

A Simple Synthesis of Protoadamantene and 2,4-Dehydroadamantane

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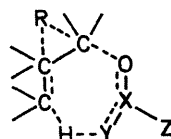
Summary 2-Adamantyl methanesulphonate has been converted by pyrolysis in 95% yield into a mixture (2:3) of protoadamantene (4) and 2,4-dehydroadamantane (5); hydroboration of protoadamantene and oxidation afforded protoadamantan-4- and -5-ones (5:4).

lit.⁶ 202.5—203.5°; elution with isopentane) and protoadamantene (35%; m.p. 179—182°, lit.⁵ 183—185°; elution with ether).

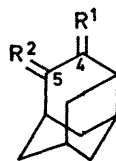
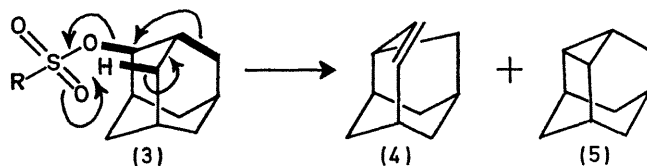
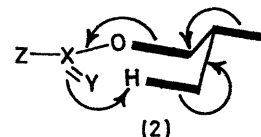
WE have for some time been interested in ester pyrolyses which afford olefins by skeletal rearrangement and may proceed *via* a seven-membered transition state such as (1).^{1,2} Such reactions have been observed with carboxylic esters,^{1,3} sulphonic esters,⁴ and xanthates.² Recorded examples include the conversion² of isobornyl methyl xanthate into camphene of high optical purity and the transformation of patchouli acetate into α - and γ -patchoulenes.³ We have used⁴ the steric requirements of this process to convert the atisane into the aconane skeleton and were struck by the rigidly defined geometry of the bonds undergoing fission and migration [structure (2)].

If this geometry is optimal, then 2-adamantyl esters *e.g.* (3) should lead in one step to protoadamantene (4),⁵ a substance of potential interest that is not otherwise readily accessible. The formation² of tricyclene from bornyl methyl xanthate suggests that 2,4-dehydroadamantane (5)⁶ might also be expected.

We have converted 2-adamantyl methanesulphonate (3), m.p. 67—68°, in 90—95% yield, into a mixture (2:3) of protoadamantene (4) and dehydro-adamantane (5). 2-Adamantyl methanesulphonate (3) (1.04g) was slowly sublimed during 20 min into a glass tube (60 × 3 cm) kept at 520 (± 10) °C and He pressure 0.5—0.7 mmHg, and partially (10 cm at exit end) packed with glass wool coated, as was the inner surface of the tube, with sodium carbonate. The pyrolysate, collected at -196°, was filtered in isopentane through alumina (grade II); removal of solvent from the eluate at <45° afforded a hydrocarbon mixture (91%), consisting of protoadamantene,⁵ dehydroadamantane⁶ and minor (<1%) amounts of adamantane and an unidentified hydrocarbon (6) (*M* 134). [Retention Indices⁷ on 1% Apiezon L, 75°: (6) 1085; (4) 1100; adamantane 1108; (5) 1126]. Chromatography over AgNO₃ (15%)-Al₂O₃ afforded after solvent removal (Vigreux column) without crystallisation dehydroadamantane (56%; m.p. 197—202°,



- (1) X = C; Y = O; Z = R (Ar)
 X = C; Y = S; Z = SR
 X = S; Y = O; Z = :O, R(Ar)



- | | R ¹ | R ² |
|------|-------------------------|-------------------------|
| (7) | H ₂ | α -OH β -H |
| (8) | H ₂ | α -H β -OH |
| (9) | α -OH β -H | H ₂ |
| (10) | α -H β -OH | H ₂ |
| (11) | H ₂ | O |
| (12) | O | H ₂ |

2-Adamantyl acetate⁸ was unchanged under similar conditions. 2-Adamantyl xanthate, m.p. 107.5—109.5°, afforded (4), (5), and adamantane (5% of each), dithiocarbonate (40%), and recovered xanthate (40%). 2-Adamantyl toluene-*p*-sulphonate⁸ gave a hydrocarbon product very similar in yield and composition to that obtained with (3); however, this ester was more difficult to handle because of its lower volatility.

Hydroboration (1 mol. equiv. of B₂H₆ in tetrahydrofuran at 25°) of protoadamantene (4) afforded the four isomeric protoadamantan-5- and -4-ols (7), (8), (9), and (10), in the proportions 2.5:1:3:1.25 [estimated as trimethyl

silyl ethers⁹ on 2% silicone elastomer 30 at 150°; R.I. (TMS ethers): (7) 1347; (8) 1364; (9) 1417; (10) 1431]. Alcohols (9) and (10) were completely identical with protoadamantan-4-*exo*- and -4-*endo*-ols.^{5,10} Oxidation of the alcohol mixture (RuO₂-NaIO₄)¹¹ afforded protoadamantan-5- and -4-ones (11) and (12) (4:5) [R.I. on 2% silicone elastomer 30 at 160°: adamantanone 1325; (11) 1338 (12) 1364], separated by preparative t.l.c. on Kieselgel G.

Protoadamantan-5-one, m.p. 222—225°, ν_{\max} (CCl₄) 1727 cm⁻¹ (unsplit, unlike protoadamantan-4-one), was further characterised by its Eu(DPM)₃-shifted n.m.r. spectrum.¹²

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