Thermolysis of Azo-compounds: a Reactivity Factor of 10^{17}

By EVAN L. ALLRED* and JERALD C. HINSHAW
(*Department of Chemistry, University of Utah, Salt Lake City, Utah* 84112)

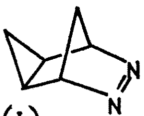
Summary Incorporation of cyclopropyl and cyclobutyl groups in the 2,3-diazabicyclo[2,2,2]oct-2-ene system has been found to increase the thermoloysis rates by factors of *ca.* 10^{17} and 10^{5}, respectively.

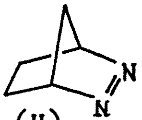
RECENT investigations indicate that certain simple cyclic azo-compounds decompose thermally by mechanisms other than radical processes.[1–4] As a case in point, (I) is 10^{11} times more reactive than (II) and gives cyclohexa-1,4-diene which involves synchronous loss of nitrogen and carbon–carbon double-bond formation.[2] We now report a comparison of the thermolyses of compounds (III)—(V).

Hydrolysis–decarboxylation with hot potassium hydroxide in methanol–water converted (VI)[5,6] into a hydrazine, which was oxidized readily with yellow mercuric oxide to (IV) (m.p. 143—144°).† Azo-compound (V)[3] was prepared from (VII)[5] by an analogous procedure. The intermediate hydrazine was oxidized with cupric chloride. For stability reasons (V) was handled as its cuprous chloride complex.

Thermolysis of (IV) in the gas phase at 150° produced a quantitative yield (>98%) of cyclo-octa-1,5-diene (determined by g.l.c.). Azo-compound (V) was liberated by dissolving the cuprous chloride complex in pyridine. Decomposition of (V) in this solvent at 25° gave quantitative yields (>98%) of both cyclohepta-1,4-diene and nitrogen.

The first-order rate constants for thermolysis of (IV) in the gas phase were measured by following the disappearance of the u.v. –N=N– absorption [λ_{max} (iso-octane) 382 nm].[7] The thermolysis of (V) is so much faster than that of (III) that its kinetics of decomposition were measured in pyridine at low temperature. Rates were determined at five temperatures between $-3{\cdot}5$ and $+12°$. This was accomplished by periodic n.m.r. integration of the developing τ 8·15 and 8·76 signals of cyclohepta-1,4-diene


(I)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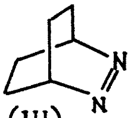
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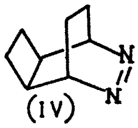
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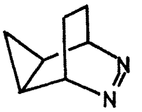
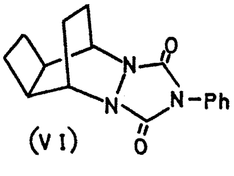

(V)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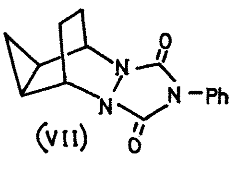
(VII)

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† Azo-compound (IV) and the cuprous chloride complex of (V) have satisfactory elemental analyses and appropriate spectral properties.

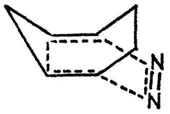
TABLE

Compound	Temp.	10^4k (sec.$^{-1}$)	E_a (kcal./mole)	$\Delta S^{\ddagger}$ (eu)	Relative rate
(V)	$-3·5°$	1·71[a]	14·9 ± 1·5	-21[b]	$1·1 \times 10^{17}$
	$+12·0°$	8·56[a]			
(IV)	$+150·2°$	0·362	39·2 ± 0·3	$+11$[b]	
	$+175·3°$	4·92			
	$-3·5°$				$6·7 \times 10^{4}$[c]
(III)[d]	$+240·0°$	212	44·6 ± 0·2	$+10·5$	
	$-3·5°$				1·0[c]

[a] Calculated from 25—30 n.m.r. integrations covering the range 0—80% reaction. [b] Average value over the temperature range for kinetics. [c] Estimation based on gas-phase results and extrapolation to $-3·5°$. [d] From other reported data.[7]

against the protons of methanol as an internal standard.[2] Some results are given in the Table.

Comparison of reactivity between (III), (IV), and (V) necessitates extrapolation of the kinetic data between gas-phase and liquid pyridine–cuprous chloride conditions. In this regard, a control experiment with (II) demonstrated that the decomposition rates of such azo-compounds are not appreciably greater in pyridine–cuprous chloride than in the gas phase. On this basis, (V) is more reactive than its bicyclic parent (III) by the astonishing factor of *ca.* 10^{17}. This represents one of the largest, if not the largest, reactivity enhancements yet exhibited by the cyclopropane group.[2,8] All the criteria, enormous reactivity, high product specificity, low E_a, and negative $\Delta S^{\ddagger}$ point uniquely to concerted nitrogen elimination and diene formation *via* transition state (VIII).[2][‡]



(VIII)

A significant rate increase and high product specificity suggest the possibility of participation by cyclobutyl bonding electrons in the thermolysis of (IV). However, these results do not unequivocally preclude a diradical decomposition pathway since diradical products such as the tricyclo[4,2,0,0^{2,5}]octanes and *cis*-1,2-divinylcyclobutane would be converted into cyclo-octa-1,5-diene under our reaction conditions.[9,10] High E_a and positive $\Delta S^{\ddagger}$ values support a diradical process.

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[‡] $\Delta S^{\ddagger}$ is -9 e.u. for thermolysis of azo-compound (I).

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