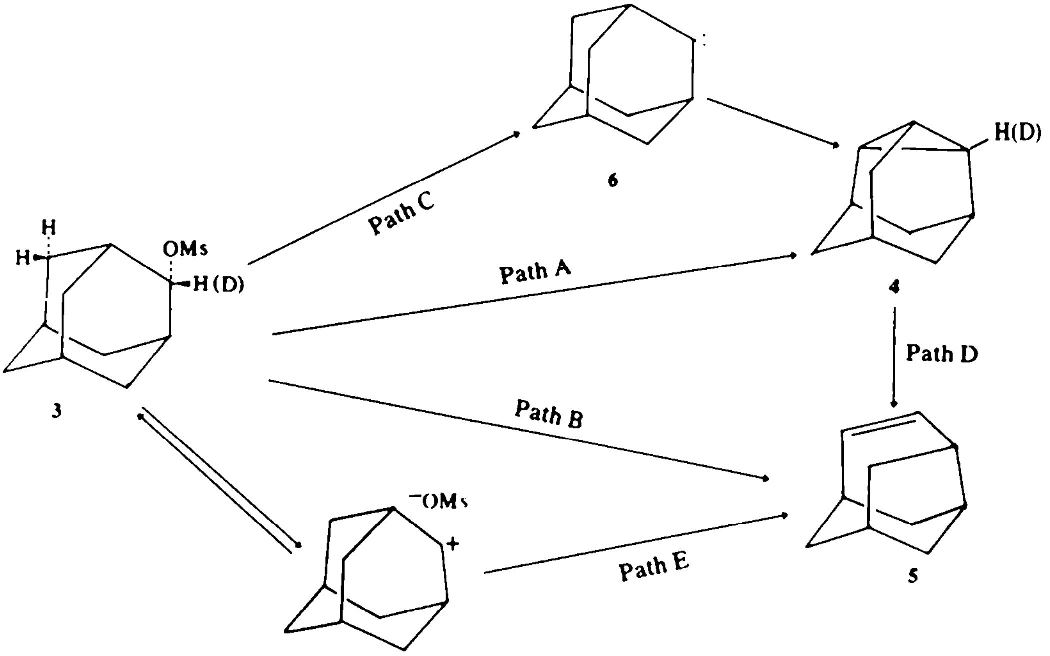
Scheme 1.

More recently, a 7-centered concerted elimination mechanism was proposed by Johnston and Overton[4] to account for the pyrolytic rearrangement of the atisane to the 7,20-secoaconane skeleton and by Kwart and Hoster[5] to explain the first acyclic example, the predominance of the less stable, unconjugated olefin ($H_2C{=}C(CH_3)CH_2Ph$) arising from the thermolysis of neophyl acetate. Several other instances of 1,3 elimination have been reported.[6]

Adamantanoid molecules are particularly well suited for the observation of 1,3 eliminations since competition by "normal" 1,2 elimination pathways are disfavored due to the necessity of forming high energy bridgehead double bonds. Thus, pyrolysis of 3-homoadamantyl acetate gave two skeletally rearranged olefins (as well as the non-bridgehead olefin, 4-homoadamantene).[7] Pertinent to the present work, pyrolysis of 2-adamantane methanesulfonate (**3**) gave cleanly and in high yield a 3:2 mixture of 2,4-dehydroadamantane (**4**) and 4-protoadamantene (**5**) (tricyclo[4.3.1.$0^{3,8}$]dec-4-ene).[8] Only trace amounts (~1%) of adamantane were formed. The synthetic utility of this reaction rests on the ease of separation of the saturated from the unsaturated products by chromatography on silica gel containing 15% silver nitrate.

We now report the extension of the homo-retroene reaction to the noradamantane and to the diamantane series. The results, along with labelling experiments on 2-adamantyl substrates, allow further mechanistic interpretations.

Pyrolysis of 2-adamantyl-2-d methansulfonate. The postulated[8] mechanistic routes leading from **3** to **4** and **5**, paths A and B, are shown in Scheme 2. However, other

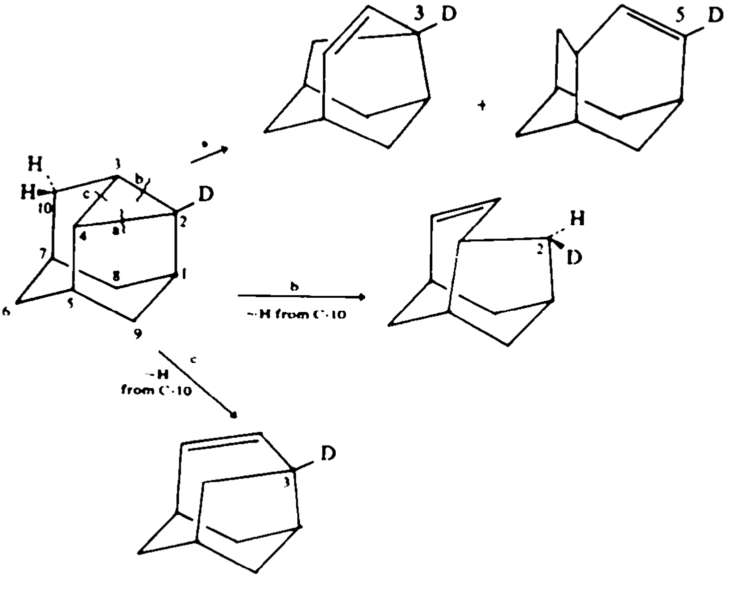


Scheme 2.

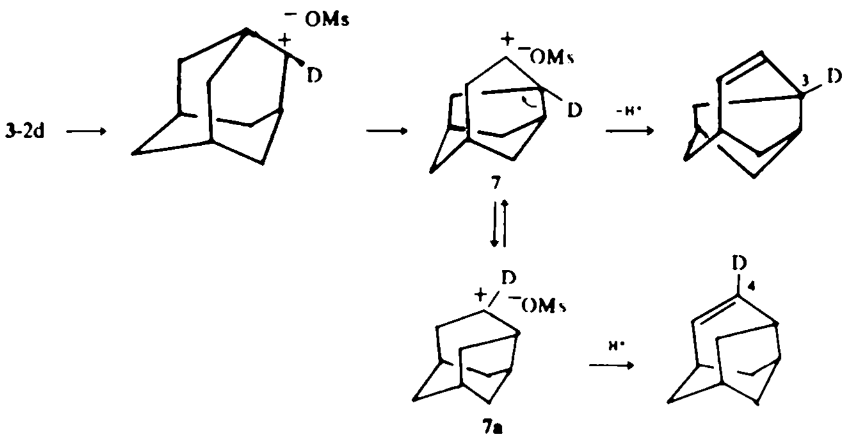
mechanistic pathways leading to the same products are conceivable.[2,3] In other cases, thermolysis of esters can involve concerted α-elimination to a carbene;[3a] thus, carbene (6) from 3 (path C, Scheme 2) could give 4.[9] The minor product (5) could be formed from 4 (path D, Scheme 2) by a consecutive rather than a competitive process. Pyrolysis of 4 has been shown to give 5, either by a 2,4-bond homolysis, or (more probably) by a $\sigma 2 + \sigma 2$ cycloreversion.[10] Still another possibility exists, that 5 be formed from 3 by a mechanism involving ion pairs[2,3a,6d,11] (path E, Scheme 2). The present investigation of the labelled ester (3-2*d*) helps to elucidate some of these questions.

3-2*d* was subjected to thermolysis at 550° and the products isolated in the usual manner. The mass spectrum of 5 indicated 99.5% monodeuterocompound (5-d); thus no label was lost in the formation of 5.[12] On the other hand, 4 contained 7–8% of nondeuterated material, formed most probably by path C; the remainder (92–3%) had to be formed by path A.

Comparison of the NMR spectra of 5d$_1$ with 5 revealed that the signal for one of the bridgehead H atoms (δ2.66) has disappeared in the former, while there remained two olefinic (δ6.19, m, splitting pattern simplified), three bridgehead ($\delta = 2.26$, broad), and eight methylene protons (δ1.27–1.90, m). Since 5-d$_1$ formed from 4d$_1$ should contain deuterium at the double bond and on a methylene group as well (Scheme 3) we conclude that 5 is not formed from 4 and that alternative pathways of elimination possessing nearly equal free



Scheme 3.



Scheme 4.

energies of activation ($\Delta\Delta G^{\neq} = 0.3$ kcal/mol) are available to **3**. The higher deuterium content of **5**, relative to **4**, indicated that the latter could not be the exclusive or even the main precursor of **5**.

The comparison of the ^{13}C-NMR spectra of **5**-d$_1$ and **5** corroborates these conclusions. From the signals for the saturated carbon atoms in **5** (δ32.0, C-10; 32.6, C-6; 34.1, C-8; 36.4, C-3; 39.6, C-1; 39.9, C-7; 42.4, C-2; 43.9, C-9), only the one corresponding to C-3 shows a marked decrease in intensity for the deuterated material (**5**-d).†

The study of **3**-2d could not distinguish between the concerted homo-retroene elimination (path B, Scheme 2) and a possible ion pair mechanism (path E, Scheme 2) for the formation of **5**. While the automerization of the protoadamantyl cation (**7**)[13] in the ion pair should result in some deuterium incorporation at C-4, the observed absence of such scrambling could result if proton abstraction from **7** by the counter ion is much faster than the transformation **7**$\rightleftharpoons$**7a** (Scheme 4).

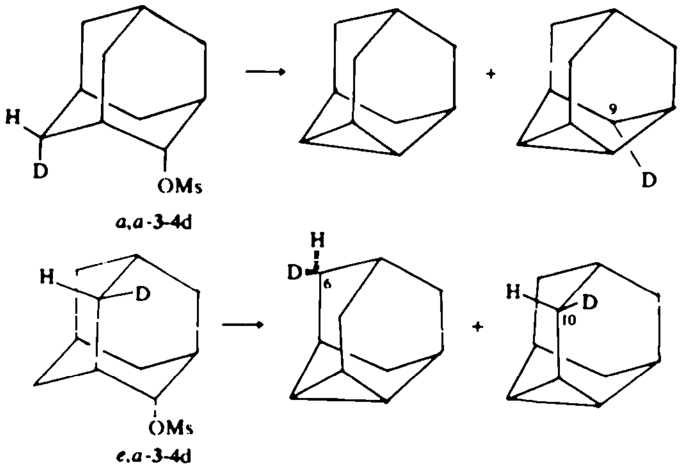
In preliminary experiments on the decomposition of 2-adamantyl-4-d mesylate (**3**-4d) in a Monel reactor, the dehydroadamantane formed exhibited similar relative signal intensities in the ^{13}C-NMR spectrum whether the starting material was the pure diaxial isomer (*a,a*-**3**-4d) or a 1:1 mixture with the axial-equatorial isomer (*e,a*-**3**-4d). The elimination from the two epimers should lead to different distributions of the label in the products (Scheme 5), but both samples contained deuterium at C-6, C-9, and C-10. This result indicates a facile epimerization of the starting material which can be best rationalized as involving some sort of reversible dissociation, e.g. via ion pairs.[14]

Whether dissociation to ion pairs is a necessary step for the homo-retroene elimination (**3**→**5**), or whether it is only a competing reaction, was assessed by investigating the 2-noradamantyl mesylates.

Pyrolysis of equatorial (**8**) *and axial* (**9**) *2-noradamantyl methanesulfonates*. Concerted elimination (Paths A and B) from the two epimeric 2-noradamantyl mesylates (**8** and **9**) should lead to different products (Scheme 6).

On the other hand, if ion pairs were involved in competition with the concerted 1,3-elimination of Path A (cf. Path E, Scheme 2), both epimers **8** and **9** should give 4-brendene (**11**) (olefins **14** and **15** are too strained to be likely products).

Equatorial 2-noradamantanol[15a] is available from the reaction of deltacyclane with sulfuric acid. Oxidation with chromic acid affords 2-noradamantanone, and subsequent reduction with LiAlH$_4$ furnishes the epimeric axial-2-noradamantanol.[15a] Both alcohols were converted to the corresponding mesylates in the usual manner.



Scheme 5.

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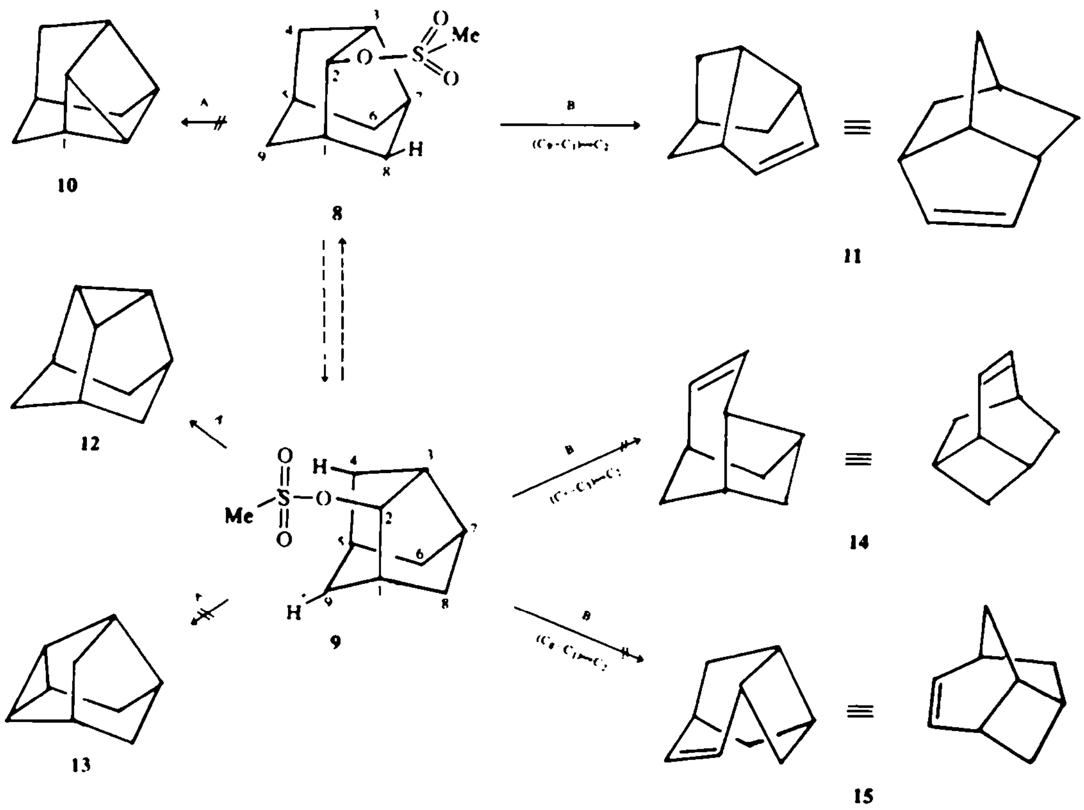
†The ^{2}H-NMR spectrum also indicates that all of the deuterium label is located at a single position. The spectrum contained a single peak corresponding to the signal absent from the ^{1}H spectrum of **5**-d$_1$ (see above).

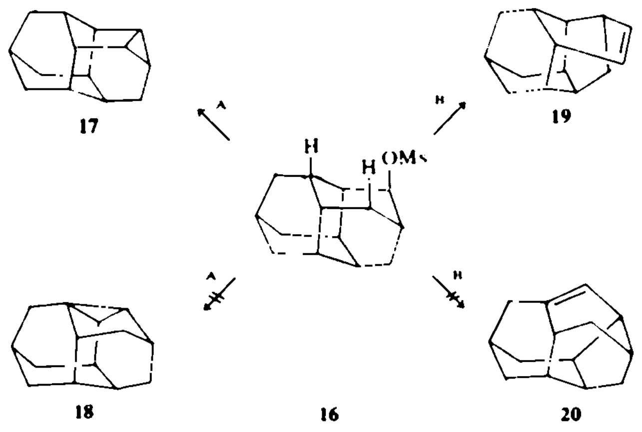


Scheme 6.

The pyrolysis of **8** at 530° afforded in 70% yield a mixture of three hydrocarbons in the ratio 68 (*m/e* 120)[16]: 28 (*m/e* 120): 4 (*m/e* 122). The major product could be easily separated from the other two by chromatography on 15% silver nitrate on silica gel and all three components were isolated by preparative glc.

As expected, the major product was identified as 4-brendene[15e] (**11**) by its spectral and physical properties, and it was converted to 4-brendanone[15e] by hydroboration-oxidation.[17] The second product (*m/e* 120) was shown to be triaxane (**12**),[18] by comparison of its ^{1}H-NMR and ^{13}C-NMR spectra with published spectra. The third product (*m/e* 122) was noradamantane.[15] The pyrolysis of **9** under identical conditions gave rise to a 1:4 ratio of hydrocarbons **11** and **12**, in 75% combined yield.

The regioselectivity observed, with the axial mesylate **9** giving much less **11** than the equatorial mesylate **8**, is not consistent with the prediction for an ion pair mechanism. The detection of some cross-over products (**12** from **8** and **11** from **9**) indicates a partial epimerization of the starting material prior to decomposition, possibly in a wall-catalyzed reaction. Indeed it was observed that pyrolysis of **8** and **9** in a gold coil reactor[7a,19] reduces the amount of cross-over product substantially. We conclude that the homo-retroene elimination in the noradamantyl series (**8** to **11**) is a concerted process. It may well be similarly concerted in the adamantyl series (**3** to **5**), but since epimerization in this case is fast compared with elimination (see above), **5** might be formed either by epimerization followed by Path B or ion pair formation followed by Path E (Scheme 2). Notwithstanding the



Scheme 7.

imperfect regioselectivity, the pyrolyses of **8** and **9** represent attractive synthetic routes to 4-brendene (**11**) and triaxane (**12**), respectively.[20]

Pyrolysis of 3-diamantyl methanesulfonate (**16**). In contrast to the 2-adamantyl (**3**) case, the two γ-H atoms equidistant to the mesylate group are no longer equivalent in **16**. Four products are conceivable (**17–20**, Scheme 7).

Pyrolysis of **16** at 550° yielded a 3:2 mixture of two hydrocarbons (along with about 1% diamantane) in 70% yield. The major product, identified by comparison with a sample prepared by an alternative route,[21] was 3,5-dehydrodiamantane (**17**). The other possible hexacyclic product, 1,3-dehydrodiamantane (**18**), calculated[21] to be appreciably more strained than **17**, was not formed. The NMR spectrum of the second product (Experimental) was consistent with the protodiamantene **19** (pentacyclo[$8.3.1.0^{2.8}.0^{4.13}.0^{7.12}$]tetradec-5-ene); again, the more strained bridgehead olefin, **20**, was not formed in the reaction.[22]

We conclude from the results of the pyrolysis of **8**, **9** and **16** that the strain in the products contributes to the determination of the regiospecificity of both paths A and B in the pyrolysis of esters.

EXPERIMENTAL

General. M.ps (Mettler FP1 apparatus) are uncorrected. Elemental analyses were performed by Hoffmann–LaRoche, Inc. The ^1H-NMR spectra were taken at 60 (Varian A-60A instrument) and 100 MHz (Varian HA-100 instrument), the ^{13}C-NMR spectra at 25.2 MHz (Varian XL-100 instrument), and the ^2H-NMR spectra at 15.4 MHz (Varian XL-100 instrument). Mass spectra (AEI-MS9 instrument) and GLC-mass spectra (E.I. Du-Pont 21–490 instrument) were determined at 70 eV.

Synthesis and pyrolysis of 2-adamantyl-2-d methanesulfonate (**3-2-d**). The mesylate **3-2-d** was synthesized as described for the unlabelled material,[8] except that 2-adamantanol-2-d (obtained from adamentanone and lithium aluminum deuteride) was employed. The pyrolysis and product separation were conducted as described previously.

2-*Equatorial-noradamantyl methanesulphonate*. Methane-sulphonyl chloride (3 ml) was added to a soln of 2-*equatorial*-noradamantanol[15a] (0.5 g, m.p. 222–224°) in pyridine (10 ml) and the mixture was stirred at room temp. for 72 hr. The mixture was then poured into ice-water (20 ml) which was extracted with ether (3 × 20 ml). The ether extract was washed with 15% HCl, satd Na_2CO_3, water, dried and filtered. Decolourising charcoal (0.1 g) was added to the filtrate and the mixture was filtered through celite after 1 hr. Evaporation of the solvent afforded a gum-like solid (0.65 g), which, on crystallization a few times in pentane-ether at −78° gave 2-*equatorial*-noradamantyl methanesulphonate (0.42 g), homogeneous on tlc, m.p. 65–66°. IR (CCl_4): 1360, 1340, 1176, and 930 cm^{-1}; NMR: δ 4.77 (1H, m), 2.97 (3H, s), and 1.40–2.77 (12H, m); *m/e* (relative intensity) 216 (1, M^+), 120(46), 105(18), 91(35), and 79(100) (Found: C, 55.6; H, 7.25. $C_{10}H_{16}O_3S$ requires: C, 55.55; H, 7.45%).

Pyrolysis of 2-equatorial-noradamantyl-methanesulphonate. 2-*Equatorial*-noradamantyl methanesulfonate (0.5 g) was sublimed slowly during 20 min at 220° into the pyrolysis tube (530 ± 20°) at 0.02 torr. The pyrolysate, collected at −196°, was extracted with isopentane (3 × 10 ml), which, after being filtered through a column of basic alumina (activity II, 10 g), was analyzed by glc (2m × 1/8 in 1% ApL, 60°). It consisted of three compounds (M^+ by gc-ms) in the ratio of 68(M^+ 120): 28(M^+ 120): 4(M^+ 122) having retention times of 3.6, 4.6 and 5.3 min respectively. The mixture was separated by preparative glc (14 ft × 1/4 in 20% ApL, 130°) to give tricyclo[$4.2.1.0^{4.8}$]non-2-ene (brendene, 0.12 g),[15c] m.p. 178–180°. IR (CCl_4): 3053, 2946, 2860 and 1603 cm^{-1}; NMR: δ_H ($CFCl_3$), 5.92 (2H, broad s), 2.94 (1H, m), 2.36 (3H, m), and 1.08–1.70 (6H, m); δ_C($CFCl_3/CDCl_3$) 139.7 (C-2, C-3), 54.2 (C-8), 43.2 (C-1, C-4), 42.3 (C-6), 39.5 (C-7), and 36.3 (C-5, C-9). (Found: M^+ 120.0939); and tetracyclo [$3.3.1.0^{2.4}.0^{3.7}$]nonane (triaxane,[18] 0.055 g) m.p. 177–178°; IR (CCl_4): 3040, 2942 and 2855 cm^{-1} NMR: δ_H ($CFCl_3$) 2.48 (4H, m), 2.04 (3H, m), 1.69 (3H, m) and 1.31 (3H, d), δ_C ($CFCl_3/CDCl_3$) 47.2 (C-6, C-8, C-9), 40.4 (C-2, C-3, C-4) and 37.2 (C-1, C-5, C-7) (Found: M^+ 120.0938; C_9H_{12} requires: M^+ 120.0939).

Noradamantan-2-one. To a stirred soln of 2-*equatorial*-noradamantanol[15a] (1.5 g) in ether (10 ml), a chromic acid soln prepared from sodium dichromate dihydrate (1 g), water (4.5 ml), and 96% H_2SO_4 (1 ml) was added. After the mixture was kept at room temp. for 2 hr, water (5 ml) was added and the ether layer was separated. The aqueous layer was extracted twice with ether and the combined ethereal soln was dried and evaporated to give noradamantan-2-one (1.4 g), m.p. 214–215° (sublimation); IR (CCl_4): 1750 cm^{-1}; NMR (CCl_4): δ 1.40–2.80(m); *m/e* (relative intensity) 136 (51, M^+), 118(9), 107(17), 92(24), 79(100) and 66(67). (Found: M^+ 136.0883. $C_9H_{12}O$ requires, M^+ 136.0888).

2-*Axial-noradamantanol*. To a stirred soln of noradamantan-2-one (1.3 g) in ether (100 ml), a slurry of LAH (0.4 g) in ether (25 ml) was added. The mixture was boiled under reflux overnight. The usual work-up afforded 2-axial-noradamantanol (1.2 g), m.p. 244–245° (sublimation); IR (CCl_4): 3640, 1100 and 1040 cm^{-1}; NMR (CCl_4): δ 4.04 (1H, approx. dd), 2.31 (1H, exchangeable with D_2O) and 1.10–2.60 (12H, m); *m/e* (relative intensity) 138(16, M^+), 120(45), 105(13), 95(31), 91(28) and 79(100) (Found: M^+ 138.104. $C_9H_{14}O$ requires: M^+ 138.104).

2-*Axial-noradamantyl methanesulphonate*. Methane sulphonylchloride (6 ml) was added to a stirred soln of 2-*axial*-noradamantanol (1.1 g) in pyridine (25 ml) and the mixture was stirred at room temp. for 72 hr. The usual work-up gave a yellow oil, which, after repeated recrystallization from ether–pentane, afforded 2-*axial*-noradamantyl methanesulphonate (1.1 g), m.p. 25–26°. IR (CCl_4): 1368, 1348, 1180, 1100, 950, 890 and 850 cm^{-1}; NMR (CCl_4): δ4.78 (1H, approx, dd), 3.03 (3H, s) and 1.20–2.70 (12H, m), *m/e* (relative intensity) 216 (2, M^+), 132 (3), 120 (93), 105 (15), 91 (32) and 79 (100) (Found: C, 55.85; H, 7.6; S, 14.6. $C_{10}H_{16}O_3S$ requires: C, 55.55; H, 7.45; S, 14.85%).

Pyrolysis of 2-axial noradamantyl methanesulphonate. 2-*Axial*-noradamantyl methanesulphonate (0.5 g) was pyrolysed under the conditions used for its epimer; a similar work-up gave a mixture (0.17 g) of tricyclo [$4.2.1.0^{4.8}$]non-2-ene and tetracyclo[$3.3.1.0^{2.4}.0^{3.7}$]nonane in the ratio of 1:4. The mixture was separated by preparative glc as before and each component was found to be identical with the authentic sample (IR and ^1H NMR comparisons).

3-*Diamantyl methanesulfonate* (**6**) *and its pyrolysis*: 3-Diamantyl methanesulfonate was prepared as above in 85% yield (NMR: δ 4.69 (1H, m), 2.90 (3H, s), 2.08 (3H, m), 1.77 (15 H, broad S)). Pyrolysis as above at 550°C afforded in 70% yield a 3:2 mixture of dehydrodiamantane[21] and protodiamantene. (NMR: δ 6.10 (2H, m), 1.15–2.80 (16H, complex m)), containing 1% diamantane (by glc).

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