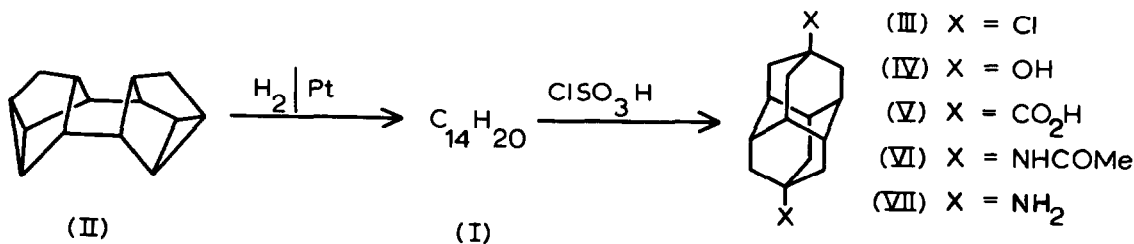


DIAMONDROID REARRANGEMENTS IN CHLOROSULPHONIC ACID. A HIGHLY REGIOSELECTIVE ROUTE TO APICALLY DISUBSTITUTED DIAMANTANES

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Although chlorosulphonic acid is an effective reagent for bridgehead chlorination of adamantane (1) and diamantane (2), there have been no reports of its use as a Lewis acid catalyst in rearrangement reactions leading to diamondoid hydrocarbons (3). We have explored the possibility of using chlorosulphonic acid as the solvent, catalyst and functionalisation reagent in the synthesis of substituted diamantanes in a single operation, and we now describe a simple, highly regioselective route to 4,9-(diapical) derivatives (4) which does not require the isolation and purification of the hydrocarbon.



A mixture of tetrahydrobinor-S (I) (2,5), obtained by hydrogenolysis of the norbornadiene dimer Binor-S (II), and neat chlorosulphonic acid (mole ratio 1:5.7) was stirred at -15°. After 9 h glc analysis revealed the presence of one major product and several minor products, one of which was diamantane. The major product was isolated in 82% yield by chromatography over silica gel and identified as 4,9-dichlorodiamantane (III) (4b). The dichloride obtained by this method provides a convenient synthetic entry into the 4,9-series. Hydrolysis with aqueous dioxan containing NaOH in an autoclave at 160° gave the 4,9-diol (IV) in high yield. Koch-Haaf carboxylation of the diol yielded the 4,9-diacid (V) with physical properties reminiscent of those of terephthalic acid: very high melting point, 456° (6), and extreme insolubility in the common organic solvents. That the diacid was formed from the diol without rearrangement was revealed by the presence in the nmr spectrum of its dimethyl ester, m.p. 189-190°, of two sharp singlets at δ 1.9 (18H) and 3.7 (6H), the former signal reappearing as two

singlets, ratio 2:1, upon addition of $\text{Eu}(\text{fod})_3$. A Ritter reaction with the diol and acetonitrile in sulphuric acid gave the diamide (VI), m.p. 399° (6), which could be hydrolysed to the diamine (VII), m.p. $238\text{--}240^\circ$, using hydrochloric acid in methanol.

Although the mechanism of the diamantane rearrangement in chlorosulphonic acid is unknown, monitoring experiments indicated that the predominant pathway leading to the 4,9-dichloride does not involve formation of diamantane with subsequent chlorination. At intermediate times small amounts of diamantane and monochlorodiamantanes were present, but the major intermediates were two new isomeric monochlorides, indicating that one substituent was already introduced before termination of the rearrangement process. Prolonged exposure of (I) or (III) to chlorosulphonic acid gave the 1,4,9-trichlorodiamantane, m.p. $184\text{--}186^\circ$, in 80-90% yield (7).

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