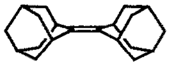
Tetrahedron Letters No. 3, pp 285 - 286.
© Pergamon Press Ltd. 1979. Printed in Great Britain.
0040-4039/79/0115-0285$02.00/0

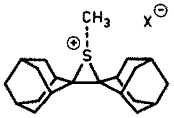
A CONVENIENT SYNTHESIS OF 4e-CHLOROADAMANTYLIDENEADAMANTANE BY MEANS OF THE REACTION OF PHENYLSULFENYL CHLORIDE WITH ADAMANTYLIDENEADAMANTANE.

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 methylsulfenyl halides with adamantylideneadamantane (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.



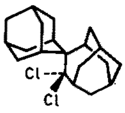
1



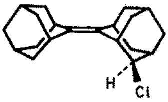
2

a; $X = ClO_4^{\ominus}$
b; $X = Br_3^{\ominus}$
c; $X = Cl^{\ominus} + Cl_3^{\ominus}$

Virtually simultaneously with our report of this reaction Garratt[2] reported that the reaction of 1 with phenylselenyl chloride leads to spiro compound 3.



3



4

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 electrophiles[4] and singlet oxygen.[5]

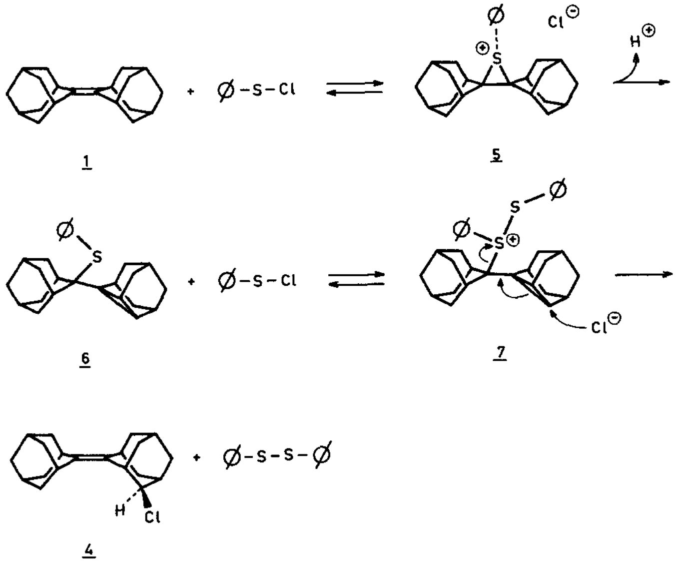
Treatment of 1 (26.8 gr. 0.1 mole) in CH_2Cl_2 (250 ml) with phenylsulfenyl chloride (31.7 gr. 0.22 mole) led to immediate evolution of HCl. After 8 hours 4 was formed nearly quantitatively as indicated by ^{1}H-NMR spectroscopy. To isolate 4 from diphenyldisulfide and a

---

‡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^{0}.*

A plausible mechanism for the 1 → 4 conversion is shown in the Scheme.[6] We were unable to detect by ^1H-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.

References:

1. J. Bolster and R.M. Kellogg, J. Chem. Soc. Chem. Comm., 630 (1978).
2. D.G. Garratt, Tetrahedron Letters, 1915 (1978).
3. J.H. Wieringa, J. Strating, and H. Wynberg, Tetrahedron Letters, 4579 (1970).
4. J. Strating, J.H. Wieringa and H. Wynberg, J. Chem. Soc. Chem. Commun., 907 (1969).
5. H. Wynberg and H. Numan, J. Am. Chem. Soc., 99, 604 (1977).
6. A.C. Udding, J. Strating, and H. Wynberg, Tetrahedron Letters, 1345 (1968).

---

*A slight excess over the theoretical 2 eqv of C_6H_5SCl leads to the best results, larger excesses result in overchlorination. (Attempts to allow C_6H_5SBr to react with 1 led only to the formation of the bromonium salt of 1). Spectra data for 4: ^1H-NMR ($CDCl_3$): δ 4.15 (1H), δ 3.2-2.65 (4H), δ 2.6-1.15(22H); ^{13}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_{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.

(Received in UK 16 November 1978)