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BROMINATION OF ADAMANTANE AND BICYCLO(2.2.2)OCTANE WITH LIQUID BROMINE

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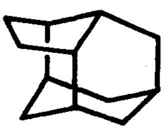
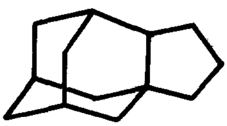
The direct bromination of adamantane with elemental bromine to give 1-bromoadamantane[1], one of the most versatile intermediates in the derivative chemistry of adamantane[2], has long been believed to proceed only slowly for no obvious reason, refluxing for three to four hours in neat bromine being the standard procedure.[1b, 3] The presumed slow rate of reaction is even used as a criterion of qualitative estimation of bridgehead reactivity of bicyclo-(3.3.1)nonane[4] and diamantane[5] relative to adamantane.

We found that adamantane could be brominated much more rapidly: Adamantane (0.31 g) was stirred in 3 ml of liquid bromine at room temperature for two hours. Glc analysis at this point revealed essentially single product and no trace of adamantane. Usual work up[1b] gave 0.35 g (91 %) of pure 1-bromoadamantane.

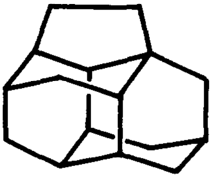
Not only adamantane itself, but also other related diamond molecules such as 1-methyladamantane, 2,4-ethanoadamantane[6] (I), 1,2-propanoadamantane[6] (II), 1,3-ethanodiamantane[6] (III) and nordiamantane[6] (IV) brominate easily at room temperature with neat bromine to give mono- to tetrabromides in high yields[7].



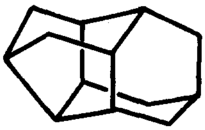
I



II



III



IV

Clearly, adamantane is more reactive towards molecular bromine than had been presumed. In fact, however, this finding is not surprising if one recalls two known facts that diamantane also brominates rapidly by stirring in liquid bromine at room temperature[5] and that solvolysis rates of 1-bromoadamantane and 1-bromodiamantane are the same order of magnitude[2]. We suggest that the capacity of molecular bromine, a Lewis acid, as the bridgehead brominating reagent has been underestimated on the following ground.

Bicyclo(2.2.2)octane, whose bridgehead carbenium ion is nearly thousand times less stable than 1-adamantyl carbenium ion[8], is found to afford its 1-bromo-derivative upon treatment with liquid bromine. The reaction is very slow even under reflux, but remarkably accelerated by the presence of boron tribromide and a trace of aluminum bromide[9]. A solution of 1.5 ml of boron tribromide and 8 mg of aluminum bromide in 10 ml of bromine was heated under reflux for 25 minutes. After cooling, 1.59 g of bicyclo(2.2.2)octane was added and the mixture stirred for three hours under reflux and overnight at room temperature. Usual work up[1b] followed by column chromatography on silica gel, crystallization from methanol and vacuum sublimation gave 0.48 g of pure 1-bromo-bicyclo(2.2.2)octane [18 %; mp 63.5-65.5°, lit[10]. 63.5-64.5°; nmr (CCl_4) two complex multiplets centered at δ 1.75 (7H) and 2.17 (6H); obsd. C, 50.60; H, 6.96; Br, 42.41] .

The direct procedure apparently provides the most convenient entry to 1-substituted bicyclo(2.2.2)octanes[11]; which have been commonly prepared by the multi-step syntheses of Grob[12] and Suzuki and Morita[10], or by the ring expansion of (1-norbornyl)carbinyl system[13].

Direct bromination of more strained polycyclic hydrocarbons including bicyclo(3.2.1)octane and twistane, as well as optimization of the 1-bromo-bicyclo(2.2.2)octane synthesis are under investigation.

References and Notes

1. (a) S. Lands, S. Kriebel and E. Knobloch, *Chem. Listy*, **48**, 61 (1954); (b) H. Stetter, M. Schwarz and A. Hirschhorn, *Chem. Ber.*, **92**, 1629 (1959).
2. R. C. Bingham and P. v. R. Schleyer, *Fortschr. Chem. Forsch.*, **18**, 1 (1971).
3. C. A. Grob, W. Schwarz and H. P. Fischer, *Helv. Chim. Acta*, **47**, 1385 (1964).
4. P. v. R. Schleyer, P. R. Isele and R. C. Bingham, *J. Org. Chem.*, **33**, 1239 (1968).
5. T. Gund, P. v. R. Schleyer and C. Hoogzand, *Tetrahedron Letters*, 1583 (1971).
6. To be published.
7. Structure of these bromides will be described in the forthcoming full accounts.
8. From relative solvolysis rates at 70°: R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3189 (1971).
9. Increase in the amounts of aluminum bromide leads to rearranged product, presumably 1-bromo-bicyclo(3.2.1)octane.
10. Z. Suzuki and K. Morita, *J. Org. Chem.*, **32**, 31 (1967).
11. Bicyclo(2.2.2)octene is commercially available.
12. C. A. Grob, M. Ohta, E. Renk and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958).
13. L. B. Humphrey, B. Hodgson and R. E. Pincock, *Canad. J. Chem.*, **46**, 3099 (1968).