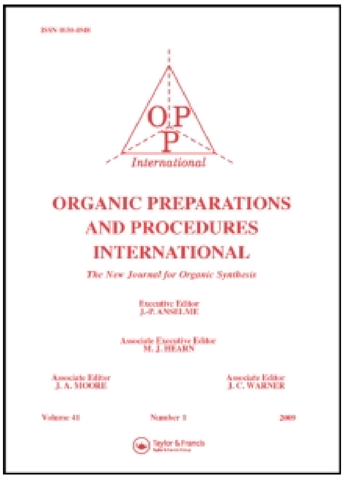


**Organic Preparations and Procedures International**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

# THE PREPARATION OF 1,3-DIBROMOADAMANTANE

T. M. Gorrie[a]; P. v. R. Schleyer[a]
[a] Department of Chemistry, Princeton University, Princeton, New Jersey

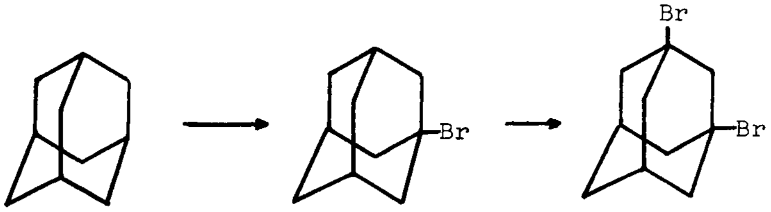
**To cite this Article** Gorrie, T. M. and Schleyer, P. v. R.(1971) 'THE PREPARATION OF 1,3-DIBROMOADAMANTANE', Organic Preparations and Procedures International, 3: 3, 159 — 162
**To link to this Article: DOI:** 10.1080/00304947109356059
**URL:** http://dx.doi.org/10.1080/00304947109356059

ORGANIC PREPARATIONS AND PROCEDURES, INT. 3(3), 159-162 (1971)

# THE PREPARATION OF 1,3-DIBROMOADAMANTANE

T. M. Gorrie[1] and P. v.R. Schleyer

Department of Chemistry, Princeton University
Princeton, New Jersey 08540



II III I

1,3-Dibromoadamantane (I) not only is an important precursor for forming other 1,3-disubstituted adamantanes,[2,3] but it also reacts in base to give the synthetically useful 7-methylenebicyclo[3.3.1]non-3-one.[4] Ionic cyclizations of such 3,7-difunctional bicyclo[3.3.1]nonanes lead to adamantane derivatives,[5] whereas photochemical cyclizations give noradamantanes.[6]

Stetter and Wulff[2] reported the preparation of I by refluxing adamantane (II) in excess bromine with boron tribromide as a catalyst. Baughman[7] found that pure boron tribromide gives only 1-bromoadamantane (III), but that trace amounts of aluminum tribromide (e.g. 1000:1 - boron tribromide: aluminum tribromide) were needed to obtain I. Most recently, Talaty *et al.*[8] followed Baughman's procedure but obtained only III; I was formed satisfactorily from II only when the ratio of boron tribromide to aluminum tribromide was around 125:1.

We report here that boron tribromide is unnecessary; I can be obtained from II (or from III) with aluminum tribromide and bromine. The bromination of adamantane is stepwise. The formation of 1,3,5-tribromoadamantane[2,3a] can be avoided by use of short reaction times and by avoiding external heating after the catalyst has been added.

## EXPERIMENTAL

To 15 ml. of bromine (reagent grade) in a round bottom flask equipped with condenser and drying tube (avoid grease) is added 5 g. (0.037 mole) of II (recrystallized once from acetone) with stirring. The reaction mixture is then heated (∿ 65°) until the generation of hydrogen bromide begins (about 5 min.). After removal of the source of heat and with continued stirring, 330 mg. (0.00063 moles $Al_2Br_6$) aluminum tribromide (freshly sublimed prior to use to insure uniform quality - avoid excessive exposure to air) is added in small portions during 15 min. The condenser is removed and replaced after each addition; care should be exercised because of the violence of the reaction. Stirring is continued 5 min. without external heating after addition of aluminum tribromide is complete; the reaction is then stopped by pouring the solution over ice and adding $CCl_4$. The time of the reaction is critical as shorter times give incomplete conversion of III to I and longer times cause generation of 1,3,5-tribromoadamantane from I. The excess bromine is decomposed with sodium bisulfite.[8] The aqueous layer is extracted 3 times with $CCl_4$ and the combined extracts are washed with water, 5% aqueous sodium bicarbonate, and dried over sodium bisulfate. The light yellow solution is evaporated in a rotary evaporator and the product is crystallized from methanol at -78°, dried and sublimed to give material, mp. 106-108° (sealed tube). The physical and spectroscopic properties are identical with those reported for 1,3-dibromoadamantane.[2,6,7,9] Yields are consistently in the range 70-80%.

The reaction can be monitored by gas chromatography. A 3' glass column packed with 5% Carbowax 20 M on Chromsorb W 80/100 may be used. A column temperature of 160° is appropriate for observation of I and III, while 100° is more suitable for following the disappearance of II, if this is desired.

1,3-Dibromoadamantane (I) can also be formed by adding 7.9 g. (0.037 mole) III to 15 ml. of bromine and refluxing for 10 min. The procedure then is otherwise the same, and the yields are similar (7.8 g., 72%).

Acknowledgements. This work was supported by grants from the National Institutes of Health (AI-07766), the National Science Foundation, the Petroleum Research Fund, administered by the American Chemical Society, and Hoffman-La Roche, Nutley, New Jersey.

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(Received April 2, 1971)