Synthesis of Adamantylideneadamantane

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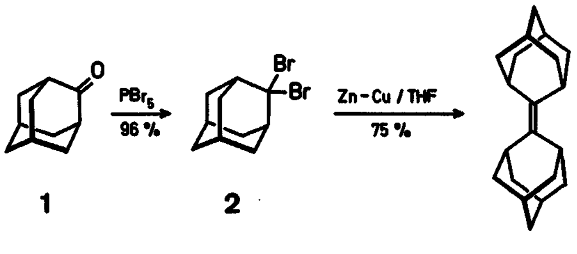
Adamantylideneadamantane (**3**) has become a compound of particular interest since its bromination affords a reasonably stable bromonium bromide, which is reported to be the first example of an isolation of the postulated intermediate in the electrophilic bromination of olefins[1].

The formation of adamantylideneadamantane (**3**) by photochemical decarbonylation of the 2-adamantylketene dimer has been reported recently[2]. A more suitable method of preparation of 3 consists of the conversion of adamantanone[3] (**1**) into *gem*-dibromoadamantane (**2**) using phosphorus(V)-bromide and debromination of **2** with a zinc-copper couple, as employed in the Simmons-Smith reaction:



1 2 3

The reaction is believed to proceed via carbene intermediates that are stabilized under the reaction conditions employed. Other methods of generation of adamantylidene carbenes (e.g., decomposition of adamantanone tosylhydrazone according to Bamford and Stevens[4] and pyrolysis of the dry lithium derivative of adamantanone tosylhydrazone[5]) do not lead to the formation of adamantylideneadamantane (**3**).

In the debromination of **2**, the quality of the zinc used proved to be rather important. Both surface and size of the granulated zinc may influence the course of the reaction. With finely divided, activated zinc dust, only a poor yield of **3** was obtained and a considerable amount of adamantane was formed as by-product. With less active, coarse zinc, a smooth reaction occurred, leading to **3** with only minor amounts of by-products. The by-products, which are readily separable from the olefin **3**, consist mainly of 2-bromoadamantane and an unknown compound that shows strong ether bands in the I.R. spectrum; the latter compound may be an insertion product formed from adamantylidene carbene and the solvent tetrahydrofuran.

2,2-Dibromoadamantane (2): Adamantanone[3] (6.6 g) was mixed with phosphorus(V)-bromide (28 g). The mixture liquified and the temperature rose to ~50° within a few minutes. The mixture was heated at 70° for 1 hr and then gradually poured into water at 60–70° with stirring. After hydrolysis was complete, the mixture was extracted with dichloromethane. The extract was washed with *N* aqueous sodium hydroxide, dried, treated with charcoal, and filtered. The solvent was removed by distillation; yield: 12.4 g (96%) of a colorless residue; m.p. 162–164° (from petroleum ether, b.p. 40–60°; Ref.[6], m.p. 165.5°).

Adamantylideneadamantane (3): Copper(II)-acetate [$Cu(OCOCH_3)_2 \cdot H_2O$; 0.25 g] was dissolved in hot acetic acid (6 ml). Zinc[7] (4.4 g) was added to the solution. The mixture was shaken and heated for a few minutes until the green color of the copper ion had disappeared. The colorless supernatant was decanted and the remaining solid washed (with decantation) with acetic acid (10 ml), then four times with ether (10-ml portions), and finally with tetrahydrofuran (10 ml). To the reagent thus obtained, tetrahydrofuran (10 ml) and 2,2-dibromoadamantane (2.0 g) were added; the mixture was cooled in ice and shaken. The temperature rose to ~30°. After the exothermic reaction had ceased, the mixture was heated to reflux for 10 min. The solid products were then filtered off and washed with ether. The filtrate and washings were combined and the solvent removed by distillation. The residue was dissolved in ether (25 ml)–2 *N* sulfuric acid (10 ml) mixture. The organic layer was separated, washed with water, dried, and evaporated to dryness. Methanol (5 ml) was added to the residue; the remaining colorless solid was filtered off, washed twice with methanol (5-ml portions), and dried in vacuo; yield: 0.69 g (75%); m.p. 181–186° after sublimation in vacuo, m.p. 184–187°.

$C_{20}H_{28}$ (268.219)	calc.	C 89.49	H 10.51
	found	89.36	10.54

Mass spectrum: M^+ 268.218.

I.R. (KBr): C—H-stretching bands at 2850, 2910, and 2970 cm^{-1}. For the rest, only weak absorptions.

N.M.R. ($CDCl_3$): δ 2.91 (s, 4 H, tertiary protons next to C=C), δ 1.55–1.95 (m, 24 H, rest of the protons).

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