

## SYNTHESIS AND RING OPENING OF 3,5-DEHYDRODIAMANTANE.

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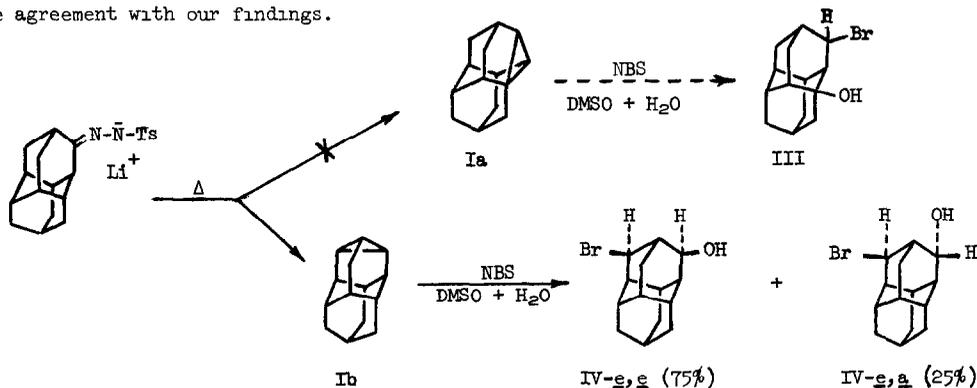
Intramolecular carbene insertion<sup>1</sup> in diamantane could give rise, in principle, to two different dehydrodiamantanes, the 1,3 (Ia) and 3,5 (Ib) isomers, by analogy with similar behavior in the adamantane<sup>2</sup> and homocadamantane<sup>3</sup> series. In order to establish the course of this reaction and to provide entries to novel disubstituted diamantane derivatives, we studied the pyrolysis of the lithium salt of diamantanone tosylhydrazone (II)

The tosylhydrazone (m.p. 173-5°, dec)<sup>4</sup> (prepared from diamantanone<sup>5</sup> by the usual procedure<sup>6</sup>) was converted to II by treatment with commercial butyl lithium in hexane, using tetrahydrofuran-ether as solvent. This salt (dried at 75-80° and 0.1 mm for one hour<sup>7</sup>) was heated at 165-170° and 0.1 mm in a sublimator. Rapid decomposition ensued. The sublimate collected was purified by column chromatography on basic alumina with pentane<sup>8</sup> to give ca. 20%<sup>9,10</sup> dehydrodiamantane (I)<sup>4</sup> (m.p. 112-4°, mass spectral parent ion and base peak at m/e 186,  $\nu$  3025, 1018 cm<sup>-1</sup> in KBr disk, nmr in CCl<sub>4</sub>,  $\delta$  2.35-1.10, complex signal)

The product I (one isomer by glc)<sup>8</sup> was reacted with N-bromosuccinimide in water-dimethylsulfoxide at room temperature<sup>7,11</sup> to give a mixture of bromohydrins (72% yield) the nmr spectrum of which contains (apart from a broad multiplet at  $\delta$  2.6-1.0 ppm for the other 16 CH<sub>2</sub>'s and one OH) two pairs of signals: (i)  $\delta$  3.85 (CHOH) and 4.44 (CHBr) ppm (0.75H each), and (ii)  $\delta$  4.02 (CHOH) and 4.98 (CHBr) ppm (0.25 H each). The equal intensity of CHOH and CHBr signals in each pair, together with the absence of another CHBr signal, rule out the bromohydrin III which should be present if 1,3-dehydrodiamantane (Ia) were a component of the carbene product. Therefore, intramolecular insertion of 3-diamantylidene gives exclusively (in the limit of our methods of detection) 3,5-dehydrodiamantane (Ib), the ring opening of Ib results in two stereoisomers of 3-bromo-5-hydroxydiamantane (IV)

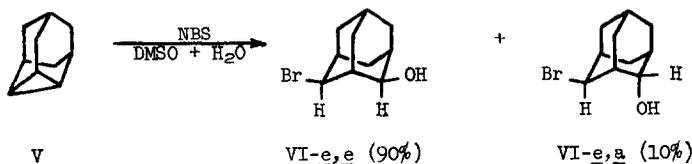
The preferential formation of Ib over Ia can be rationalized on the basis of the higher strain in the latter. Molecular mechanics calculations give a strain energy difference of 10-12

kcal/mol between Ia and Ib (2,4-dehydroadamantane (V) is indicated to be less strained than Ib, by ca. 5 kcal/mol)<sup>12</sup> Although these values are not quantitatively accurate, they are in qualitative agreement with our findings.



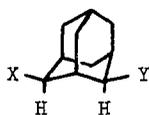
The bromohydrins IV could be separated by column chromatography (silica gel, benzene) The minor product eluted first, m p 134.8-135.9.<sup>4</sup> The major product with longer retention time (m.p. 165.8-167.0)<sup>4</sup> was assigned structure IV-e,e by analogy with the main product obtained from V under similar conditions (the CHBr and CHOH chemical shifts for the adamantane bromohydrins correspond quite closely to those for the corresponding adamantane bromohydrins,<sup>13</sup> e.g., IV-e,e vs VI-e,e (see below))

Since, in contrast to our results with Ib, the analogous ring opening of 2,4-dehydroadamantane (V) was reported to give complete stereoselectivity,<sup>11,13</sup> we reinvestigated this reaction. In our hands, treatment of V with N-bromosuccinimide in dimethylsulfoxide-water as above<sup>7,11</sup> gave a crude product with an nmr spectrum displaying not only the CHOH and CHBr signals of VI-e,e at  $\delta$  3.88 and 4.48 (lit.<sup>13</sup> 3.88 and 4.45), respectively (ca. 0.9 H each), but also two signals at  $\delta$  4.09 and 5.00, respectively (ca. 0.1 H each)



Two structures are possible for the minor product from V 2-e-bromo-4-a-hydroxyadamantane (VI-e,a) and 2-a-bromo-4-e-hydroxyadamantane (VI-a,e). (The fourth possible isomer, VI-a,a, is known and has different chemical shifts.<sup>14</sup>) In order to differentiate between these structures by nmr, it is not possible to calculate the chemical shifts for VI-e,a and VI-a,e using the values

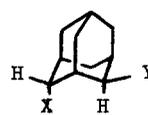
for the corresponding monosubstituted adamantanes and simple additivity assumptions,<sup>15</sup> since it was found that simple additivity does not hold for 2,4-disubstituted adamantanes<sup>13,16</sup> However, the nmr spectra of stereoisomeric 2,4-dihydroxy (VIIA, X=Y=OH)<sup>13</sup> and 2,4-dibromoadamantanes (VIIB, X=Y=Br)<sup>17</sup> show that a change in the group Y from the equatorial position (as in VII-e,e) to the axial position (as in VII-e,a), results in a displacement in chemical shift of CHX,  $\Delta \delta$  0.43 for Y=OH (VIIA) and 0.65<sup>17a</sup> to 0.70<sup>17b</sup> ppm for Y=Br (VIIB). If the difference is assumed to be the same for the bromohydrins VIIC (VI), the chemical shift for CHBr in VI-e,a should be  $\delta$  4.91 (4.48 + 0.43), and that for  $\delta$  CHOH in VI-a,e should be  $\delta$  4.53-4.58 (3.88 + 0.65 to 0.7)



VII-e,e



VII-e,a



VII-a,e

A X = Y = OH,    B X = Y = Br,    C X = Br, Y = OH (VI)

A similar treatment of the difference in the chemical shifts for the CHX signals between VII-e,e and VII-a,e, gives  $\Delta \delta$  values of 0.22<sup>13</sup> and 0.23<sup>17a</sup> to 0.29<sup>17b</sup> ppm, for Y=OH (in VIIA) and Y=Br (in VIIB) respectively, predicting  $\delta$  CHOH in VI-e,a 4.11 to 4.17 and  $\delta$  CHBr in VI-a,e 4.70 ppm

The experimental values ( $\delta$  CHOH 4.09,  $\delta$  CHBr 5.00) agree best with VI-e,a as the structure of the minor product of ring opening of V. Likewise, the minor product obtained from Ib is assigned structure IV-e,a (The correspondence between  $\delta$  values for CHBr and  $\delta$  CHOH protons in IV-e,a and VI-e,a is quite close)

Our results show that the opening of the three-membered rings of V and Ib with N-bromo-succinimide in water-dimethylsulfoxide, is not stereospecific (inversion at both sites) as reported,<sup>11</sup> but some addition with inversion-retention also takes place. This is in line with the findings for addition of halogens,<sup>11</sup> but at variance with other additions to V<sup>11,18</sup>

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