OXIDATIVE BROMINATION OF ADAMANTANE UNDER MILD CONDITIONS

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UDC 542.944:546.14:542.943.7:547.518

1-Bromoadamantane is a key compound in the synthesis of many adamantane derivatives [1-3]. In the preparation of this compound from adamantane, either a large excess of bromine or excess of adamantane is used. Attempts to synthesize 1-bromoadamantane by bromination in the presence of an oxidizing agent have been unsuccessful. Thus, for example, a mixture of adamantanol and nitroadamantane is formed in a system containing 1 part adamantane, 1.5 parts Br_2 and 7 parts HNO_3 [3].

We have found that the use of trifluoroacetic acid as the solvent permits the quantitative preparation of 1-bromoadamantane at 20°C by the action of stoichiometric amounts of bromine or an alkali bromide in the presence of nitrogen-containing oxidizing agents, namely, NO_2, alkali nitrates or alkali nitrites taken in either stoichiometric amounts or, in the presence of O_2 or air, catalytic amounts. In the latter case, the reaction rate is significantly reduced.

A suspension of adamantane in CF_3CO_2H was stirred with bromine or an alkali bromide and an oxidizing agent until complete homogenization was noted. Then the solvent was distilled off in vacuum for reuse. 1-Bromoadamantane, mp 116-118°C, was isolated by sublimation at 90°C (1 mm) from the residue either directly (Table 1, experiment 1) or after extraction with pentane and evaporation of the extract (experiments 2 and 3).

The presence of water in the reaction mixture significantly complicates the isolation of the desired product.

TABLE 1

Experiment no.	Reagents (mole ratio)	Time, h	Yield of $C_{10}H_{15}Br$,%
1	$C_{10}H_{16} : Br_2 : NO_2 = 2 : 1 : 2$	0,5	98
2	$C_{10}H_{16} : KBr : NaNO_3 = 3 : 3 : 2$	2	97
3	$C_{10}H_{16}KBr : NaNO_2 = 1 : 1 : 0{,}1–0{,}01$ (in the presence of O_2 or air)	15–20	98

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M. V. Lomonosov State University, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, p. 698, March, 1987. Original article submitted October 27, 1986.

0568-5230/87/3603-0637$12.50