CHLORINATION OF ADAMANTANE AND ALKYLADAMANTANES WITH CHLOROSULFONIC ACID

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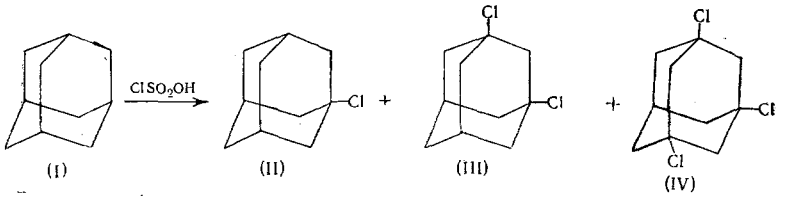
We established that adamantane and alkyladamantanes react under mild conditions with chlorosulfonic acid to yield chlorides. In adamantane from one to three hydrogen atoms are replaced by chlorine, while in 1,3-dimethyladamantane from one to two hydrogen atoms are replaced by chlorine, depending on the reaction time. The replacement occurs stepwise, which makes it possible to obtain both the intermediate and end chlorination products in good yield. Thus, the addition of adamantane (I) to chlorosulfonic acid, taken in an 8-10-fold weight excess relative to (I), followed by holding the reaction mixture at –5°C for 1 h, gave, after the usual workup, 1-chloroadamantane (II) in 60.7% yield, mp 163-164°; holding the reaction mixture for 60 h gave 1,3-dichloroadamantane (III) in 80.7% yield, mp 130-131°, while holding the reaction mixture for 240 h gave 1,3,5-trichloroadamantane (IV) in 70% yield, mp 102°



(I) (II) (III) (IV)

In a similar manner, from 1,3-dimethyladamantane were obtained 1,3-dimethyl-5-chloroadamantane in 75% yield, bp 84-87° (4 mm) n_D^{20} 1.4964, and 1,3-dimethyl-5,7-dichloroadamantane in 83% yield, mp 92-93°, while from 1,3,5-trimethyladamantane was obtained 1,3,5-trimethyl-7-chloroadamantane in 92% yield, mp 85-86°.

The structure of the obtained chlorides was confirmed by the NMR spectra, which do not contain the signals characteristic for the $H-\overset{|}{C}-Cl$ grouping. All of the obtained compounds had a satisfactory elemental analysis.

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