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INDENODIAZETINE: PREPARATION AND THERMAL DIAZETATION

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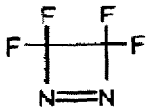
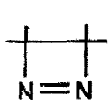
Summary. The preparation of an aryl substituted diazetine and the kinetics for its thermal decomposition to nitrogen and alkene are reported.

The thermal loss of nitrogen from diazetines is of particular interest because, although the process is highly exothermic (~50 kcal/M[1,2]), the known examples require temperatures of greater than 130°. The stability is probably related to orbital symmetry considerations for this forbidden $2\pi + 2\pi$ reaction. As yet detailed mechanistic studies have been limited because of a lack of synthetic routes to this ring system. The known cases along with activation parameters (if measured) for thermal decomposition to nitrogen and alkene are listed below. Decomposition of 5 has been shown to occur with retention of stereochemistry: *meso* 5 ⟶ Z and *dl* 5 ⟶ E-3,4-dimethyl-3-hexene[2]. The problem of



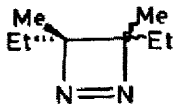
1[3] $\Delta H^{\ddagger}$ 38 kcal/M
$\Delta S^{\ddagger}$ 16 eu



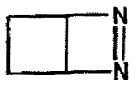
2[1] 31.8
0.3

3[4] 33.1
5.4

4[4] 33.7
3.0



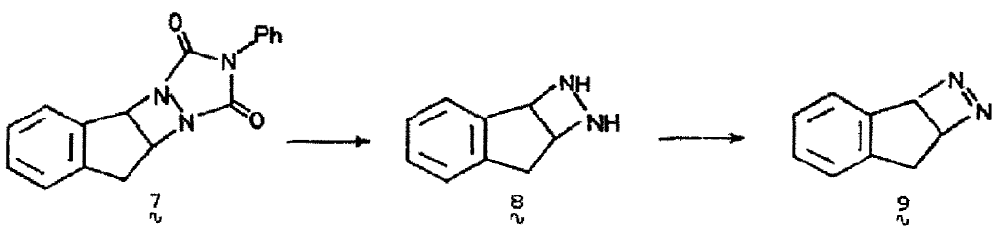
5[2]



6[5]

whether the process is concerted or stepwise involving diradicals is still in doubt. We report here the synthesis of a phenyl substituted diazetine and evidence from its thermal decomposition for a stepwise mechanism.

The known indene:N-phenyltriazolinedione adduct 7[6] was hydrolyzed (t-BuOK, DMSO, H_2O) at room temperature to the diazetidine 8 which was not isolated. Oxidation in the usual way with cupric chloride[7] gave the red isolable copper complex of 9. The diazetine 9 was freed by ice-cold aqueous KOH and extracted into pentane at 0°. Evaporation of the



7 8 9

pentane at 0° gave 9 as established by spectral evidence[8] and quantitative conversion to indene on warming above room temperature.

Kinetics for the thermal decomposition of 9 were determined spectrophotometrically and gave excellent first order plots[9]. Calculated activation parameters are $\Delta H^{\ddagger}$ = 25.8 ± 0.6 kcal/M and $\Delta S^{\ddagger}$ = 10.8 ± 0.3 eu. The change in activation energy for loss of nitrogen on going from 2 to 9 is approximately 6 kcal/M. The best model for comparison with the diazetines is the thermal decomposition of acylic azo compounds. Extensive results on these systems indicated a concerted two-bond cleavage for symmetrical cases (i.e. 10) and a rate determining single-bond cleavage for cases where the radical stability

$(CH_3)_3C-N=N-C(CH_3)_3$	$\Delta H^{\ddagger}$	42.4 kcal/M	$PhCH(CH_3)-N=N-CH_3$	$\Delta H^{\ddagger}$	38 kcal/M
10[11]	$\Delta S^{\ddagger}$	16.2 eu	11[12]	$\Delta S^{\ddagger}$	13 eu

of the two possible alkyl groups is very different (i.e. 11)[1,10]. The similar difference in activation energy between 10 and 11 (4.4 kcal/M) when compared to 2 and 9 suggests the same transition state difference may be present in the diazetines: concerted loss of nitrogen from 2 and stepwise from 9. The synthetic procedure we describe here, for the preparation of 9 may provide access to additional diazetines required to confirm this suggestion.

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8. nmr ($CDCl_3$), δ 3.2-3.5 (2H,m), 5.15-5.30 (1H,m), 5.88 (1H, broad s), 7.2-7.5 (4H,m), UV, λ max 350 nm.
9. Rate constants (temperature): 8.18×10^{-5} s^{-1} (20.8°), 38.6×10^{-5} s^{-1} (30.6°), 117×10^{-5} s^{-1} (39.5°) in benzene solvent.
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