9-Azabicyclo[6,1,0]nona-2,4,6-triene and Derivatives Thereof

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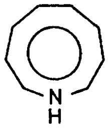
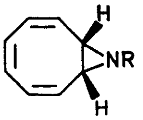
Summary The title substance was synthesized by two independent routes and was converted into various *N*-substituted derivatives displaying widely different heat sensitivities.

While *N*-ethoxycarbonyl- and *N*-cyano-9-azabicyclo[6,1,0]-nona-2,4,6-triene are known,[1,2] the parent aziridine (**2a**) is unknown. We report here its preparation and the thermal behaviour of some *N*-substituted variants.

Compound (**2a**) [air-sensitive white crystals, m.p. 50·5—51·5 °C; *m/e* 119 (M^+, 45%)] was prepared by irradiation of 1*H*-azonine (**1**)[3,4] (Pyrex-filtered; 0 °C; in de-aerated light petroleum; *ca.* 5 h) with a 450 W Hanovia light source as well as by careful treatment of urethane (**2c**)[1] with LiAlH at 0°. Structure (**2a**) was confirmed by its conversion into (**2c**) on treatment with ethyl chloroformate and its catalytic (Rh–C) hydrogenation followed by treatment with ethyl chloroformate to yield a perhydro-urethane identical (i.r., g.l.c.) with an authentic sample [*m/e* 197 (M^+, 60%)] prepared by hydrogenation of (**2c**).

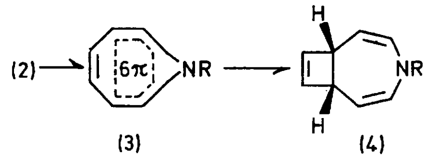


(1)



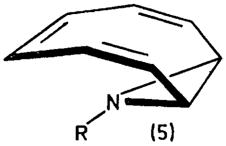
(2)

a; R = H
b; R = $CONMe_2$
c; R = CO_2Et
d; R = COMe
e; R = SO_2Ph
f; R = Cl
g; R = CN



(3) (4)

a; R = CO_2Et
b; R = COMe



(5)

The only reports on the thermolysis of the general system (2) are that (**2c**) thermally rearranges to (**4a**)[1] and that (**2g**) is susceptible to thermal decomposition.[2] Further, discussion of the mechanism of the rearrangement (2) to (4) is limited to comparison[5] to a simple Cope process and the demonstration[2b] that it cannot occur within the restrictions imposed by orbital symmetry[6] if either the remote double bond or the lone pair on nitrogen or both were to participate in the thermal bond relocation. The ease with which (**2**) would rearrange to (**4**) might be expected[2b] to be an inverse function of 'lone-pair' availability for participation in (**3**). To test this we prepared, (**2b**), m.p. 81—82°, (**2d**), and (**2e**), m.p. 74—75° by treatment of (**2a**) with *NN*-dimethylcarbamoyl chloride, acetyl chloride, and benzenesulphonyl chloride respectively, and determined their relative thermal sensitivities together with that of (**2c**). The results (Table) establish that the thermal stability of (**2**) is a sensitive function of *N*-substitution. Also comparison between (**2b**), (**2c**), and (**2d**), all of which contain the fragment N–CO shows a thermal sensitivity: [*k*(**2b**) > *k*(**2c**) ≫ *k*(**2d**)]† which is entirely consistent with the predicted destabili-

Table
Thermal response of (**2b**)—(**2e**)

Compound	Relative thermal sensitivity[a]	Product
(**2b**)	Stable (>21 h) at 76°	—
(**2c**)	$t_{\frac{1}{2}}$ *ca.* 75 min at 56°	(**4a**)
(**2d**)	$t_{\frac{1}{2}}$ *ca.* 19 min at 56°	(**4b**)[b]
(**2e**)	Stable (>21 h) at 76°	—

[a] Monitored by n.m.r. spectroscopy in C_6D_6. [b] Characterized by its n.m.r. spectrum which is analogous to that of (**4a**) (also characterized spectrally).[1]

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† Thermolysis does occur at higher temperatures, *e.g.*, for (**3b**) $t_{\frac{1}{2}}$ (110°) *ca.* 4 h and for (**3e**) $t_{\frac{1}{2}}$ (110°) *ca.* 5 h. Preliminary n.m.r analysis of the thermolysates indicates substantial decomposition and the absence of (**4**).

zation of (**3**)‡ with increased lone-pair participation.§ The thermal insensitivity of (**2e**)† does not conflict with this, for whereas the SO_2Ph group is known to be strongly electron withdrawing the effect here is believed to be chiefly inductive,¶ *i.e.*, one which does not *directly* affect the lone pair on nitrogen.

We also prepared the *N*-chloro derivative (**2f**) by treatment of (**2a**) with *N*-chlorosuccinimide and are currently studying its possible conversion into the nitrenium ion.

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‡ In terms of electron-withdrawing capacity, COMe > CO_2Et > $CONH_2$. *E.g.*, σ_p^- (COMe) = +0·874, σ_p^- (COEt) = +0·678. and σ_p^- ($CONH_2$) = +0·627 (J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", (Wiley, New York, 1961, p. 211).

§ We note that (**3**) may only be formed from the 'folded' conformation (**5**) (see *e.g.*, A. G. Anastassiou and R. C. Griffith, *J. Amer. Chem. Soc.*, 1971, **93**, 3083). The adverse effect that this conformational restriction may have on the freedom of nitrogen inversion will be discussed later.

¶ We thank Professor D. C. Dittmer for useful discussions.

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[5] G. Schröder, 'Cyclooctatetraen,' Verlag Chemie, Weinheim Germany, 1965, p. 33.
[6] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Academic Press, New York, 1970.