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THE REACTION OF BENZENESELENENYL CHLORIDE WITH ADAMANTYLIDENEADAMANTANE

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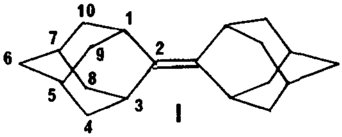
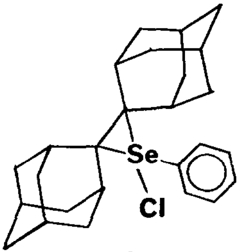
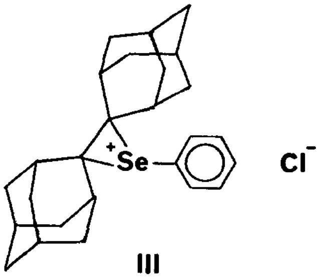
Some years ago the isolation of a uniquely stable bromiranium tribromide was reported[1] for the reaction of bromine with the heavily hindered alkene: Adamantylideneadamantane (I). Further studies indicated that chlorination also gave a stable species believed to be chloriranium salt.[2] In neither case was a normal 1,2-addition product isolable. Epoxidation using m-chloroperbenzoic acid in CH_2Cl_2 did however proceed quantitatively indicating sufficient space between the adamantane moieties for attack by the oxidative species.[3] Studies carried out by Olah and coworkers[4] have subsequently suggested that the species isolated from the halogenation reactions are not the σ-bonded ionic species initially proposed, but two-electron three-centered bonded π complexes. The unique behaviour of the double bond in (I) suggested to us that it might be possible to isolate a thermally stable episelenurane (II) or seleniranium salt (III) (both postulated intermediate in the areneselenenylation of alkenes[5]) from the reaction of (I) with benzeneselenenyl chloride.



I



II



III

The reaction of benzeneselenenyl chloride with (I) in anhydrous methylene chloride at 20°C under equimolar conditions was very slow taking 10 to 14 days to reach completion (under equivalent conditions simple alkenes such as 2,3-dimethyl-2-butene react essentially instantaneously). After evaporation of the solvent half of the alkene initially present was recovered along with diphenyl diselenide and a colorless crystalline solid (IV) of empirical formula, $C_{20}H_{28}Cl_2$ (elemental analysis, mass spectroscopy). Repeating the reaction using 2 mole equivalents of C_6H_5SeCl gave (IV) in an isolated yield of 97%. An ionic structure was ruled out on the basis of (IV)'s solubility in non polar media such as pentane and carbon tetrachloride. A symmetrical vicinal dichloride (Va) was also ruled out on the basis of the following spectroscopic evidence:

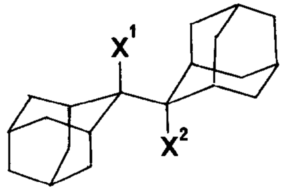
Mass spectrum: M^+ at m/e 338, M-HCl at m/e 302, M-Cl at m/e 303, M-Cl_2 at m/e 268 ($C_{20}H_{28}$). Metastable peaks at m/e 236.5, ($C_{20}H_{28}Cl^{+\cdot} \rightarrow C_{20}H_{28}^{+\cdot}$); 192 ($C_{20}H_{28}^{+\cdot} \rightarrow C_{17}H_{23}^{+\cdot}$);

189 ($C_{20}H_{28}^{+\cdot} \rightarrow C_{17}H_{21}^{+\cdot}$); and 166 ($C_{20}H_{28}^{+\cdot} \rightarrow C_{16}H_{19}^{+\cdot}$). There were no peaks at m/e 169 (M/2) or 266 (M-2HCl) as could be anticipated for a structure such as (Va).

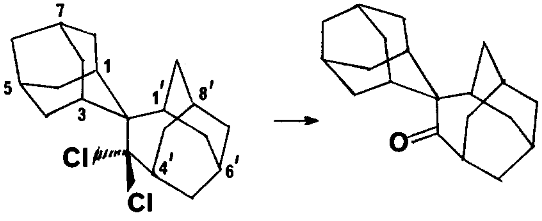
Proton NMR spectrum ($CDCl_3$): major features are four multiplets each integrating as one proton at δ 4.28, 3.03, 2.47, and 2.27 ppm; remaining protons as for adamantanes.[6] The presence of four distinct methine protons is clearly incompatible with the vicinal dichloride (Va).

Carbon-13 NMR Spectrum ($CDCl_3$): eleven observable carbon resonances;[6] δ 68.4 s $>CCl_2$; 39.6 d; 39.4 t; 38.9 t; 37.1 t; 35.8 t; 32.6 d; 32.3 d; 30.5 d; 28.4 t; 27.7 d ppm relative to TMS.

The structure which appears to best account for the spectral properties of (IV) is 3',3'-dichlorospiro[adamantane-2,2'-homoadamantane].



Va $X^1 = X^2 = Cl$
b $X^1 = Cl$ $X^2 = SeC_6H_5$



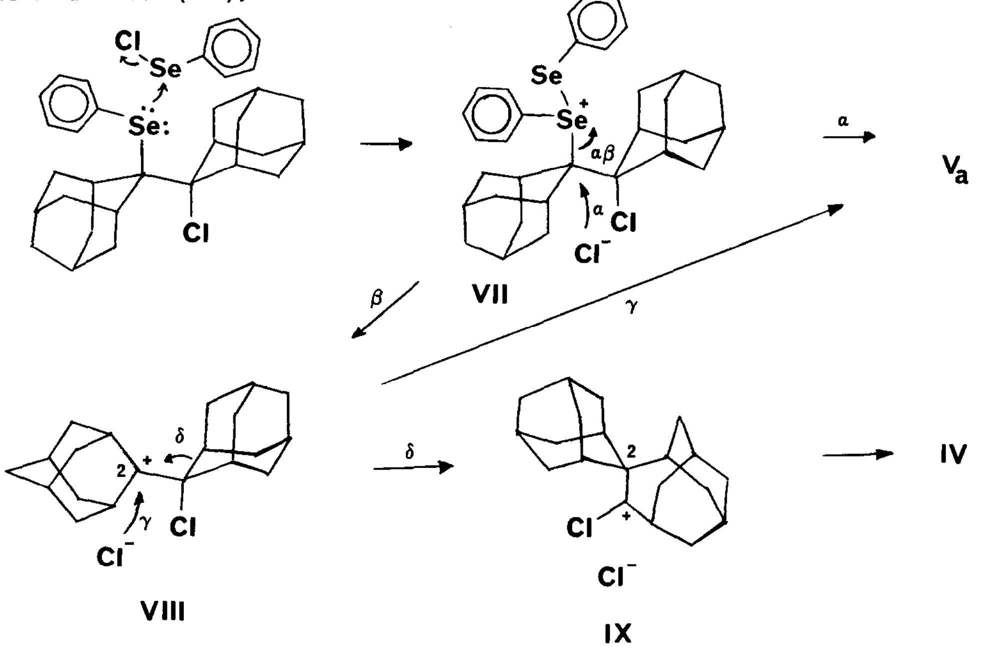
IV VI

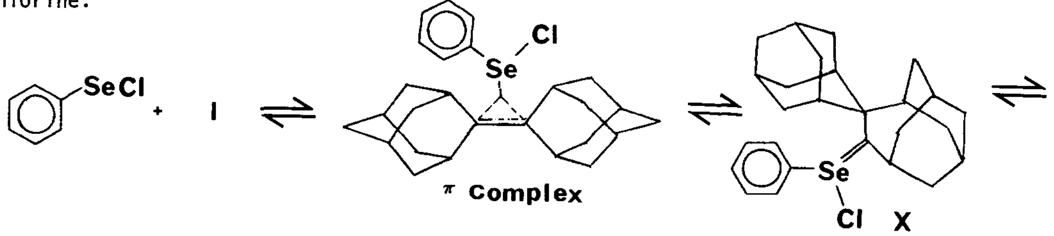
Chemical evidence for the spirocyclic system was obtained by the hydrolysis of (IV) in conc. H_2SO_4 at 25° C which gave the previously reported compound (VI); spiro[adamantane-2-2'-homoadamantan-3-one], mp 178-179 lit. 177-178.5°.[3] ir. 5.86 μ, in 55% yield after 48 hours; the remainder was unreacted (IV). An attempt to hydrolyze (IV) under basic conditions (1 N aqueous NaOH) was only partially successful, yielding approximately 5% of (VI), plus unreacted (IV) after three weeks at room temperature.

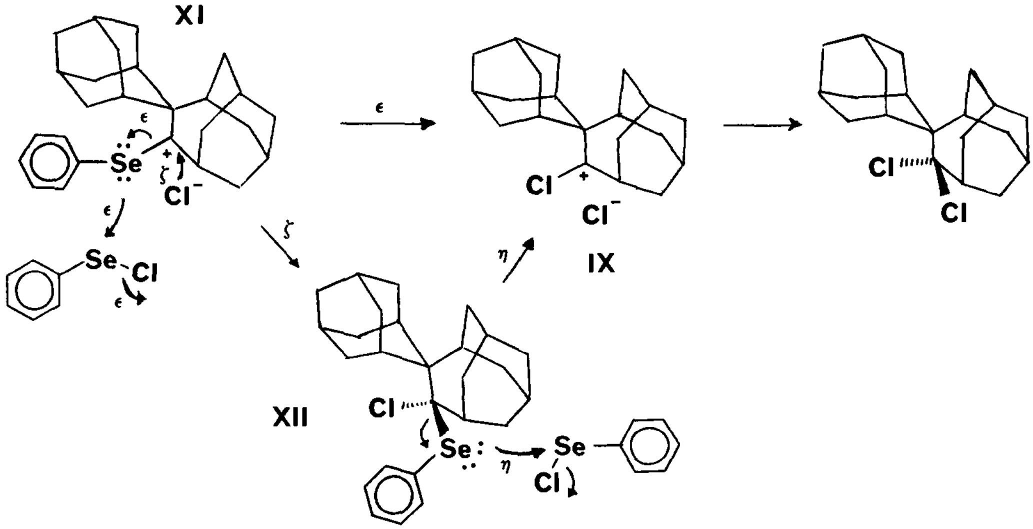
The presence of (IV), and the absence of a stable selenium containing species such as (II) or (III) was initially surprising in view of the halogenation results, since the stericly less bulky and more reactive halogens would normally be expected to pass beyond the σ complex ion stage more readily and thus give rise to normal adduct or rearrangement products. Furthermore, it was argued by Olah and coworkers that the steric restriction placed on the movement of halogen atoms during halogenation, by the C-8 and C-10, and C-8' and C-10' protons, prevents the halogen complexes from being either rapidly equilibrating ion pairs, a mixture of bridged and equilibrating pairs of partially bridged ions and that therefore the halogen adducts are most likely π-bonded complexes. This ascertainment was also substantiated by the ability of the bromine complexes to irreversibly transfer the bromine to cyclohexene or tetramethylethylene, forming the corresponding dibromide and adamantylideneadamantane. These data thus suggest that the formation of (IV) occurs via a mechanistic path which does not necessitate the presence of either (II) or (III).

The formation of dichloroalkanes from the reaction of β-chloroalkyl phenyl selenide with an equivalent of areneselenenyl chloride are known,[7] however, thus suggesting that a normal addition product (Vb) might be formed on the reaction coordinate.

The formation of (IV) from (Vb) appears to require the intermediacy of an even more bulky selenonium salt (VII), followed by loss of diphenyl diselenide to yield the carbonium ion (VIII) which must rearrange to ion (IX), faster than nucleophilic attack by chloride ion at C-2 yielding (Va), if (IV) is to be formed. A more plausible mechanism, however, seems to be one which invokes a much earlier rearrangement as shown in scheme II where, for relief of steric strain, the first formed π-complex rearranges to the alkylidene selenurane (X) or the selenocarbonium ion (XI), which then reacts with an additional equivalent of C_6H_5SeCl, possibly via (XII) to form the chlorocarbonium ion (IX) which reacts with chloride ion to yield (IV). This difference in reactivity for benzeneselenenyl chloride with (I) compared to bromine or chlorine might be attributed to the greater ability of an arylseleno group to delocalize charge relative to that of bromine or chlorine.[8]







ACKNOWLEDGEMENTS

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2. J.H. Wieringa, J. Strating and H. Wynberg; Tetrahedron Lett. (52) 4579 (1970).
3. (a) H. Wynberg, E. Boelema, J.H. Wieringa and J. Strating; Tetrahedron Lett. (42) 3613 (1970)
   (b) G.B. Gill and D. Hands; Tetrahedron Lett. (2) 181 (1971).
4. G.A. Olah, P. Schilling, P.W. Westermain and H.C. Lin; J. Amer. Chem. Soc. 96 (11) 3581(1974)
5. (a) D.G. Garratt and G.H. Schmid; Can. J. Chem. 52 (6) 1027 (1974).
   (b) G.H. Schmid and D.G. Garratt; Tetrahedron Lett. (46) 3991 (1975).
6. A structure such as Va would be expected to exist essentially only in the anti conformer[3] and thus, because of symmetry, give rise to only seven carbon resonances and 3 types of methine protons integrating as 2 : 2 : 7 protons.
7. D.G. Garratt; Ph.D. thesis, University of Toronto, 1975.
8. Compare, for example, the additions to 1-phenylpropenes and the bridging ability shown (cyclic ion vs. open carbonium ion) ArSe > Br > Cl.