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THE IONIC BROMINATION OF DIAMANTANE

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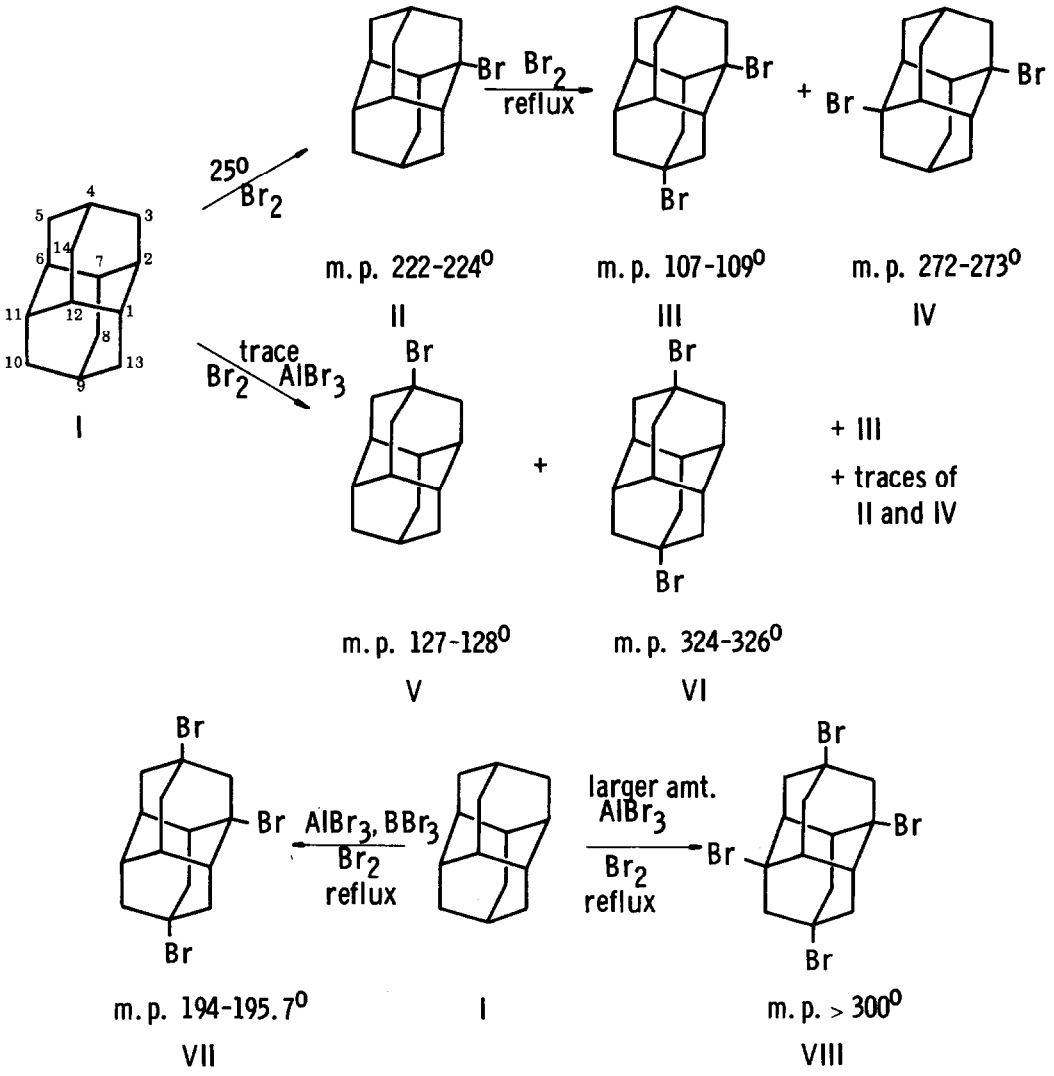
In contrast to the behavior of adamantane[1], the ionic bromination of diamantane (I)[2,3] is a much more complicated process. In refluxing bromine, adamantane gives only the bridgehead monobromide[1]. By the use of Lewis acid catalysts and increasing severity of conditions: two, three and finally four bromines can be introduced, all at the available bridgehead positions[1].

Because of its high symmetry, all bridgehead positions of adamantane are equivalent and they all bear a 1,3-relationship to each other. Because of its lower symmetry and larger size, diamantane (I) has two different types of bridgeheads and these can be in 1,2; 1,3; 1,4 and 1,6-relationships to one another. Colloquially, we designate the C-1, 2, 6, 7, 11 and 12 positions as the "belt" bridgeheads, and the C-4 and C-9 bridgeheads as "apical". The remaining hydrogens of diamantane are secondary.

The belt position of diamantane (C-1, I) is most reactive toward ionic substitution[3,4], and this position is more reactive than the bridgeheads of adamantane[5]. Thus, diamantane but not adamantane can be brominated by stirring with liquid bromine at room temperature for 2 hours; the product (80% yield) is 1-bromodiamantane (II). 1-Bromoadamantane cannot be brominated further by refluxing bromine in the absence of catalyst, but 1-bromodiamantane gives the two possible 1,4-type products: 1,4-dibromodiamantane (III) and 1,6-dibromodiamantane (IV). These two dibromides can be separated easily by solubility differences; IV, the higher melting isomer, crystallizes preferentially from hexane. IV also elutes first with hexane on alumina chromatography.

CHART I

SUMMARY OF DIAMANTANE BROMINATION RESULTS.



The apical isomer, 4-bromodiamantane (V), was finally obtained by two routes. Interestingly, traces of aluminum bromide catalyst produce a significant change in the course of the bromination, and some attack at the apical position takes place. In the presence of $AlBr_3$, bromination gives typically (see Table I) a mixture of the two monobromides, II and V, the dibromides, III and IV, and a new dibromide, 4,9-dibromodiamantane (VI). This new dibromide (VI) had an even higher melting point than IV and even lower solubility; these properties facilitated its separation from the reaction mixture. The components of the bromination mixture, including V, can be separated by alumina chromatography. V can also be prepared (along with diamantane) by partial reduction of VI with tri-n-butyl tin hydride[3].

With more $AlBr_3$ catalyst, diamantane gave first 1,4,9-tribromodiamantane (VII) and then 1,4,6,9-tetrabromodiamantane (VIII) (see Table I). The location of two of the bromine atoms in these polybromides at both apical positions (C-4 and C-9) was confirmed by chemical conversion: $AlBr_3$-catalyzed bromination of 4,9-dibromodiamantane gave both VII and VIII.

In general, polybromination of diamantane is controlled by inductive effects by the first bromine already present. Subsequent attack is at positions as far removed from the first bromine substituent as possible, but belt positions are inherently more reactive than apical ones. Typical reaction conditions are summarized in Table I.

The structures were assigned from their characteristic nmr spectra. In each case the apically substituted derivatives exhibit simpler spectra than the belt substituted isomers. The observed spectra are in every case those expected by following the additivity rules derived for 1 and 2-substituted adamantanes[6]. The apical position of (I) behaves like the adamantane bridgehead position, whereas the belt position is bridgehead in nature in relation to one cyclohexane ring and secondary with respect to the other component ring.

Table I

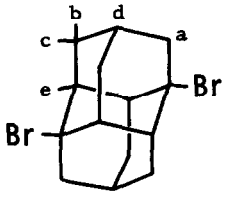
Experimental Conditions for Bromination of Diamantane.

I(g)	Br_2(ml)	$AlBr_3$(g)	Temp.	Time, hrs.	Products Major	Minor	Trace
2.0	10		Room	2	II		IV
2.0	10		Reflux	16	III, IV		
10.0	30	0.50	50°	3	III, V, VI	II, IV	
2.0	10	0.08 (+0.2ml BBr_3)	Reflux	2	VII		III, IV, VI
2.0	10	2.0	Reflux	1	VIII		

Table II

Example of Analysis of NMR Spectra

Proton type	Area	δ Calc[6]	δ Found	Appearance
a	4	2.20	2.42	Doublet
b	4	1.50	1.62	Half of AB Quartet J~12Hz
c	4	2.21	2.62	Half of AB Quartet J~12Hz
d	2	1.83	1.78	Broad
e	4	2.12	2.28	Broad



IV

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References and Footnotes.

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