## A Novel Route to the 2-Aza-adamantyl System *via* Photochemical Ring Contraction of Epoxy 4-Azahomoadamantanes

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Epoxy 4-azahomoadamantanes rearranged to give, on photolysis, N-acyl-substituted 2-aza-adamantanes as the only products.

Although several synthetic routes to the 2-aza-adamantyl system have been reported, all of them require elusive multistep procedures or starting materials, such as bicyclo[3.3.1]nonane-3,7-dione, bicyclo[3.3.1]nona-2,6-diene, and 3-endo-aminobicyclo[3.3.1]non-6-ene, that are not readily accessible. We now report a novel and convenient

route to the 2-aza-adamantyl system (4) utilizing a facile photochemical ring contraction of the epoxy 4-azahomoadamantanes, (3) (Scheme 1).

The required precursors (3a—d) were prepared by *m*-chloroperbenzoic acid (*m*-CPBA) oxidation of the azahomoadamantenes (2a—d), which are readily obtainable from the

Table 1. The epoxy 4-azahomoadamantanes (3) obtained from (2).a

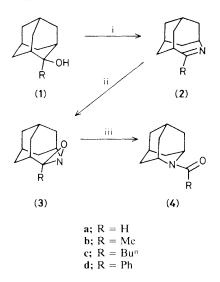
Imine	(3)	Reaction time/h	Yield/%c	M.p./°C	δ 3-H and 6-H <sup>d</sup>
(2a)	(3a)	3h	61	>300	3.90(s), 2.60(s)
(2b)	( <b>3b</b> ) <sup>f</sup>	12	91	65—68	3.82(s), 2.35(s)
(2c)	(3c)	15	71	Oil	$3.74 (s), 2.35 (s)^{e}$
(2d)	( <b>3d</b> )	12	63	105107	$3.93(s), 2.99(s)^{e}$

"Imine (2) was oxidized by m-CPBA (1.1 equiv.) in CHCl<sub>3</sub>-5% aqueous NaHCO<sub>3</sub> at 5—20 °C. <sup>b</sup> In CH<sub>2</sub>Cl<sub>2</sub>-solid NaHCO<sub>3</sub>, <sup>c</sup> Yield of isolated pure product after chromatography (Woelm neutral alumina–CH<sub>2</sub>Cl<sub>2</sub>), <sup>d</sup> In CDCl<sub>3</sub> (60 MHz), <sup>e</sup> In CCl<sub>4</sub>, <sup>†</sup> For a low yield synthesis by peracetic acid oxidation see T. Sasaki, S. Eguchi, and N. Toi, *J. Org. Chem.*, 1978, 43, 3810.

Table 2. The N-acvl-2-aza-adamantanes (4) obtained from (3).

<b>(3)</b>	Conversion/%b	Product	Yield/% <sup>6</sup>	M.p./°C	δ 3-H and 6-H <sup>c</sup>
(3a)	28	( `	67	165167	4.52 (s), 3.73 (s)
(3b)	46	(4D)	50	Oil	4.72 (s), 3.93 (s)
(3c)	50	(4c)	60	Oil	4.73 (s), 3.98 (s)
(3d)	44	( <b>4d</b> ) <sup>d</sup>	44	8891	4.93(s), 3.90(s)

<sup>a</sup> A 4.7—6.0 mm solution of (3) in cyclohexane was irradiated with a 60 W low pressure Hg lamp through a quartz filter under argon for 0.5 h at 20—30 °C. <sup>b</sup> Based on isolated amounts of (3) and (4). <sup>c</sup> In CCl<sub>4</sub> (60 MHz). <sup>d</sup> Reported as an oil in ref. 1(b); a trace of (2d) was also produced.



**Scheme 1.** i, NaN<sub>3</sub>-CHCl<sub>3</sub>-MeSO<sub>3</sub>H (ref. 3); ii, *m*-CPBA-CHCl<sub>3</sub>-NaHCO<sub>3</sub>; iii, *hv*-cyclohexane.

corresponding 2-hydroxyadamantanes (1a—d).<sup>3</sup> A mixture of (2a) with m-CPBA (1.1 equiv.) in CH<sub>2</sub>Cl<sub>2</sub>-NaHCO<sub>3</sub> stored at 5—20 °C, followed by the usual work-up and short column chromatography (Woelm neutral alumina-CH<sub>2</sub>Cl<sub>2</sub>) gave (3a) as sublimable crystals (61%).<sup>‡</sup> The other epoxy 4-azahomo-adamantanes (3b—d) were obtained using a similar method (Table 1)

Compounds (3) in cyclohexane were irradiated for 0.5 h with a low pressure Hg lamp through a quartz filter under argon. In each case a single product was formed after a short

time; longer periods gave a complex mixture. The initial product in each case was isolated by chromatography (Merck, alumina 60 PF<sub>254</sub>, type E–CH<sub>2</sub>Cl<sub>2</sub>) and characterized as the corresponding *N*-acyl-2-aza-adamantane (4) by microanalytical and spectral data. The i.r. spectra showed a strong carbonyl absorption at *ca.* 1640 cm<sup>-1</sup>, and the <sup>1</sup>H n.m.r. spectra showed two broad one-proton singlets at δ 4.93—4.52 and 3.90—3.73 characteristic of bridgehead protons adjacent to nitrogen. The results are summarized in Table 2.

The above facile and exclusive photochemical ring-contraction of (3) is rationalized in terms of stereoelectronic control theory, *i.e.*, the geometrical arrangement of the nitrogen lone pair and the skeletal C-5–C-6 bond in an *anti*-relation in the 4-azahomoadamantane (3), is favourable for the rearrangement.

This ring-expansion and ring-contraction sequence of the adamantane skeleton thus provides a novel and convenient route to the 2-aza-adamantvl system.

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 $<sup>^\</sup>dagger$  All new compounds had spectral and microanalytical data in agreement with the assigned structures.