A convenient synthesis of 4e-chloroadamantylideneadamantane by means of the reaction of phenylsulfenyl chloride with adamantylideneadamantane

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A CONVENIENT SYNTHESIS OF 4e-CHLOROAdamANTYLIDENEAdamANTANE
BY MEANS OF THE REACTION OF PHENYLSULFENYL CHLORIDE WITH
ADAMANTYLIDENEAdamANTANE.

John Bolster, Richard M. Kellogg*, Egbert W. Meijer, and Hans Wynberg
Department of Organic Chemistry, The University,
Nijenborgh, 9747 AG Groningen, The Netherlands

We have reported that the reaction of methylsulfonyl halides with adamantylidene-adamantane (1) leads to the formation of a thiiranium salt (2), which in some instances can be isolated.¹ On treatment with nucleophiles the salt (2a) can undergo either desulfurization or demethylation.

Virtually simultaneously with our report of this reaction Garratt² reported that the reaction of 1 with phenylselenenyl chloride leads to spiro compound 3.

We have now investigated the reaction of phenylsulfenyl chloride with 1; this is found to afford an excellent preparative route to 4e-chloroadamantylideneadamantane 4.[‡] Up to now 4 has only been available through direct chlorination of 1, followed by a tedious isolation procedure.³ Derivatives of 1, obtainable through 4, are of much interest in connection with, for example, studies of additions of electrophiles⁴ and singlet oxygen.⁵

Treatment of 1 (26.8 gr. 0.1 mole) in CH_2Cl_2 (250 ml) with phenylsulfenyl chloride (31.7 gr. 0.22 mole) led to immediate evolution of HCl. After 8 hours 4 was formed nearly quantitatively as indicated by $^1\text{H-NMR}$ spectroscopy. To isolate 4 from diphenyldisulfide and a

[‡]Equatorial with respect to the 2,4-substituted cyclohexyl ring. See also H. Numan and H. Wynberg, *J. Org. Chem.*, **43**, 2232 (1978).

small amount of unreacted 1 the reaction mixture - after evaporation of CH_2Cl_2 - is put in an ice bath and CCl_4 (350 ml) was added, followed by an excess of Br_2 to generate the bromonium salts,⁴ which are isolated by filtration and subsequently repeatedly rinsed with a solution of Br_2 in CCl_4 to remove the last traces of diphenyldisulfide. The salt of 4 decomposes on washing with ether whereas that of 1 is stable. The red solution of 4 and Br_2 thereby obtained is washed with Na_2SO_3 until colorless and is dried over MgSO_4 . Removal of the solvent gives 25.6 gr. (0.085 mole, 85%) of spectroscopically pure 4.³ An analytically pure sample of 4 is obtained by recrystallization from CH_3OH and sublimation, m.p. 144-145°.*

A plausible mechanism for the 1 $\rightarrow$ 4 conversion is shown in the Scheme.⁶ We were unable to detect by $^1\text{H-NMR}$ the thiiranium salt (5), although this seems a reasonable intermediate.

The chain of events subsequent to formation of (5) represents one of the few reactions courses open to the thiiranium ion.

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*A slight excess over the theoretical 2 eqv of $\text{C}_6\text{H}_5\text{S-Cl}$ leads to the best results, larger excesses result in overchlorination. (Attempts to allow $\text{C}_6\text{H}_5\text{SBr}$ to react with 1 led only to the formation of the bromonium salt of 1). Spectra data for 4: $^1\text{H-NMR}$ (CDCl_3): δ 4.15 (1H), δ 3.2-2.65 (4H), δ 2.6-1.15 (22H); $^{13}\text{C-NMR}$ (C_6D_6 , δ 128 ppm) δ 137.134 (1C, sp^2), δ 131.411 (1C, sp^2), δ 68.134 (1C, d, $J_{\text{C-H}} = 132$ Hz). The absorptions for the rest of the carbon atoms lie between δ 39.882 and 28.069; mass spectrum: m/e 302/304 (3:1); i.r. (KBr): 1095, 975, 798 and 710 cm^{-1} . A satisfactory elemental analysis was obtained.