$_{\pi}2_s$].[13,14] Thus, the reactivity sequences of Table I offer indirectly via early and late transition states a highly valuable criterion for the presence or absence of concertedness.

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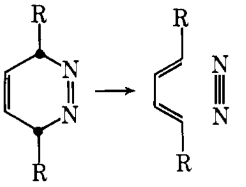
Received August 4, 1976

Concerted Cycloreversion in Solution: Medium Influence on Nitrogen Extrusion

Sir:

The thermal deazetation of azoalkanes **1** provides a striking contrast to the behavior of the saturated derivatives **2**. For the former, nitrogen extrusion is rapid, stereospecific, and product specific never leading to ring closure products. Berson and co-workers have suggested that these reactivity traits be adopted as basic criteria for concerted cycloreversion.[1]



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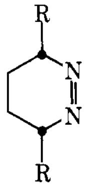


2

Replacement of the carbon-carbon double bond in **1** by an anti-fused cyclopropane ring as in **3** also leads to product specificity and enormous rate enhancements for N_2 loss (up to 10^{17}).[2,3] Unlike the unsaturated species cyclopropanated azoalkanes are stable enough to permit kinetic evaluation of the decomposition rates. The results have led Allred and colleagues to propose a fourth measure for concertedness, namely, a negative activation entropy.[2a,b] The four polycyclic derivatives on which the suggestion was based (**3–6**) have been associated with $\Delta S^{\ddagger}$ (25 °C) = −21, −13, −5, and −6 eu, respectively. A $\Delta S^{\ddagger} = -8$ eu has likewise been recorded for the benzo derivative **7**.[4] With few exceptions[5-10] other kinetic measurements on the decomposition of cyclic and acyclic azoalkanes yield positive $\Delta S^{\ddagger}$ values. For these reactions radicals are the generally accepted intermediates.[9,11]

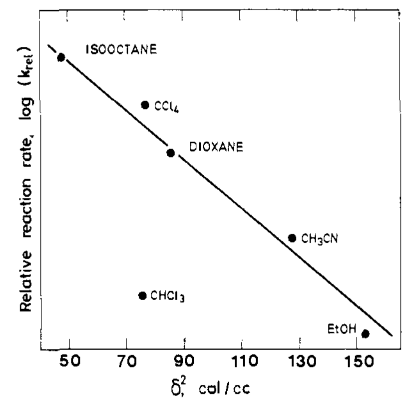
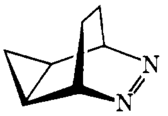


Figure 1. Log (k_{rel}) for the cycloreversion of azo **3** at 25 °C in various solvents plotted against the internal solvent pressure, δ^2.



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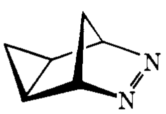

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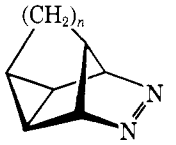
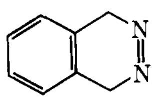


5, $n = 2$
6, $n = 3$



7

Negative and low positive activation entropies have been observed for the concerted, thermal decomposition of acyclic peresters and interpreted in terms of restricted internal rotations in the transition state.[12] A similar rationale for the rigid bicyclic azo structures is not easily constructed. We speculated that a possible clue to understanding the phenomenon might reside in the fact that $-\Delta S^{\ddagger}$'s have been reported *only* for azo decompositions in solution. Positive values are consistently found in the gas phase.[11] To test the effect of solvent on the behavior of a reasonably well-established cycloreversion as well as the source of the unusual activation parameters, we have reinvestigated the kinetics of compound **3** in media of widely differing polarity.

The substrate was isolated from its cuprous bromide complex and recrystallized from hexane below 0 °C (best mp 29.5–30.0°, lit.[13] 25–30 °C; NMR (−5 °C, $CDCl_3/Me_4Si$, 90 MHz) 5.47 (2 H, s, hw = 8.3 Hz), 1.58–0.42 ppm (8 H, m); uv, λ_{max}(isooctane) (ϵ_{min}) 366 (80), 377 nm (180)). Gradual

Table I. Relative Rates, Activation Parameters and Error Limits for the Cycloreversion of Cyclopropylazoalkane **3**[a]

Solvent	10^3k, s^{-1}	k_{rel}	$\Delta G^{\ddagger}$, kcal/mol	E_a, kcal/mol[b]	ln A	$\Delta S^{\ddagger}$, eu[b]	Confidence limits for $\Delta S^{\ddagger}$[c] 95%	99%
Isooctane	8.5	14.9	20.3	22.1 ± 0.4	32.5	4.1 ± 1.1	±3.0	±4.2
CCl_4	4.5	7.9	20.7	22.6 ± 0.2	32.8	4.7 ± 0.8	±2.5	± 3.7
Dioxane	3.1	5.4	20.9	22.9 ± 0.3	32.9	4.9 ± 0.7	±2.1	±3.0
Pyridine	2.4	4.2	21.0	24.3 ± 0.4	34.9	8.9 ± 1.3	±3.2	±4.6
CH_3CN	1.4	2.4	21.4	23.0 ± 0.2	32.3	3.6 ± 0.5	±1.4	±2.1
$CHCl_3$	0.94	1.6	21.6	24.1 ± 0.3	33.6	6.3 ± 0.9	±2.0	±3.0
EtOH (96%)	0.57	1.0	21.9	23.5 ± 0.1	32.2	3.4 ± 0.8	±0.8	±1.2

[a] At 25 °C. [b] Error limits represent the standard deviation from the least-squares line. [c] Cf. E. S. Swinbourne, "Analysis of Kinetic Data", Thomas Nelson and Sons Ltd., London, 1971, pp 40–43.

warming of solutions of **3** to room temperature leads to quantitative formation of 1,4-cycloheptadiene as previously documented.[2a,13] The fragmentation rates in several solvents at five temperatures were monitored by following the decrease in the uv absorption band at 366 nm.[14] Each run was performed at least in duplicate, followed to two-three half-lives and evidenced a clean first-order process. The average correlation coefficient for over 90 rate constant plots is 0.9993. Activation parameters and error limits are presented in Table I.

In all solvents a positive $\Delta S^{\ddagger}$ is observed. Consideration of the lower limit of the standard deviation, a measure of precision, is insufficient to change the sign of the activation entropy in any given case. Application of the much more stringent confidence limit criterion, a measure of accuracy, leads to a zero or a positive $\Delta S^{\ddagger}$ even at the 99% level. While $\Delta S^{\ddagger}$ is in fact a sum of changes in the degrees of freedom for substrate, the substrate-solvent complex, and the solvent itself,[15] it appears that the positive experimental values reflect simple intuitive expectations for a fragmentation process of the type posited for compounds **3–7**. Consequently we conclude that no distinction between a concerted or a radical pathway in the extrusion of nitrogen can be made from the sign of the entropy of activation. Once a pericyclic mechanism has been determined by other means, however, entropy differences may be useful for a more detailed analysis of the reaction. As a case in point, $\Delta S^{\ddagger}$ for the concerted expulsion of N_2O from azo *N*-oxides corresponding to **1** ranges from −5 to +6 eu.[16] A viable interpretation is possible only by taking substrate-solvent interactions into account.[16,17]

The previous kinetic investigation of the cyclopropyl azoalkane **3** was conducted upon a solution of its cuprous chloride complex in pyridine and led to E_a = 14.9 kcal/mol and $\Delta S^{\ddagger}$ = −21 eu (ca. +5 °C).[2a] In the same solvent we find E_a = 24.3 kcal/mol and $\Delta S^{\ddagger}$ = +9.0 eu (+5.0 °C). The very great differences are possibly due to the presence of CuCl in the reaction medium. Solutions of the copper salt in pyridine are unfortunately highly absorbing and prevent kinetic evaluation by uv. Alternatively the negative $\Delta S^{\ddagger}$ values for **3–6** may be a consequence of the inaccuracies inherent in the previous method of measurement (NMR). In spite of the divergence of the activation parameters, rate constants in pyridine at 25 °C differ only by a factor of 2. Thus the conclusions of Allred, Hinshaw, and Johnson[2a,b] regarding the rate enhancement effect of the cyclopropyl moiety are preserved.

Although solvent studies alone are not sufficient to distinguish radical from concerted processes, they provide important supplementary information. The decomposition of **3** to cycloheptatriene and nitrogen is an electroneutral reaction and consequently its course can be influenced by solvation and internal volume effects.[18] Ordinarily the rates of formation of radicals are insensitive to medium composition. However, solvation is detectable by observation of a compensating spread in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.[19,20] The near constancy of these values for **3** (Table I) suggests the absence of an activated complex leading to a biradical, provided that steric hindrance to solvation is absent.[21] Under these conditions regular solution theory suggests that internal volume effects arising from the internal pressure of the solvent should be manifest.[18,22] A plot of δ^2 (= P_{internal}) vs. log k (Figure 1) for **3** reveals the fact that the rate of deazetation decreases with increasing solvent polarity and P_{internal}. An inverse solvent dependence of the same order of magnitude is evident for the bimolecular reverse, the Diels–Alder reaction.[23,24]

The internal pressure of the solvent is a measure of its resistance to disruption and its ability to restrict the motion of solute molecules. The fragmentation of cyclopropyl azoalkane **3** via a cycloreversion mechanism is thus predicted to be slowest in the solvent with the greatest P_{internal} (EtOH), whereas the opposite ought to obtain for cycloaddition as is observed. Further support for a continuity of mechanisms in these cases resides in the finding that the irregular solvent induced variation of the activation parameters (Table I) resembles that for the cycloaddition of cyclopentadiene to itself.[23a] The solvent effects for **3** are consequently in agreement with mechanistic arguments derived from relative rate enhancements. Furthermore they suggest that rate studies of electroneutral reactions in different media and perhaps as a function of pressure[24,25] should aid in the discrimination of radical, concerted, and concerted-radical[6,26] reactions.

Acknowledgment. We are grateful to the NATO Research Grants Program for partial funding of the work and to Henrik Olsen (University of Copenhagen) for stimulating discussion.

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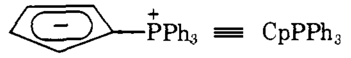
The Synthesis and Structure of Mercuric Halide Complexes of Triphenylphosphonium Cyclopentadienylide. The First X-ray Structure of a Mercury Cyclopentadienyl

Sir:

We wish to report the synthesis and characterization of the initial examples of a new class of metallocenes, the cationic metal halide complexes of triphenylphosphinium cyclopentadienylide, I.



$\equiv$ CpPPh$_3$

I

Stirring 0.2401 g (0.736 mmol) of CpPPh$_3$ with 0.3360 g (0.738 mmol) of mercuric iodide in 50 ml of dry, deoxygenated (N$_2$) tetrahydrofuran (THF) at room temperature resulted in the formation of a dark yellow precipitate after a few minutes. Upon filtration 0.3155 g (55%) of the 1:1 adduct, CpPPh$_3$HgI$_2$, mp 191-192 °C dec, was obtained. More of the product could be precipitated by addition of petroleum ether (60-90 °C), but it was of slightly lesser quality. The complex has been air-stable at room temperature for more than a year. Anal. Calcd for C$_{23}$H$_{19}$HgI$_2$P: C, 35.35; H, 2.46; Hg, 25.69; I, 32.51; P, 3.97. Found: C, 35.46; H, 2.61; Hg, 25.38; I, 32.27; P, 2.96. NMR (CDCl$_3$) 6.33-6.72 (m, 4 H, Cp), 7.48-4.98 (bs, 15 H, phenyl); IR (KBr) 1350, 1110, 1080, 1008, 837, 805, 760, 700, 555, 537, 520; λ_{max} (THF) 2400 (17 200), 2500 (19:200), 2640 sh (13 300), 2890 (4000).

By identical procedure the mercury(II) bromide (mp 188-189 °C dec) and chloride (mp 183-184 °C dec) complexes were prepared. Both display long-term stability in the solid form.

The nature of the metal-cyclopentadienyl interaction in complexes of CpHgX (X = Cl, Br, and Cp) has been a subject of debate for nearly 2 decades; both fluxional σ-bonding and π-bonding have been argued.[1] Evidence clearly favors the former view,[2] but the most direct probe, namely, x-ray diffraction, has been frustrated by the inability to grow light-stable single crystals. This has now been accomplished for the mercuric iodide complex of I.

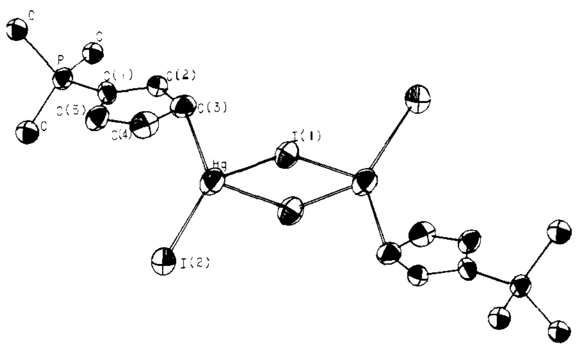


Figure 1. ORTEP of [(C$_6$H$_5$)$_3$PC$_5$H$_4$HgI$_2$]$_2$.

Table I. ^{13}C NMR Chemical Shift Data for Mercury(II)-Ylide Complexes

Compound	Solvent	Cyclopentadienyl chemical shifts (ppm)^a		
		C(1)	C(2),C(5)	C(3),C(4)
CpPPh$_3$	CDCl$_3$	127	116.9	114.3
CpPPh$_3$HgI$_2$	CDCl$_3$	—	121.5	111.9
CpPPh$_3$HgCl$_2$	Me$_2$SO-d_6	—	123.5	110.8

^{a} Center of the ^{31}P-^{13}C splitting pattern (C-H decoupled).

Automated x-ray diffractometer single-crystal measurements were made of 4052 independent reflections of a yellow crystal of [(C$_6$H$_5$)$_3$PC$_5$H$_4$HgI$_2$]$_2$: triclinic, $P\bar{1}$, a = 10.786 (2) Å, b = 11.412 (2) Å, c = 11.016 (2) Å, α = 116.01 (2)°, β = 104.93 (2)°, γ = 92.60 (2)°, Z = 1. Full-matrix least-squares refinement of a model with 154 parameters (Hg, I, P. and C atoms of the cyclopentadiene ring anisotropic) gave R_1 = 0.060, R_2 = 0.052. A drawing of the structure (neglecting the phenyl groups) is shown in Figure 1. The compound exists as a dimer bridged by two iodine atoms, Hg-I (1) distances 2.982 (1) and 2.937 (1) Å, external Hg-I (2) distance 2.681 (1) Å. The phosphorus atom is attached to the cyclopentadiene ring at C(1), (P-C(1), 1.748 (7) Å, C(1) has triangular planar coordination) and the Hg atom is attached at C(3) (Hg-C(3), 2.292 (8) Å, C(3) has tetrahedral coordination). The cyclopentadiene ring distances, C(1)-C(2), 1.375 (10), C(2)-C(3), 1.429 (10), C(3)-C(4), 1.432 (12), C(4)-C(5), 1.367 (11), C(5)-C(1), 1.467 (10) Å, imply double bonds localized at C(1)-C(2) and C(4)-C(5). The bond angles about C(1) (125.2 (6)°, 125.5 (6)°, 109.0 (6)°, sum = 359.7°) are very similar to those found for the triphenylphosphonium cyclopentadienylide ylide.[3] The P-C distance is longer in the mercury substituted ylide (1.748 (7) vs. 1.718 (3)), but the double bond distances in the ring, though nominally shorter (1.375 (10) and 1.367 (11) vs. 1.392 (4) and 1.376 (4) Å for the CpPPh$_3$ ylide), are not significantly different. The coordination about the Hg atom is essentially tetrahedral, with the main distortions being the bridging iodine angles (I(1)-Hg-I(1′), 93.76 (2)°) and angle involving the Cp group (C(3)-Hg-I(2), 131.5 (2)°).

Attachment of the mercury at the 3-position is somewhat of a surprise because C(1) is actually the position of greatest electron density,[4] and C(2) is the position of bonding suggested by superdelocalizabilities (S$_E$), localization energies (L$_r$), and the free valences (F$_r$) of the reaction intermediate in electron transfer theory.[4] In agreement with these reaction indices, electrophiles and even Diels-Alder dienophiles result in substitution at the 2-position. There are no previous examples of reaction at C(3). A possible explanation lies in the steric interaction between the bulky triphenylphosphonium group and the metal halide.[5]

The ^{13}C NMR spectra reveal much about the structure of the mercury complexes in solution (Table I). The mercury is bound to the cyclopentadienyl site and not the phenyls; this is evidenced by the greater chemical shifts (upfield and downfield) of the cyclopentadienyl carbons compared to the phenyl carbons, and the broadening and diminution of the cyclopentadienyl signals. The C(1) absorption of the mercury complexes apparently falls in the phenyl region as all attempts to locate it have been unsuccessful. It is clear that in solution mercury does not remain limited in its attachment to C(3); the fact that both C(2) (and C(5)) and C(3) (and C(4)) are nearly