

7-Azabicyclo[2.2.1]heptane *N*-Imide as an Intermediate in the Thermal Decomposition of *N*-Amino-7-azabicyclo[2.2.1]heptane and the Corresponding Benzenesulphonamide

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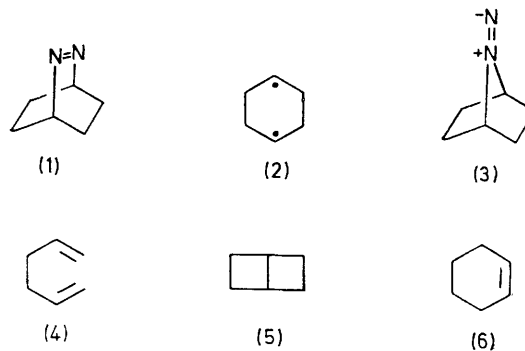
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Summary An intermediate in the thermal decomposition of *N*-amino-7-azabicyclo[2.2.1]heptane and the corresponding benzenesulphonamide derivative, whose structure is consistent with the formulation 7-azabicyclo[2.2.1]heptane *N*-imide, affords on thermal fragmentation the hydrocarbon products hexa-1,5-diene, bicyclo[2.2.0]hexane, and cyclohexene and does not rearrange to the corresponding stable 2,3-diazabicyclo[2.2.2]oct-2-ene isomer.

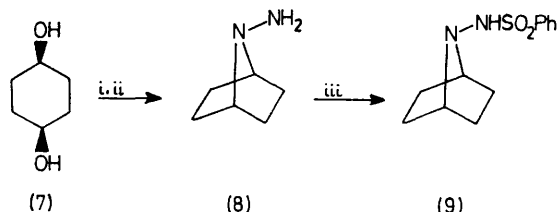
2,3-DIAZABICYCLO[2.2.2]OCT-2-ENE (1) undergoes thermal decomposition at 200 °C (E_a 44.5 kcal mol⁻¹) to afford nitrogen and hexa-1,5-diene (4).¹ If the diradical, cyclohexane-1,4-diyl (2), intervenes in this reaction, ring closure to bicyclo[2.2.0]hexane (5) as well as the cleavage product (4) might be expected.² However, (5) is not stable at 200 °C (E_a 36 kcal mol⁻¹) and has been shown to rearrange to hexa-1,5-diene (4).² *N*-Imides (*N*-aminonitrenes)³ are potential sources of diradicals and decompose at lower

temperatures than the isomeric azo-compounds. We report here a study of the thermal decomposition of the *N*-imide (3), an isomer of the azo-compound (1).

N-Amino-7-azabicyclo[2.2.1]heptane (8) and the benzenesulphonamide derivative (9) were prepared by the route



in the Scheme. For the generation and thermal decomposition of (3) a solution of (9) in diglyme [(MeOCH₂CH₂)₂O] was heated at 25 °C (and also at 120 °C) with BuⁿOCH₂CH₂ONa. Products observed by analytical vapour-



SCHEME. Reagents: i, MeSO₂Cl; ii, H₂NNH₂·H₂O; iii, PhSO₂Cl.

phase chromatography (v.p.c.) were hexa-1,5-diene (4), bicyclo[2.2.0]hexane (5), and cyclohexene (6). As an alternative method for generation of (3), oxidation with HgO of (8) in benzene at 25 °C afforded (4) and (5) (Table).

TABLE

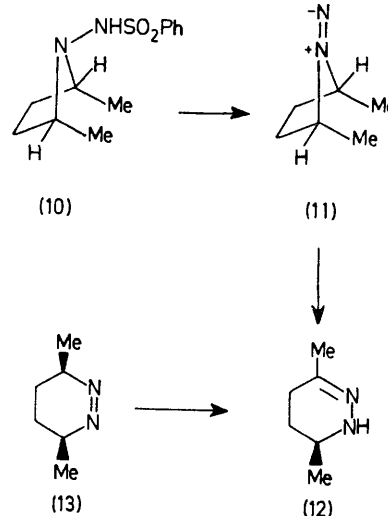
Reactant	Conditions ^a	Ratio (4):(5):(6)	Yield (%) from (7) ^b
(8)	A	76:24: ^c	6.2
(9)	B	76:24: ^c	24.5
(9)	C	73:24:3	92.6

^a A: HgO in benzene, 25 °C; B: diglyme + BuⁿOCH₂CH₂ONa at 25 °C; C: diglyme + BuⁿOCH₂CH₂ONa at 120 °C. ^b Yield of total hydrocarbons. ^c < 1.

The α-elimination route and the HgO oxidation procedure gave similar products in similar ratios. This is consistent with the cleavage and closure products arising from a common intermediate, the *N*-imide (3). Thermal decomposition of the presumed intermediate (3) affords a significant amount of the closure product (5) consistent with (though not proof of) the intermediacy of the diradical (2).

N-Imides are known to undergo competitive rearrangement to hydrazones as well as fragmentation with extrusion of nitrogen.³ Since some of their azo-isomers with enolizable hydrogen atoms are known to isomerize rapidly to their corresponding hydrazones, the possible intermediacy of azo-intermediates in the *N*-imide → hydrazone rearrangement has been discussed.^{3,4} We have found that decomposition of (10) affords the hydrazone (12) as well as hydrocarbon products and nitrogen presumably from a common *N*-imide precursor.⁵ The azo-compound (13) which has enolizable hydrogen atoms is thermally stable relative to

N-imide fragmentation but is known to isomerize rapidly in the presence of acid or base to its more stable hydrazone tautomer (12). Whether the *N*-imide → hydrazone rearrangement proceeds through an azo-compound such as (13) is not known.



The decomposition of the bicyclic *N*-imide (3) affords an opportunity to test for the occurrence of the *N*-imide → azo-compound rearrangement. The azo-compound (1) should be thermally stable at 25 °C (and 120 °C) and stable in the presence of base owing to the steric restriction that requires the corresponding hydrazone to possess an unfavourable bridgehead double bond. We could determine in this case whether the intermediate *N*-imide rearranges to any significant extent to its more stable azo-isomer. Under v.p.c. conditions under which the authentic azo-compound (1) was stable and observable, we were not able to detect (1) (< 1%) arising from either the α-elimination of (9) or the oxidation of (8). These results are consistent with the view that some *N*-imide → hydrazone rearrangements do not proceed by the indirect route involving the azo-isomer, but rather proceed directly to the hydrazone.³

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⁴ B. V. Ioffe and L. A. Kartsova, *Tetrahedron Letters*, 1973, 623.

⁵ P. B. Dervan and T. Uyehara, *J. Amer. Chem. Soc.*, 1976, **98**, 2003.