A Simple and Unambiguous Route to Adamantene: Debromination of 1,2-Dibromoadamantane with Bis(trimethylsilyl)mercury

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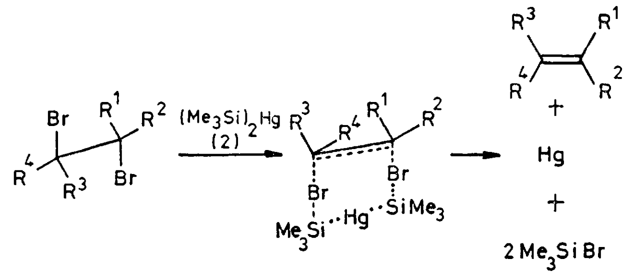
Summary In a process extensible, in principle, to the preparation of other anti-Bredt alkenes, reaction in boiling benzene of 1,2-dibromo- or 1,2-di-iodo-adamantane with bis(trimethylsilyl)mercury, which dehalogenates 1,2-dibromoalkanes in a concerted, 'four-centre' manner, leads to the unambiguous generation of adamantene, as shown by trapping by 1,3-diphenylisobenzofuran (30—35% yield of adduct) and 2,5-dimethylfuran (16% yield of adduct).

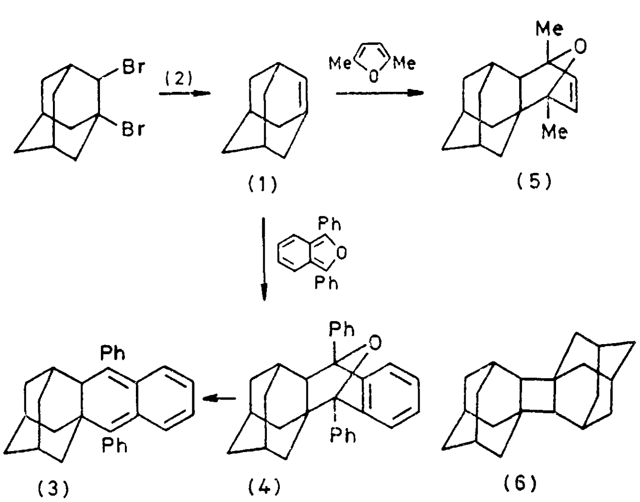
We report a simple route to adamantene (**1**) which not only leads unambiguously to this elusive species,[1] but is also extensible, in principle, to other anti-Bredt alkenes.

Our route depends on the dehalogenating properties of bis(trimethylsilyl)mercury (**2**)[2] which is known to debrominate 1,2-dibromoalkanes in a concerted, 'four-centre' manner (Scheme 1).[3]



Scheme 1

Thus, reaction of (**2**) (2·5 mol equiv.) with 1,2-dibromoadamantane (1 mol) in the presence of 1,3-diphenylisobenzofuran (5 mol) in boiling benzene after five days gave the hydrocarbon (**3**), 35%, m.p. 204—206 °C.† Taken with the concerted nature of the debromination (*vide supra*), this observation points to the generation of adamantene, its subsequent trapping by the diene, and deoxygenation of the resulting cycloadduct (**4**) to give the product (**3**) (Scheme 2). In support of this it is known[4] that diphenylisobenzofuran adducts readily lose oxygen under reducing conditions; moreover, in our case, mercury (II) oxide was a by-product.



Scheme 2

1,2-Di-iodoadamantane behaved similarly, giving the hydrocarbon (**3**) in 30% yield, while similar reaction of 1,2-dibromoadamantane in the presence of 2,5-dimethylfuran as trap gave the 1:1 adduct with adamantene (**5**; 16%), with ^{1}H n.m.r. spectrum identical with that previously reported.[1d] In the absence of the above 1,3-dienic traps, 1,2-dibromoadamantane gave dimers of adamantane (*e.g.* **6**) in low yield.

It is noteworthy that previous attempts to trap adamantene of different genesis *via* [2 + 4] cycloaddition with furan and its derivatives have led to adducts in zero to low (<9%) yields.[1c–e]

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† All new compounds had the expected ^{1}H and ^{13}C n.m.r. and mass spectra and elemental analysis.

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