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THE FUNCTIONALIZATION OF DIAMANTANE (CONGRESSANE)

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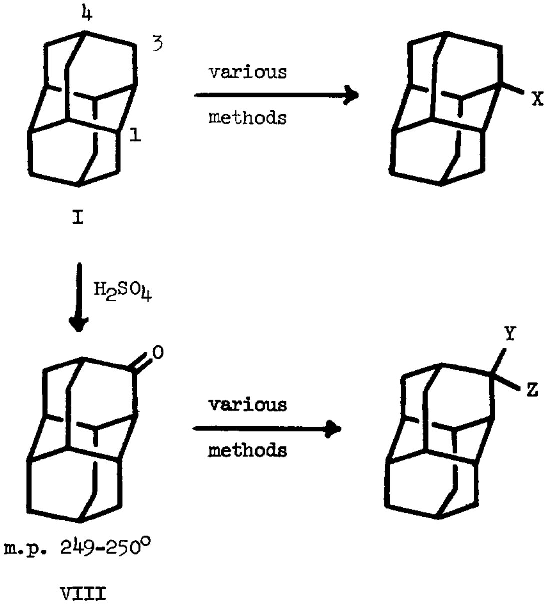
Diamantane (I)[1,2] (formerly called "Congressane")[2] has now become readily available through rearrangement of tetrahydro-Binor-S.[3] We have developed methods to functionalize diamantane to give the three possible types of monosubstituted derivatives. In this preliminary report, we summarize some of the basic chemistry of this interesting relative of adamantane.[4]



		m.p.
II,	X=Br	209-211°
III,	X=COOH	201-202.2°
IV,	X=OH	291-292°
V,	X=CH_3	215-218°
VI,	X=$NHCOCH_3$	167-168°
VII,	X=$NH_3^+Cl^-$	360°

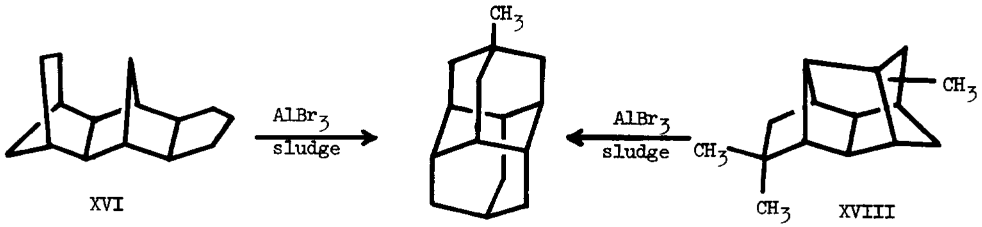
	Y	Z	m.p.
IX	OH	H	256-257°
X	OTs	H	124.2-124.6°
XI	Br	H	93-94°
XII	Cl	H	157-158°
XIII	CH_3	OH	149-150°
XIV	=CH_2		125-126°
XV	CH_3	H	117-118°

Three positional diamantane isomers are possible since the molecule has two types of bridgeheads (C-1 and C-4) as well as methylene groups (C-3), all six of which are equivalent. Our objective was to find ways to substitute each of these three positions easily and selectively. This goal has been met in two (C-1 and C-3) of the three cases, and a workable although cumbersome method to obtain 4-substituted derivatives has been developed.

The 1-position of diamantane (I) is more reactive than adamantane[4] towards ionic substitution. When I is stirred with liquid bromine at room temperature a good yield of 1-bromodiamantane (II) is obtained.[5] Similarly, the Koch-Haaf carboxylation of diamantane (I) gives the 1-carboxylic acid (III).[6] Other 1-derivatives have been prepared from II by conventional procedures: IV (by hydrolysis), V (by reaction with CH_3MgBr),[7] VI (by the Ritter reaction),[8] and VII (by hydrolysis of VI).

The best entry to methylene-substituted adamantanes is the sulfuric acid oxidation procedure of Geluk and Schlattmann.[9] When diamantane is used instead of adamantane, a 60% yield of 3-diamantanone (VIII) results. Reduction of this ketone with $LiAlH_4$ gave 3-diamantanol (IX) from which tosylate X, bromide XI (with PBr_5), and chloride XII (with $SOCl_2$) could easily be prepared. Methyl Grignard reagent reacted with VIII to give 3-methyl-3-diamantanol (XIII). Dehydration of this tertiary alcohol with H_3PO_4 yielded 3-methylenediamantane (XIV), and reduction of the latter produced 3-methyldiamantane (XV).

In principle, because of their equatorial character, 4-substituted diamantanes should be the most stable thermodynamically. Both 1- and 3-derivatives are axial to one of the cyclohexane rings which make up the diamantane structure. Reactions governed by thermodynamic control should thus give 4-substituted adamantanes. However, we have been able to realize this expectation in only one instance. Rearrangement of <u>exo</u>-tetrahydrotricyclopentadiene (XVI)[10] with $AlBr_3$-sludge catalyst[1] gave a product containing the various methyldiamantanes (and other materials) from which 4-methyldiamantane (XVII) could be isolated by distillation; crystals of XVII formed in 3% yield.[11] Somewhat better results were obtained by isomerization of XVIII,[12] which gave a 15% glc yield of XVII (50% of the product mixture).

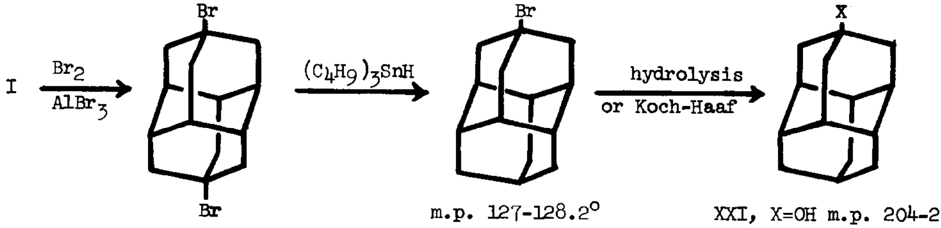


XVI

XVIII

XVII, m.p. 98.6-99.6°

The introduction of functional groups at C-4 has been accomplished indirectly. Bromination of diamantane (I) with refluxing bromine in the presence of a small amount of $AlBr_3$ catalyst gives mostly a mixture of dibromides.[5] The residue remaining when this mixture is treated with pentane is 4,9-dibromodiamantane (XIX), the highest melting of the diamantane dibromides we have prepared.[5] Reduction of XIX with 1 mole of tributyl tin hydride gave a mixture of starting material, diamantane, and 4-bromodiamantane (XX). XX could be hydrolyzed to 4-diamantanol (XXI) while Koch-Haaf reaction under high dilution conditions[13] gave the 4-carboxylic acid (XXII).



m.p. 324-326°

XIX

m.p. 127-128.2°

XX

XXI, X=OH m.p. 204-206°

XXII, X=COOH m.p. 278.5-279.9°

The diamantane derivatives described here were characterized by their nmr, ir and mass spectra; all gave acceptable microanalytical data. The nmr spectra were especially revealing, since diamantane derivatives follow nearly the same additivity rules as do 1-substituted[14] and 2-substituted[15] adamantanes. By utilizing the known shielding or deshielding effects of the various substituents,[14,15] it is actually possible to predict with good accuracy the nmr spectra of diamantane derivatives. This makes the identification of these compounds very easy.

The preparation and properties of homodiamantanes, nor- and bisnor-diamantanes, protodiamantanes, and di- and polysubstituted diamantane derivatives will be reported later. Diamantanes can also be used to synthesize, by ring opening reactions, a number of interesting adamantanes.

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References and Footnotes

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(5) Several dibromo- and polybromodiamantanes result from more vigorous reaction conditions. These products will be described subsequently.

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(10) Sample kindly provided by P. Starcher, Union Carbide Corporation.

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(12) The preparation of XVIII and its rearrangement were carried out by Dr. E. Osawa.

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