ratio is very insensitive to changes of solvent or temperature, the spread of the values for a given structure being confined within about a factor of 2 in most cases. As the structure of the substrate is varied, the selectivity values fluctuate more markedly. Beyond the not surprising observation that R_1 migration in solvolysis becomes relatively more favorable as the ring system gets larger and hence more tolerant of the trigonal center so produced, a detailed rationalization of these responses to structural changes at present would be mere speculation. However, the major effect emerges in a comparison of the deaminative and solvolytic reactions, where in a given structure deamination invariably produces an increase in the preference for ring expansion. In some cases, the effect amounts to a factor of as much as 100 or more in the selectivity ratio.

In our opinion, the experimental finding that deamination increases selectivity in the present cases and decreases it in the previous examples[2] involves no contradiction. The apparent paradox is resolved by (and therefore serves to validate) the hypothesis of ground-state conformational control proposed by Cram and McCarty.[6]

The "normal" very large preference for phenyl over methyl migration in solvolytic rearrangements of 3-phenyl-2-butylarenesulfonates is much diminished or even reversed in the corresponding deaminations.[6] Since the energies of the transition states for deaminatively induced rearrangement probably do not lie far above the barriers for internal rotation, the choice of a migrating group depends strongly on the distribution of conformations in the diazonium ion ground state. In the 3-phenyl-2-butyl system, where ground-state conformations appropriate to migration of either methyl or phenyl do not differ greatly in energy, the effect is to counteract whatever factors cause the "normal" migratory superiority of phenyl over methyl.[6]

In the present cases, the strongly preferred ground-state conformations are those in which the leaving group is as far as possible from the bulky bicyclic ring system. Unless the "normal" migratory aptitude ratio in solvolytic reactions is already overwhelmingly favorable to ring-member migration (a circumstance neither expected theoretically nor observed experimentally), the large ground-state conformational preference will result in an enhanced relative importance of ring-member migration in deamination, the effect observed here.

---

[6] D. J. Cram and J. E. McCarty, *J. Amer. Chem. Soc.*, **79**, 2866 (1957).

[7] This investigation was supported in part by predoctoral fellowships of the National Institute of General Medical Sciences. The dates and identifying numbers are given in ref 8.

[8] (a) 1965–1966, National Science Foundation Trainee, 1966–1969, No. 5 FO1 GM33291-03; (b) 1967–1970, No. 7 FO1 GM37475-O3.

[9] National Science Foundation Graduate Fellow, 1966–1969.

[10] Dow Chemical Company Fellow, 1964–1966.

* Address correspondence to this author at Yale University.

Jerome A. Berson,* James W. Foley,[7,8a] J. Michael McKenna[9]
Helmut Junge, Dennis S. Donald, Richard T. Luibrand[7,8b]
Nitya G. Kundu, William J. Libbey, Mohindar Singh Poonian
Joseph J. Gajewski,[10] John B. E. Allen

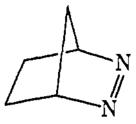
Department of Chemistry, Yale University
New Haven, Connecticut 06520
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received August 4, 1970

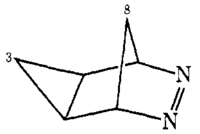
The Influence of Geometry on Cyclopropyl Participation in the Thermolysis of Azo Compounds

Sir:

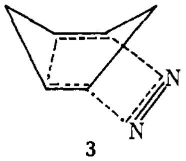
Recent work in this laboratory[1] has shown that azo compound **2** thermally decomposes faster than **1** by the enormous factor of 10^{11}. All criteria for the mechanism of the decomposition of **2** point uniquely to synchronous loss of nitrogen and diene formation *via* transition state **3**.[1] This has prompted our investigation of the factors responsible for the extraordinarily accelerated rate of decomposition. We now report a study of azo compounds **4**, **5**, and **6**.



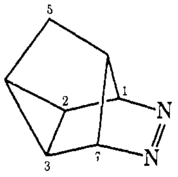
1



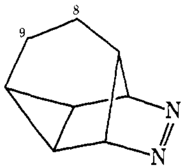
2



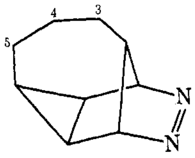
3



4

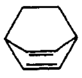


5

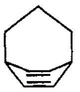


6

7



8



9

Syntheses of **5** and **6** were accomplished by a variation of the published method used for **4**.[2] Reaction of 4-phenyl-1,2,4-triazoline-3,5-dione[3] with dienes **8**[4,5] and **9**[6,7] gave the expected 1:1 homo Diels–Alder adducts,[8,9] mp 210–210.5° and 169–169.5°, respectively. Hydrolysis–decarboxylation with hot potassium hydroxide in methanol–water converted the adducts to hydrazines. Oxidation of the latter with cupric chloride gave the cuprous chloride complexes of **5** and **6**. The azo compounds were liberated by treatment of the complexes with aqueous ammonia at −20°. They were extracted into cold $CDCl_3$.

Thermolysis of **5** in $CDCl_3$ at 50° gave **8** (gpc and nmr analyses) and nitrogen as products. Similarly, **6** in $CDCl_3$ decomposed at 25° to **9** and nitrogen. In accord with a previous report,[2] thermolysis of **4** in the

---

[1] E. L. Allred, J. C. Hinshaw, and A. L. Johnson, *J. Amer. Chem. Soc.*, **91**, 3382 (1969).

[2] R. M. Moriarty, *J. Org. Chem.*, **28**, 2385 (1963).

[3] J. C. Stickler and W. H. Pirkle, *ibid.*, **31**, 3444 (1966).

[4] Diene **8** was prepared from bicyclo[2.2.2]oct-5-en-2-one (P. K. Freeman, D. M. Balls, and D. J. Brown, *ibid.*, **33**, 2211 (1968)) by treatment of the tosylhydrazone with methyllithium (R. H. Shapiro and M. J. Heath, *J. Amer. Chem. Soc.*, **89**, 5734 (1967)).

[5] K. Tori, Y. Takano, and K. Kitahonoki, *Chem. Ber.*, **97**, 2798 (1964).

[6] Diene **9** was prepared by oxidation of *trans*-bicyclo[3.2.2]non-8-ene-6,7-dicarboxylic acid (K. Alder and H. H. Mölls, *ibid.*, **89**, 1960 (1956)) with lead tetraacetate.

[7] A. J. Baker, A. M. Chalmers, W. W. Flood, D. D. MacNicol, A. B. Penrose, and R. A. Raphael, *Chem. Commun.*, 166 (1970).

[8] The reactions were carried out at reflux temperatures in acetone for **8** and in dioxane for **9**.

[9] All isolated compounds gave satisfactory elemental analyses except for the cuprous chloride complex of **6**. Thus far, we have been unable to prepare a pure sample of the latter. All compounds, including **5** and **6**, gave spectral data in accord with their assigned structures.

Table I. Thermolysis Rate Data for Some Azo Compounds

Compd	Temp, °C	10^4k, sec^{-1}	E_a, kcal/mol	$\Delta S^{\ddagger}$, eu	Rel rate
1[a]	+180.8	8.35	37.3 ± 0.3	+8.7	
	−3.5				1[c]
2[b]	−3.5	1.04[d]	17.7 ± 1.6[e]	−13[f]	2.2×10^{11}
4	+150.0	2.33	36.5 ± 0.3	+8.3	
	−3.5	4.34×10^{-11} [c]			9.2[c]
5[b]	+50.0	3.31	23.3 ± 0.4[e]	−5[f]	
	−3.5	2.46×10^{-3} [g]			5.2×10^{8}
6[b]	−3.5	0.90[d]	19.6 ± 0.9[e]	−6[f]	1.9×10^{11}

[a] From other reported data.[11] [b] In $CDCl_3$. [c] Estimation based on gas-phase results and extrapolation to −3.5°. [d] Taken from the Arrhenius plot of the kinetics covering the temperature range from +10 to −5°. [e] Calculated from 15–20 nmr measurements covering the range 0 to *ca.* 80% reaction. [f] Average values over the temperature range for kinetics. [g] Extrapolated to −3.5° from the data at higher temperatures.

gas phase at 150° gave **7**; no formation of quadricyclene was observed.[10]

First-order rate constants for the thermolysis of **4** in the gas phase at 121–150° were measured by following the disappearance of a uv -N=N- absorption [λ(isooctane) 338 nm].[11] The thermolyses of **5** and **6** are so much faster than that of **4** that their kinetics of decomposition were measured in the liquid phase in $CDCl_3$ at lower temperatures. Rates were determined at five temperatures between +50 and +33° for **5** and +9 and −5° for **6**. This was accomplished by periodic nmr measurement of the developing vinyl proton signals of the diene product against the vinyl protons of 2,5-dimethylfuran internal standard. Some results are summarized in Table I.

Comparison of reactivity between **1**, **4** and **2**, **5**, **6** necessitates extrapolation of the kinetic data between gas- and liquid-phase conditions. Control experiments with **1** have demonstrated that the decomposition rates of such azo compounds are not appreciably greater in the liquid phase than in the gas phase. On this basis, **4** is 10^7–10^{10} times less reactive than structurally similar **5**, **6**, and **2**. All of the criteria, enormous differences in reactivity, E_a, and $\Delta S^{\ddagger}$, suggest different decomposition mechanisms. The striking match in reactivity, E_a, and $\Delta S^{\ddagger}$ for **1** and **4** points to decomposition of **4** *via* a diradical pathway.[1,11–14] A similarity in reactivity, E_a, and $\Delta S^{\ddagger}$ for **2**, **5**, and **6** indicates that **5** and **6** decompose by concerted processes[1,15–17] involving transition states like **3**.[18]

Of the possible rationalizations for the remarkable differences in the decomposition of **4** and **5**, **6** the explanation which we prefer is that based on differences in strain in the transition states. Thus, if **4** were to follow a concerted pathway, the one-carbon bridge C_5 would cause severe strain in the transition state as C_1, C_2, C_3, and C_7 rehybridize to give diene **7**. This effect is eased substantially by the two-carbon bridge C_8C_9 in **5**. The constraint is reduced further in **6** by the three-carbon bridge $C_3C_4C_5$.[19] An additional factor which may be of relevance here is the difference in the orientation of the cyclopropyl ring. For **5** and **6** the cyclopropyl orbitals are more favorably oriented for overlap as the C–N bonds break. In both regards, molecular models show that the angle situation has become similar for **6** and **2**.

Earlier it was suggested that relief of steric interaction between C_3 and C_8 hydrogens may make a contribution to the 10^{11} rate enhancement found with **2**.[1] However, since **2** and **6** have the same reactivity such a factor contributes little, if anything, to the reactivity of **2**. The low reactivity of **4** compared to **2** indicates that relief of strain involved in opening of the cyclopropyl ring is not a major factor. The indications are that the exceptional acceleration is electronic in origin.

Acknowledgment. We express appreciation to the National Science Foundation for support of this work with Grant No. GP-9478. Special thanks are due Dr. J. C. Hinshaw for helpful discussion and for providing us with compound **2**.

---

(10) Control experiments showed that quadricyclene would have survived the experimental conditions and could have been detected if it had been formed to an appreciable extent.

(11) S. G. Cohen, R. Zand, and C. Steel, *J. Amer. Chem. Soc.*, **83**, 2895 (1961).

(12) E. L. Allred and R. L. Smith, *ibid.*, **91**, 6766 (1969).

(13) M. P. Schneider and R. J. Crawford, *Can. J. Chem.*, **48**, 628 (1970); R. J. Crawford and A. Mishra, *J. Amer. Chem. Soc.*, **88**, 3963 (1966), and other papers in the series.

(14) W. R. Roth and M. Martin, *Justus Liebigs Ann. Chem.*, **702**, 1 (1967); W. R. Roth and M. Martin, *Tetrahedron Lett.*, 4695 (1967).

(15) E. L. Allred and J. C. Hinshaw, *Chem. Commun.*, 1021 (1969).

(16) J. A. Berson and S. S. Olin, *J. Amer. Chem. Soc.*, **91**, 777 (1969).

(17) M. Martin and W. R. Roth, *Chem. Ber.*, **102**, 811 (1969).

(18) The negative $\Delta S^{\ddagger}$ values are quite surprising for dissociative transition states like **3**. While we have no rationale for this observation at present, we find it most intriguing.

(19) Although the differences in strain for the dienes have not been reported, inspection of models indicates the order of decreasing strain is **7** > **8** > **9**.

Evan L. Allred,* Albert L. Johnson
Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

Received November 9, 1970

Asymmetric Homogeneous Hydrogenation with Rhodium(I) Complexes of Chiral Phosphines

Sir:

There has been recent interest in asymmetric hydrogenations catalyzed by soluble rhodium catalysts of the Wilkinson type.[1–4] For example, asymmetric hydrogenation of α-phenylacrylic acid was accomplished

---

(1) (a) W. S. Knowles and M. J. Sabacky, *Chem. Commun.*, 1445 (1968). Correcting for the optical purity of the phosphine (69%), the asymmetric synthesis of hydratropic acid was 22%. (b) See also *Chem. Eng. News*, **48**, 41 (July 11, 1970), where it is reported that 28% asymmetric synthesis has now been achieved.

(2) L. Horner, H. Siegel, and H. Buthe, *Angew. Chem.*, **80**, 1034 (1968); *Angew. Chem., Int. Ed. Engl.*, 7, 942 (1968).

(3) J. D. Morrison, "13th Annual Report on Research," Petroleum Research Fund, American Chemical Society, Washington, D. C., 1968, p 223.

(4) J. D. Morrison and R. E. Burnett, Abstracts of Papers, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, No. ORGN 85.