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NEW METHOD OF POLYHALOADAMANTANE SYNTHESIS

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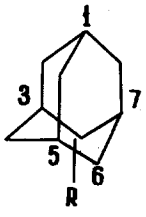
We have demonstrated earlier, that treatment of adamantane with chlorosulfonic acid leads to its chlorination. Depending on the time of interaction either mono-, di- or trichloroadamantanes can be obtained [1] . Now it has been shown, that the maximum concentration (60%) of the 1-chloride (1) is reached within 1 hour. Further degree of substitution and its direction depend upon the ratio of the reagents. Thus 1,3-dichloride (II), m.p. 131-133°, was obtained in a 90 per cent yield, by treating adamantane with 4 moles of chlorosulfonic acid for 100 hours at 20°. Further increase of the percentage of chlorosulfonic acid leads to accumulation of trichlorides (III) and (IV) in a ratio also dependent on the excess of chlorosulfonic acid. The maximum yield of 1,3,5-trichloride (III) is obtained when the molar ratio of adamantane to $HOSO_2Cl$ is 1:17. The highest percentage of 1,3,6-trichloride (IV) was obtained by using 8 moles of $HOSO_2Cl$.



I R = 1-Cl
II R = $1,3-Cl_2$
III R = $1,3,5-Cl_3$
IV R = $1,3,6-Cl_3$
V R = $1,3,5,7-Cl_4$
VI R = $1,3-Br_2$
VII R = $1,3,6-Br_3$
VIII R = $1,3,5,7-Br_4$
IX R = $1,3-(PhOH)_2$

Chromatographic fractionation of the trichloride mixture gave III, m.p. 102 - 102,5°, and IV, m.p. 148-150°, NMR 4,08 δ (C_6-H). Relation of the yields of chlorinated adamantanes on reaction conditions is shown in F.1.

Though tetrachloride was never formed in any of the experiments we obtained 1,3,5,7-tetrachloroadamantane (V) by chlorination of 1,3,5 -trichloride with $HOSO_2Cl$ at 50°. The yield of the compound with m.p. 196-197° (199-201[2])

was 87 per cent. The substitutive bromination of chloroadamantanes was achieved by treatment with Br_2 in the presence of $AlBr_3$. Thus 1,3-dibromoadamantane (VI), m.p. 100-105°, was obtained from II. Trichloride (IV) gives quantitatively 1,3,6-tribromoadamantane (VII), m.p. 166-168° (169-170° [3]), by refluxing with bromine and $AlBr_3$ for 24 hours. Similar treatment of tetrachloride (V) leads to 1,3,5,7-tetrabromoadamantane (VIII), m.p. 239 - 243 (246-248 [4]).

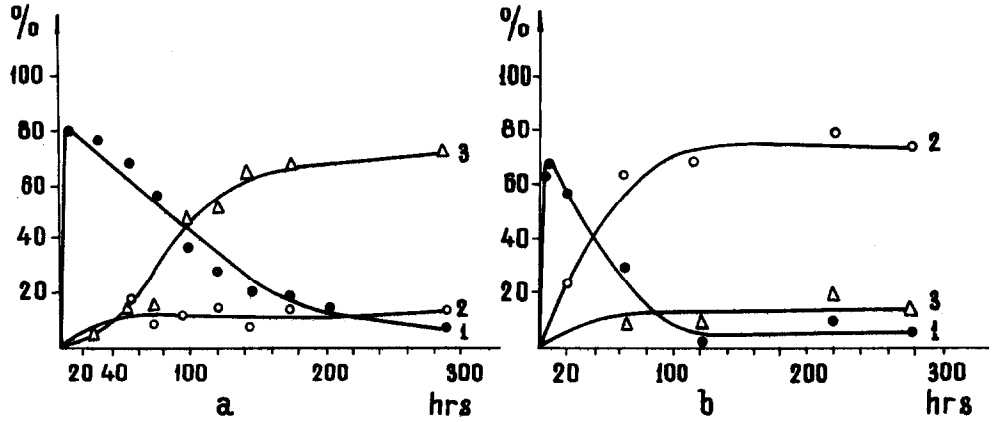


Fig. 1. Chlorination of adamantane with chlorosulfonic acid at 20°.

a - Adamantane: $HOSO_2Cl$ = 1:8,4 M; b - Adamantane: $HOSO_2Cl$ = 1:17 M;

1 - 1,3-Dichloroadamantane; 2 - 1,3,5-Trichloroadamantane;

3 - 1,3,6-Trichloroadamantane

High reactivity of chlorine atoms is exemplified by interaction of dichloroadamantane with phenol. The reaction proceeds without any catalysts and leads to 1,3-bis(4-hydroxyphenyl)adamantane (IX), m.p. 199-202°, in 85 per cent yield.

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