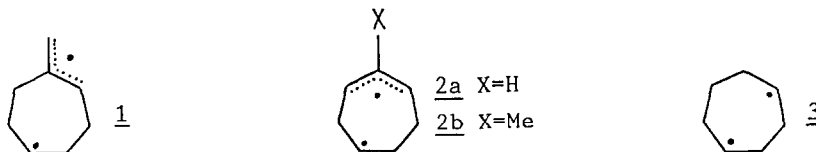


1,4-CYCLOHEPTYLENE AND THE RELATED ALLYLIC DIRADICALS.
THERMAL NITROGEN EXTRUSION FROM 6,7-DIAZABICYCLO[3.2.2]NON-6-ENES

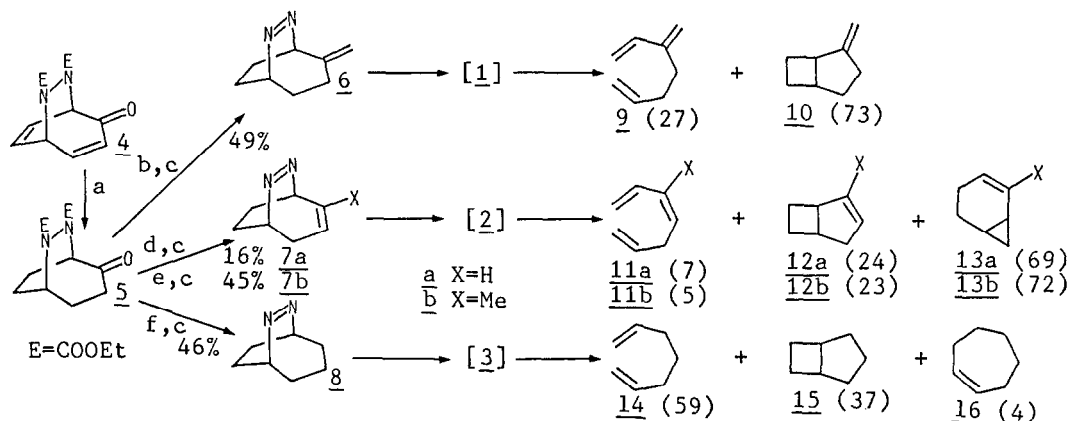
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Summary: Thermal nitrogen extrusion of 2-methylene-6,7-diazabicyclo[3.2.2]non-6-enes and 6,7-diazabicyclo[3.2.2]nona-2,6-dienes proceeded easily to give closure and cleavage products via the corresponding 5-methylene-1,4-cycloheptylenes and 4-cyclohepten-1,3-ylenes, respectively.

Recently we have reported sulfide extrusion from the methyl sulfonium salts of 8-thiabicyclo[3.2.1]oct-2-enes and the related sulfonium salts by metyllithium that would give the allylic diradicals (1 and 2) as the reactive intermediates.¹⁾ Upon investigation we ascertained that there was no information obtained from studies on certain procedures, such as nitrogen extrusion²⁾ from bicyclic azo compounds 6-8, to generate diradicals intermediates 1-3.³⁾ On the other hand, the fact that the reactivity of azo bridged compounds is enhanced by vinyl substituents on the bridgehead carbons⁴⁾ suggests easy nitrogen extrusion from 6 and 7 in which a sp² carbon is adjacent to the bridgehead carbon. Herein we report thermolysis of 6-8 and a preliminary stereochemical test of closure of diradical intermediates 1 and 2b.



Azo compounds 6,⁵⁾ 7a, and 8⁶⁾ were prepared from the Diels-Alder type 1,4-addition product of tropone and diethyl azodicarboxylate (4)⁷⁾ as shown in Scheme 1. Solution thermolysis of the azo compounds (0.02 M in degassed cyclohexane, sealed tube) was investigated in the temperature range of 115-180 °C for 6 and 7 and 190-230 °C for 8 and the results are shown in Scheme 1. Those hydrocarbon products were isolated by preparative gas chromatography and were identified spectroscopically.^{8,9)} Quantitative nitrogen extrusion to the hydrocarbons was confirmed by NMR studies of each azo decomposition in benzene-d₆.¹⁰⁾ The product composition (determined by GC and given in each parenthesis) was not influenced by temperature, except for slow rearrangement of 11 at 180 °C.



Scheme 1. Synthesis and thermolysis of 6,7-diazabicyclo[3.2.2]non-6-enes.^{a)}

a) (a) Ref. 7. (b) i) $\text{Ph}_3\text{P}=\text{CH}_2$; ii) KOH, MeOH. (c) i) AcOH; ii) NaOH; iii) O_2 . (d) i) NaBH_4 ; ii) $\text{PPh}_3\text{-CCl}_4$; iii) KOH, MeOH. (e) i) $\text{Ph}_3\text{P}=\text{CH}_2$; ii) I_2 , PhMe; iii) KOH, MeOH. (f) H_2NNH_2 , KOH, $\text{HOCH}_2\text{CH}_2\text{OH}$.

Table 1. Kinetic parameters for pyrolysis of 6,7-diazabicyclo[3.2.2]non-6-enes

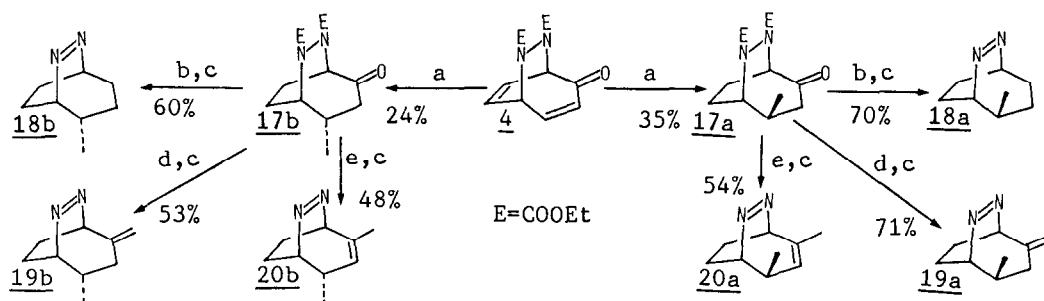
Diazene	k_{rel} (150 °C)	$\frac{\Delta H^\ddagger}{\text{kcal mol}^{-1}}$	$\frac{\Delta S^\ddagger}{\text{cal deg}^{-1} \text{mol}^{-1}}$	$\frac{\Delta G^\ddagger (150 \text{ °C})}{\text{kcal mol}^{-1}}$
<u>6</u>	23400	35.2	13.6	29.4
<u>7a</u>	3670	36.4	12.7	31.0
<u>8</u>	1	41.7	8.8	38.0

Azo compound 8 gave the cleavage product as the major one, while 6, 7a, and 7b predominantly gave the closure products. No hydrogen-shift products were derived from 6 and 7.

Table 1 shows kinetic parameters for the thermal decomposition of 6, 7a, and 8. First order rate constants which give linear Arrhenius plots were based on the rate of appearance of the respective major products (10, 13a, or 14). In comparison with the free energy for the deazetation of 8, those for 6 and 7a are lower by 8.6 and 7.0 kcal mol^{-1} , respectively. In each case, the lowering of the free energy of activation is smaller than an estimated allylic stabilization energy (ca. 12 kcal mol^{-1}).¹¹⁾ The difference may reflect the conformationally restricted overlap between the pi-orbital of the carbon-carbon double bond and the stretching carbon-nitrogen sigma-orbital, if the rate determining step is cleavage of the carbon-nitrogen sigma-bond.

Next we did a stereochemical test of the closure process of the deazetations. To this end, we prepared methylated azo compounds 18a-20b as shown in Scheme 2. Copper (I)-catalyzed 1,4-addition of methylmagnesium iodide to 4 followed by catalytic hydrogenation gave a mixture of 17a and 17b. These were separable by silica gel column chromatography. Stereochemistry of the substituents was confirmed by LIS studies on the $^1\text{H-NMR}$ spectra of 20a and 20b.

Conditions and the results of the solution thermolysis are summarized in

Scheme 2. Synthesis of methylated diazenes.^{a)}

a) (a) i) MeMgI-CuI; ii) H₂, Pd-C. (b) H₂NNH₂, KOH, HOCH₂CH₂OH. (c) i) AcOH; ii) NaOH; iii) O₂. (d) i) Ph₃P=CH₂; ii) KOH, MeOH. (e) i) Ph₃P=CH₂; ii) I₂, PhMe; iii) KOH, MeOH.

Table 2. Decomposition of methylated 6,7-diazabicyclo[3.2.2]non-6-enes^{a)}

Di-azene	Temp °C	Time h	Product (composition/%)			
			Cleavage	Closure		Others
				Retention	Inversion	
<u>18a</u>	220	4	<u>21</u> (52)	<u>22a</u> (37) ^{b)}	<u>22b</u> (7) ^{b)}	<u>23a</u> , <u>23b</u> ^{c)}
<u>18b</u>	220	4	<u>21</u> (56)	<u>22b</u> (23) ^{b)}	<u>22a</u> (17) ^{b)}	<u>23a</u> , <u>23b</u> ^{d)}
<u>19a</u>	140	1	<u>24</u> (12)	<u>26a</u> (82)	<u>26b</u> (5)	<u>25</u> (1)
<u>19a</u>	180	1	<u>24</u> (2)	<u>26a</u> (81)	<u>26b</u> (6)	<u>25</u> (11)
<u>19b</u>	140	1	<u>24</u> (25)	<u>26b</u> (66)	<u>26a</u> (8)	<u>25</u> (1)
<u>19b</u>	180	1	<u>24</u> (9)	<u>26b</u> (62)	<u>26a</u> (12)	<u>25</u> (17)
<u>20a</u>	140	1.5	<u>27</u> (4)	<u>28a</u> (11), <u>29a</u> (62)	<u>28b</u> (10), <u>29b</u> (13)	
<u>20a</u>	180	0.5	<u>27</u> (3)	<u>28a</u> (11), <u>29a</u> (60)	<u>28b</u> (13), <u>29b</u> (13)	<u>30</u> (1)
<u>20b</u>	140	1,5	<u>27</u> (3)	<u>28b</u> (3), <u>29b</u> (47)	<u>28a</u> (24), <u>29a</u> (24)	
<u>20b</u>	180	0.5	<u>27</u> (2)	<u>28b</u> (3), <u>29b</u> (39)	<u>28a</u> (26), <u>29a</u> (24)	<u>30</u> (6)

a) Determined by GLC unless otherwise noted. b) Determined by ¹H-NMR.

c) 3.6% and 0.4%, respectively. d) 2.7% and 1.3%, respectively.

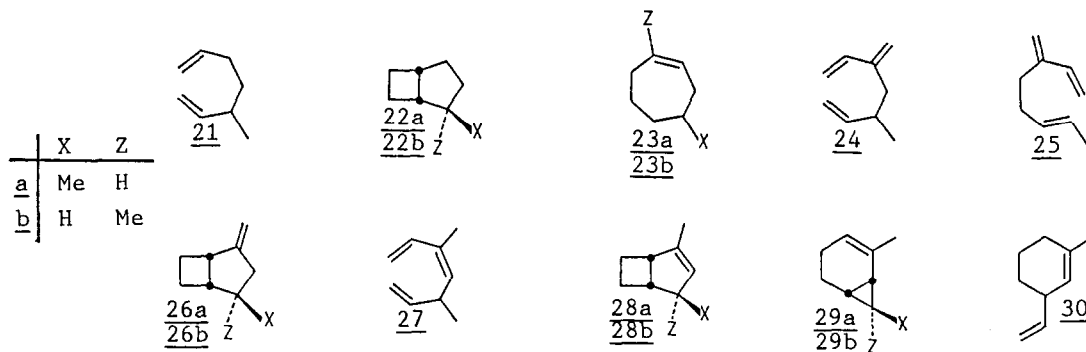


Table 2. Those products were isolated and identified spectroscopically.¹²⁾ Bicycloheptanes 22a and 22b and 2-methylene derivatives 26a and 26b were stable under the respective reaction conditions. Interconversion between 28a and 28b was observed; less than 2% from the former and less than 1% from the later

after heated at 180 °C for 1 h. Triene 24 reached thermal equilibrium with 25 (7 : 93) within 3 h at 180 °C. Slow rearrangement of 29b into 30 at 180 °C was confirmed independently.

Table 2 shows that i) retention is prior to inversion in each case, except for the reaction of 20b at 180 °C; ii) the ratios of retention to inversion for a series are larger than respective those for b series in which retention products are thermodynamically less stable; iii) retention takes extreme preference over inversion in the both cases of 19a and 19b; iv) for the reactions of 20a and 20b, retention gives 29 mainly, while inversion gives 28 and 29 equally.

Although stereochemical tests of cleavage are lacking, these results indicate that the hydrocarbons would be formed via the diradical intermediates (such as 1-3) which have reacted before reaching conformational equilibrium. Nitrogen extrusion of the diazenes possessing a C-C double bond at such a position may involve allylic diazenyl diradicals, but we could not find any strong reasons to adopt such diazenyl diradicals, instead of the allylic diradicals, for the explanation of the stereochemical results.

References

- 1) T. Uyehara, M. Takahashi, and T. Kato, *Tetrahedron Lett.*, 25, 3999 (1984).
- 2) For a recent review, see; P. S. Engel, *Chem. Rev.*, 80, 99 (1980).
- 3) For photochemical reaction of 13, see; W. J. Leigh and R. Srinivasan, *J. Am. Chem. Soc.*, 105, 514 (1983).
- 4) P. S. Engel, C. J. Nalepa, D. W. Horsey, D. E. Keys, and R. T. Grow, *J. Am. Chem. Soc.*, 105, 7102 (1983) and references cited therein.
- 5) All new compounds reported here exhibited satisfactory spectral and analytical characteristics.
- 6) M. L. Heyman and J. P. Snyder, *Tetrahedron Lett.*, 1973, 2859.
- 7) Y. Kitahara, I. Murata, and T. Nitta, *Tetrahedron Lett.*, 1967, 3003.
- 8) The authentic samples of following compounds, shown with the CAS registry number, were prepared: 10 [28436-00-2], 12a [7095-65-0], 13a [2566-57-6], 14 [3070-53-9], 15 [278-07-9], and 16 [628-92-2].
- 9) Compound 12b was derived from bicyclo[3.2.0]heptan-2-one.
- 10) Noticeable solvent effects were not observed.
- 11) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, London, Sydney (1968), p. 43.
- 12) The authentic specimens of 22a, 22b, 26a, 26b, 28a, and 28b were prepared as follows. Treatment of bicyclo[3.2.0]hept-3-en-2-one (31) with (Me)₂CuLi gave 4-exo-methylbicyclo[3.2.0]heptan-2-one (32a) selectively. The endo-methyl isomer (32b) was prepared selectively from 4-methylbicyclo[3.2.0]hept-3-en-2-one, derived from 31, by catalytic hydrogenation. Wolff-Kishner type reductions of 32a and 32b gave 22a and 22b, respectively. Compounds 26a and 26b were derived from 32a and 32b, respectively, by treating with methylenetriphenylphosphorane. Respective transformations of 32a and 32b into 28a and 28b are Grignard reactions with MeMgI followed by dehydration in the presence of KHSO₄.

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