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THE SYNTHESIS AND DECOMPOSITION OF A NORBORNYL ENDO Δ^2- 1,2,3-TRIAZOLINE[1]

L.H. Zalkow and R.H. Hill

Georgia Institute of Technology, School of Chemistry, Atlanta, Georgia 30332 U.S.A.

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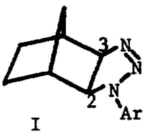
The recent observation[2,3] that norbornyl exo Δ^2-1,2,3-triazolines (I) give on pyrolysis, in addition to the expected exo-aziridines (II) and imines (III), endo aziridines (IV), prompted us to investigate the behavior of the corresponding endo triazolines (V) under similar conditions.



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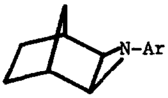

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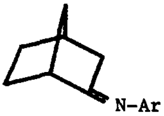

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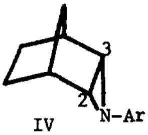

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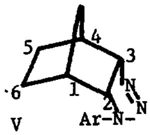
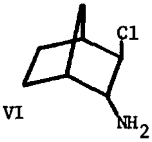


V

Unfortunately, endo triazolines cannot be obtained directly from bicyclic olefins, such as norbornylene, by the most universal synthetic method, namely, 1,3-dipolar cycloaddition of azides, since this reaction has been shown to proceed exclusively with exo orientation[2,4,5,6].

We now wish to report the synthesis of the first such endo norbornyl triazoline by a method which appears to be of general applicability[7]. The requisite endo-2-amino-exo-3-chloronorbornane (VI) was prepared from norbornylene by sequential treatment with nitrosyl chloride[8], then urea[9]



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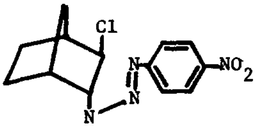


VII

to give the chloro oxime, the acetate of which was reduced with diborane[10] to give VI, which was isolated as its HCl salt [m.p. 195-200°; $\nu_{\max.}^{\mathrm{KBr}}$ 3400, 2925, 1960, 1590, 1570, 1495, 1475 cm^{-1}][11]. Chloroamine VI was also made by the same procedure via the p-nitrobenzoate ester of the intermediate oxime. The hydrochloride salt of VI was coupled with p-nitrobenzenediazonium chloride in a buffered solution to give VII in 61% yield [m.p. 112-115°, $\nu_{\max.}^{\mathrm{KBr}}$ 3380, 3315, 1600, 1500, 1320, 1250 cm^{-1}]^{11}. The latter intermediate was converted into the endo triazoline V (Ar = p-$NO_2C_6H_4$) in 64% yield by treatment with sodium ethoxide in ethanol in the presence of one equivalent of silver nitrate [m.p. 120-130°; $\nu^{max.}_{KBr}$ 1595, 1500, 1378, 1320 cm^{-1}; M^+-N_2, m/e 230]^{11}. The NMR spectrum (in $CDCl_3$) of V (Ar = p-$NO_2C_6H_4$) clearly showed that the triazoline ring was endo by the appearance of the C-2 proton as a doublet of doublets (J = 12.0, 4.25 Hz) centered at δ4.02 and the C-3 proton as a doublet of doublets (J = 12.0, 5.50 Hz) centered at δ5.09[7]. In contrast to this, the exo triazoline I (Ar = p-$NO_2C_6H_4$)[12] shows the C-2 proton as a doublet (J = 9 Hz) centered at δ 3.79 and the C-3 proton as a doublet (J = 9 Hz) centered at δ 4.77.

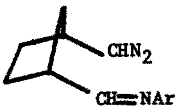
Photolysis of V, as expected[2], gave cleanly the endo aziridine IV (Ar = p-$NO_2C_6H_4$) with the C-2 and C-3 protons appearing in the NMR spectrum as a triplet (J = 2 Hz) centered at δ 2.93. Table 1 indicates the results obtained on pyrolysis[13] of the endo and exo aziridines.

Table 1.

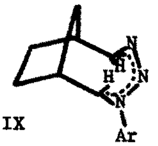
Pyrolysis of Triazolines (Ar = p-$NO_2C_6H_4$) in Decalin at 165-170°

Triazoline	Endo Aziridine IV	Exo Aziridine II	Imine III	Polymer
Exo I	8.8%	48.5%	42.3%	0
Endo V	17.5%	34.4%	48.2%	80%

We have previously suggested[2] that exo triazolines (I) yield endo aziridines (IV) via intermediate diazoimines (VIII), which could arise by a thermally allowed retro 1,3-dipolar cycloaddition reactions.



VIII



IX

Now with the observation that endo triazolines (V) yield exo aziridines (II) on pyrolysis, further support for such an intermediate is provided. However, because of the large amount of polymer produced in the pyrolysis of the endo triazoline, under the conditions recorded in Table 1, we cann conclusively state that a common intermediate is involved in the pyrolysis of exo and endo triazolines and more than one pathway may be operative. As might be expected on thermodynamic grounds, the endo triazoline begins to evolve nitrogen (in decalin) about 30° below that observed for the exo triazoline (165°). Attempts to observe, by NMR, the interconversion of exo and endo triazolines via intermediate VIII or via an intermediate such as IX, which could arise by a thermally allowed disrotatory electrocyclic ring opening of either triazoline, have so far not met with success. Likewise, we have so far not succeeded in trapping intermediate VIII with carboxylic acids. Further studies are underway.

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