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SYNTHESIS AND SOME REACTIONS OF VINYLIDENEADAMANTANE[1]

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Allenes embodying or substituted with adamantane skeleton have attracted much attention recently in view of their unique properties such as extreme thermostability.[2,3] We wish to report here a facile synthesis of vinylidene-adamantane (3) as one of such allenes and some of its reactions.

Reaction of methyleneadamantane (1)[4] with dichloro- and dibromocarbenes generated from the corresponding haloforms and 50% aqueous KOH by the phase-transfer method[5] (benzene as the organic phase and benzyltriethylammonium chloride as the catalyst) at 5-10° afforded dichloro- (2a) and dibromocyclopropane derivatives (2b) in 40 and 54% yields respectively after usual work-up and dry distillation (0.5 mmHg). 2a and 2b were characterized as follows:[6] 2a n_D^{19} 1.5413; δ ($CDCl_3$) 2.3-1.5 (m, 14H) and 1.16 (s, 2H); M^+ m/e 230, 232 and 234 (ca.10:6:1 ratio). 2b: mp 50-51°; δ ($CDCl_3$) 2.3-1.5 (m, 14H) and 1.40 (s, 2H); M^+ m/e 318, 320 and 322 (ca. 1:2:1 ratio).

Treatment of 2b with n-BuLi (1.2 equivalent of 15% n-hexane solution) in ether at -8-0° for 1 h. afforded exclusively vinylideneadamantane (3) which was isolated as a colorless oil in 83% yield after chromatography (silica gel-n-pentane) and had the following physical data: n_D^{18}1.5468; ν (neat) 1980 cm^{-1}; δ ($CDCl_3$) 4.56 (s, 2H) and 2.65-1.53 (m, 14H). The similar treatment of 2a with n-BuLi (3.0 equivalent) gave also 3 in 49% yield.

3 was thermally very stable and did not change on heating at 190° for 4 days in benzene but on heating at 260° for 1 week 3 decomposed to afford a

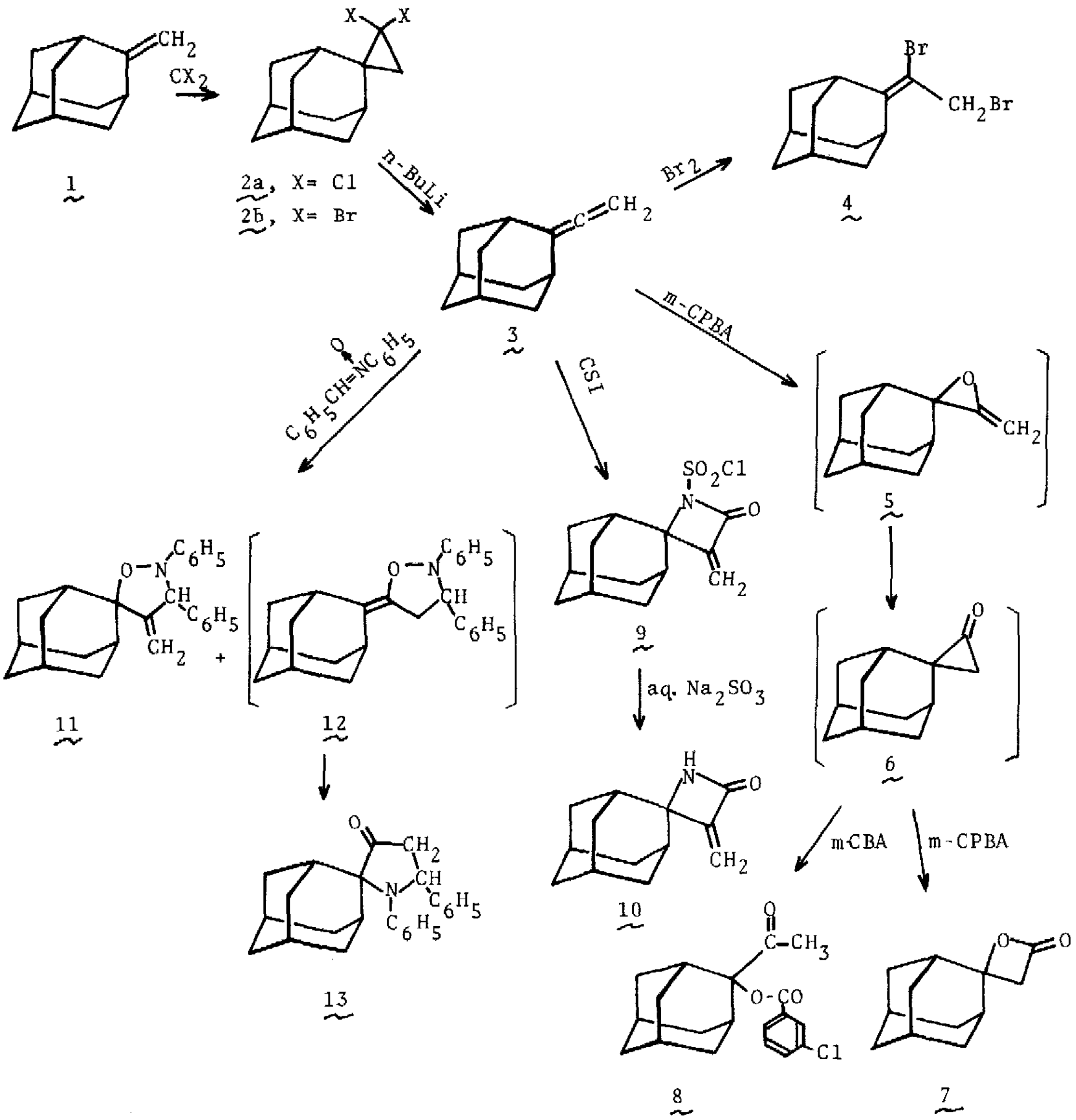
complex mixture of unidentified products which involved yet *ca*. 30% unchanged **3**.

Treatment of **3** with bromine in $CHCl_3$ at room temperature afforded adduct **4** quantitatively as an oil: n_D^{20}1.5348; ν (neat) 1620 and 650 cm^{-1}; δ ($CDCl_3$) 4.25 (s, 2H) and 2.5-0.67 (m, 14H). The observed regiospecific addition was in accord with that reported for 1,1-dialkylallene.[7]

Epoxidation of **3** with *m*-chloroperbenzoic acid (m-CPBA) in CH_2Cl_2 at room temperature yielded a complex mixture of products, from which β-lactone **7** and ester **8** were isolated in 7 and 15% yields respectively after chromatography on a silica gel column. The structures were assigned as shown in Scheme based on analytical and spectral data. **7**: mp 63-65°; ν (KBr) 1815 cm^{-1}; δ ($CDCl_3$) 2.97 (s, 2H) and 2.5-1.3 (m, 14H); M^+ *m/e* 192. **8**: n_D^{19}1.5557; ν (neat) 1735 and 1720 cm^{-1}; δ ($CDCl_3$) 8.2-7.2 (m, 4H), 2.15 (s, 3H) and 2.7-1.6 (m, 14H); M^+ *m/e* 332 and 334 (3:1 ratio). Since allene oxide-cyclopropanone isomerization is well known,[8] the formation of **7** could be rationalyzed by an initial formation of **5**, followed by the isomerization to **6** and its Baeyer-Billiger rearrangement. The formation of **8** could be explained also by considering the isomerization of **5** to **6**, followed by its reaction with *m*-chlorobenzoic acid.[9]

On treatment with chlorosulfonyl isocyanate (CSI) at -78° for 15 hr, **3** afforded a 1:1 adduct **9** (41%): mp 106-108°; ν (KBr) 1805 and 1640 cm^{-1}; δ ($CDCl_3$) 5.97 (s, 1H), 5.87 (s, 1H) and and 2.2-1.5 (m, 14H), which was converted to **10** in 93% yield with 20% aqueous sodium sulfite solution: mp 163-166°; ν ($CDCl_3$) 3200 and 1760 cm^{-1}; δ ($CDCl_3$) 8.0 (broad s, 1H, disappeared on deuteration), 5.68 (d, *J*=1.5 Hz, 1H), 5.36 (d, *J*=1.5 Hz, 1H), and 2.2-1.5 (m, 14H). The observed regiospecific addition was in accord with that reported for 1,1-dialkylallene.[10]

In order to examine the 1,3-dipolar cycloaddition reactivity of **3**, reactions with benzonitrile oxide and C,N-diphenylnitrone were carried out. Although no adduct was obtained with benzonitrile oxide generated *in situ* from benzhydroxamoyl chloride and triethylamine in ether, with diphenylnitrone in toluene under refluxing for 15 hr **3** gave a complex mixture of products. Purification on a silica gel column afforded adducts **11** and **13** in 16 and 17% yields respectively and they were characterized as follows (Scheme). **11**: mp 86-88°; ν (KBr) 1660,



Scheme

1600, 900, 760 and 695 cm^{-1}; δ (CDCl$_3$) 7.7-6.8 (m, 10H), 5.20 (d, *J*=2.5 Hz, 1H), 4.87 (t, *J*=2.5 Hz, 1H), 4.72 (d, *J*=2.5 Hz, 1H), and 2.7-1.3 (m, 14H). **13**: mp 169-172°; ν (KBr) 1725, 1600, 770 and 700 cm^{-1}; δ (CDCl$_3$) 7.7-7.1 (m, 10H), 4.69 (t, *J*=8.0 Hz, 1H), 3.00 (d, *J*=8.0 Hz, 2H) and 2.8-1.0 (m, 14H). The formation of 3-pyrrolidinone derivative **13** could be rationalyzed by thermal rearrangement of an initial adduct **12**.[11]

Above results indicate that vinylideneadamantane **3** exhibits chemically normal reactivity, though **3** is thermally very stable.

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