SHORT COMMUNICATIONS

Substitution Reaction of 1-Bromoadamantane in Dimethyl Sulfoxide: Simple Synthesis of 1-Azidoadamantane[1]

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Recent interest in the chemistry of adamantane[2] and the biological activity of its derivatives[3] has given stimulus to synthesize many adamantylamine derivatives[4] including adamantylhydrazine.[5] We wish to report a simple synthesis of 1-azidoadamantane (II), a good precursor of adamantylnitrene. For this purpose, the direct substitution reaction of 1-bromoadamantane (I) with sodium azide in dipolar aprotic solvents has been examined, though direct substitution reactions of I in strongly acidic conditions have been well established.[6]

A mixture of I (0.43 g) and sodium azide (1.3 g) in dry dimethyl sulfoxide (20 m*l*) was heated with stirring at 100°C for 2 days. The mixture was poured onto ice-water to give colorless precipitates which afforded fine needles (0.105 g, 29.6%) with a mp of 80—81°C after recrystallization twice from aqueous methanol. This product was characterized as 1-azidoadamantane (II) from analytical (Found: C, 67.38; H, 8.65; N, 23.37%. Calcd for $C_{10}H_{15}N_3$: C, 67.76; H, 8.53; N, 23.71%) and infrared spectral data (ν_{N_3} 2110 cm^{-1}). Compound II afforded 1-aminoadamantane on treatment with lithium aluminium hydride in ether, which was identified by the same retention time with that of an authentic sample[7] on g.l.c. analysis,[8] and by the superimposable infrared spectrum on that of an authentic sample.[7] The yields of II in other conditions are summarized in Table 1, in which the best yield was 35.2%. From the water layer,

$$\underset{\text{I}}{\text{Ad-Br}} + \text{NaN}_3 \rightarrow \underset{\text{II}}{\text{Ad-N}_3} + \text{NaBr}\,.$$

$$\underset{\text{III}}{\text{Ad-O-S}^+(\text{CH}_3)_2\text{Br}^-} \qquad \text{Ad-} = \text{1-adamantyl}$$

1-hydroxyadamantane (IV) was isolated in *ca.* 30% yield as the main by-product. Similar reaction in dimethylformamide or in hexamethylphosphoramide gave no II, most of the strating material being recovered. A facile substitution of I in dimethyl sulfoxide suggests a characteristic interaction of I with the solvent to give an intermediate salt like III[9] which could give II with azide anion and IV on hydrolysis. Although the yields are not satisfactory as yet, the facile preparation of II might make it possible to explore the chemistry of adamantylnitrene.

TABLE 1

Solvent	React. time (days)	React. temp. (°C)	Yield of II (%)
Dimethyl sulfoxide	1	100	13.4
Dimethyl sulfoxide	2	100	29.6
Dimethyl sulfoxide	3	100	31.9
Dimethyl sulfoxide	6	100	30.7
Dimethyl sulfoxide	14*	100	35.2
Dimethylformamide	3	100	0
Hexamethylphosphoramide	3	100	0

* The reaction was carried out in a sealed tube.

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[1] Synthesis of Adamantane Derivatives. X. Previous paper: T. Sasaki, S. Eguchi, T. Toru and K. Ito, submitted to this Bulletin.

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[8] Silicone SE-30 column (2 m) at 180°C.

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