

## Evidence for a Reverse Diels–Alder Mechanism in the Thermolysis of an Azo-compound

By JERALD C. HINSHAW and EVAN L. ALLRED\*

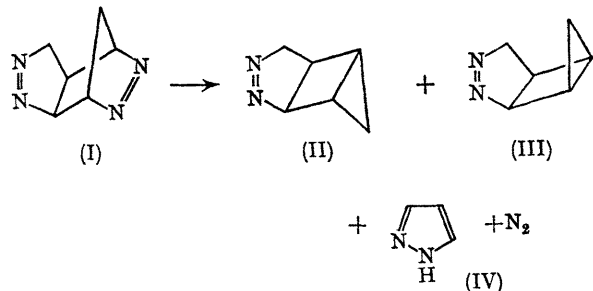
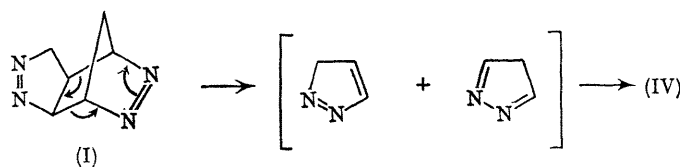
(Department of Chemistry, University of Utah, Salt Lake City, Utah 84112)

UNTIL now, all reported thermolyses of cyclic azo-compounds,<sup>1–5</sup> occurred by mechanisms which gave extrusion of molecular nitrogen. We now report that thermolysis of the azo-compound (I)† has a contribution from a reaction pathway which does not involve loss of nitrogen.

Thermolysis of (I) (m.p. 105–106°) under nitrogen at 120° was complete in 5 hr. and gave 0.75 mol. of nitrogen. Gas-phase chromatographic analysis of the product showed only three components in a ratio of 50:25:25; these were readily separated by preparative gas phase chromatography (Carbowax 20 M on Chromosorb W column) and were identified as (II),† (III),† and (IV), respectively. Component (IV) had physical and spectral properties identical with authentic pyrazole.

involving diradical-like intermediates which cyclize to give the bicyclo[2,1,0]pentane structures.<sup>2</sup> Compound (I) shows the same propensity for inversion of configuration as the 2,3-diazabicyclo[2,2,1]hept-2-ene system.<sup>2,4</sup>

The formation of pyrazole (IV) could be by a reverse Diels–Alder reaction, *e.g.*



The observed product distribution indicates that (II) and (III) are formed *via* a nitrogen-elimination route, probably

The proposed intermediates (V) and (VI) are not isolated because of ready hydrogen shifts to give the more-stable pyrazole (IV).<sup>6</sup> The structural analogy between (I) and *exo*-dicyclopentadiene which yields cyclopentadiene monomer by a reverse Diels–Alder reaction is obvious.<sup>7,8</sup> It is interesting that this reaction occurs readily at 120° with (I) but that *exo*-dicyclopentadiene is distilled unchanged at 170°.<sup>8</sup>

The thermolysis of (I) is apparently the first example of an azo-compound which decomposes by competitive reverse Diels–Alder and nitrogen-elimination mechanisms.<sup>7,9</sup>

We thank the National Science Foundation for support of this work.

(Received, November 4th, 1968; Com. 1500.)

† For the synthesis and characterization of compounds (I)–(III), see E. L. Allred and J. C. Hinshaw, *J. Amer. Chem. Soc.*, 1968, **90**, 6885.

<sup>1</sup> P. D. Bartlett and N. A. Porter, *J. Amer. Chem. Soc.*, 1968, **90**, 5317.

<sup>2</sup> E. L. Allred and R. L. Smith, *J. Amer. Chem. Soc.*, 1967, **89**, 7133.

<sup>3</sup> R. J. Crawford and L. H. Ali, *J. Amer. Chem. Soc.*, 1967, **89**, 3908; R. J. Crawford and A. Mishra, *ibid.*, 1966, **88**, 3963; and references therein.

<sup>4</sup> W. R. Roth and M. Martin, *Annalen*, 1967, **702**, 1; W. R. Roth and M. Martin, *Tetrahedron Letters*, 1967, 3865, 4695.

<sup>5</sup> D. E. McGreer and W. S. Wu, *Canad. J. Chem.*, 1967, **45**, 461, and references therein.

<sup>6</sup> R. Fusco, "The Chemistry of Heterocyclic Compounds; Pyrazole, Pyrazolines, Pyrazolidines, Indazoles, and Condensed Rings", ed. A. Weissberger, Interscience, New York, 1967, vol. 22, p. 4.

<sup>7</sup> H. Kwart and K. King, *Chem. Rev.*, 1963, **63**, 415, and references therein.

<sup>8</sup> W. C. Herndon, C. R. Grayson, and J. M. Manion, *J. Org. Chem.*, 1967, **32**, 526.

<sup>9</sup> J. Sauer, *Angew. Chem. Internat. Edn.*, 1966, **5**, 211; C. G. Overberger, J. P. Anselme, and J. G. Lombardino, "Organic Compounds with Nitrogen–Nitrogen Bonds", Ronald Press, New York, 1966.