

6,2-hydride shift in norbornyl cation¹⁰ (overall $\Delta F^\ddagger = 5.9$ kcal/mol¹¹) can be combined with the data pertaining to eq 1 and 2 to give a monotonic curve that extrapolates to near-zero substituent effect at zero overall ΔF^\ddagger .

(10) J. A. Berson, R. G. Bergman, J. H. Hammons, and A. W. McRowe, *J. Amer. Chem. Soc.*, **89**, 2581 (1967).

(11) G. A. Olah and A. M. White, *ibid.*, **91**, 3957 (1969).

(12) The partial support of this work by National Institute of General Medical Sciences Predoctoral Fellowship No. 5 FO1 GM 33291 (1966-1969) and by an NSF Traineeship (1965-1966) is gratefully acknowledged.

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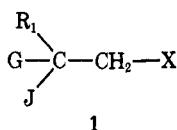
Received August 4, 1970

Deaminative and Solvolytic Ring Expansion. Relative Migratory Aptitudes of Ring Members and β Substituents¹

Sir:

The intermediates in carbonium ion processes usually distribute themselves among several competing reaction pathways with far less discrimination in nitrosative deaminations than in solvolytic reactions.² Although agreement has not been universal on the mechanistic details of deaminations, there seems to be general acceptance of the hypothesis that loss of molecular nitrogen is an exceptionally facile process. This compresses the energy scale for the hierarchy of possible reactions that follow upon (or accompany) it and hence damps out the selectivity.² We were startled therefore to find (in the course of other studies) a widespread apparent reversal of this behavior. The present paper documents a number of examples of selectivity which are much *greater* in deaminatively induced ring expansions than in the solvolytic counterparts.

The competing paths we use to examine selectivity are the migration of a β substituent (R_1) and the migration of a β ring member (G, J) in carbinyl derivatives of the general formula 1.³ The groups G and J



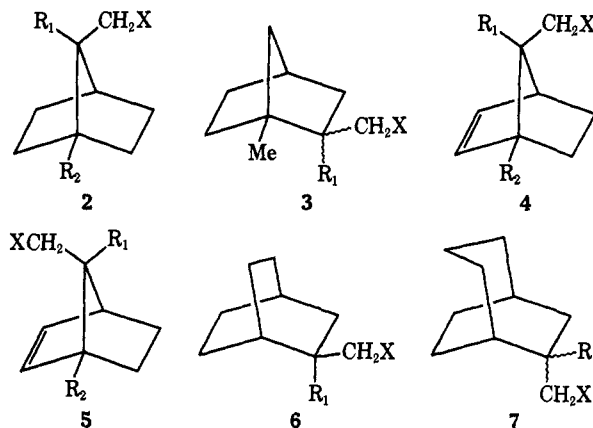
correspond to ring members of the series of bicyclic substrates 2-7.

(1) This work was supported in part by grants from the National Institute of Arthritis and Metabolic Diseases (AM-07505), the National Science Foundation (GP-6212X and GP-11017X), the Petroleum Research Fund (Type C grant), administered by the American Chemical Society, and the Wisconsin Alumni Research Foundation. An institutional grant to Yale University (GU-2730) is also gratefully acknowledged.

(2) For an excellent review with references to the extensive literature, see E. H. White in "The Chemistry of the Amino Group," S. Patai, Ed., Wiley, New York, N. Y., 1968, Chapter 8.

(3) In many cases, direct displacement of the leaving group X without rearrangement occurs in these systems, but since there is sometimes an appreciable bimolecular component in this type of reaction,⁴ we exclude it from consideration here.

(4) (a) J. A. Berson, M. S. Poonian, and W. J. Libbey, *J. Amer. Chem. Soc.*, **91**, 5567 (1969); (b) J. A. Berson, D. S. Donald, and W. J. Libbey, *ibid.*, **91**, 5580 (1969).



The selectivity (ring expansion/migration of the β substituent) is based upon the total amount of product of each type in each of the reactions. Some of the details of product characterization already have been reported^{4,5} and others will appear in forthcoming papers.

The data shown in Table I indicate that in the solvolytic reactions (X = OBs, ONs, or Br), the selectivity

Table I

Substrate	R_1	R_2	Medium	Selectivity (ring exp/ $\sim R_1$)	
				X = ONs ^a	X = NH ₂ ^b
2	H	H	HOAc	17 \pm 3 ^a	>200
			HCO ₂ H	23	
			Aq dioxane ^c	15	
2	CH ₃	H	HOAc	7.5	>200
			Aq HOAc	3	241 ^e
2	H	CH ₃	HOAc	3	
			HCO ₂ H	11	
			Aq dioxane ^c	2	
3	<i>exo</i> -H		Aq HOAc		325 ^e
			HOAc	7.9	
			Aq acetone ^d	3.3	
3	<i>endo</i> -H		Aq dioxane ^c	3.9	
			Aq HOAc		16
			HOAc	6.5	
3	<i>endo</i> -H		Aq acetone ^d	5.8	
			Aq dioxane ^c	5.1	
			Aq HOAc		7.5
4	H	H	HOAc	1.5	96 ^e
			HOAc		>200
			Aq HOAc		>200 ^e
5	H	H	HOAc, AgClO ₄	1 ^f	
			HOAc	18	29
			Aq HOAc		82
4	CH ₃	H	HOAc, AgClO ₄	2-4 ^{f,g}	
			HOAc	2.5	>200 ^e
			HOAc	40	59 ^e
4	H	CH ₃	HOAc	0.3	62 ^e
			HOAc	3.2	17 ^e
6	H		Aq dioxane ^c	0.5	7.5, ^h 7.5 ⁱ
7	<i>exo</i> -H		HOAc	0.17	
7	<i>endo</i> -H		HOAc	0.14	

^a In some cases, *p*-bromobenzenesulfonates were used. ^b Deamination with sodium nitrite in acetic acid or 9:1 H₂O-HOAc (v:v) unless otherwise indicated. ^c 60:40 dioxane-H₂O (v:v). ^d 75:25 acetone-H₂O (v:v). ^e X = NH₂Cl. ^f X = Br. ^g Ratio increases with temperature between 25 and 125°. ^h At 25° with a small amount of HOAc added. ⁱ At 100° with a small amount of HOAc added.

(5) J. A. Berson, J. J. Gajewski, and D. S. Donald, *ibid.*, **91**, 5550 (1969).

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 examples² 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.

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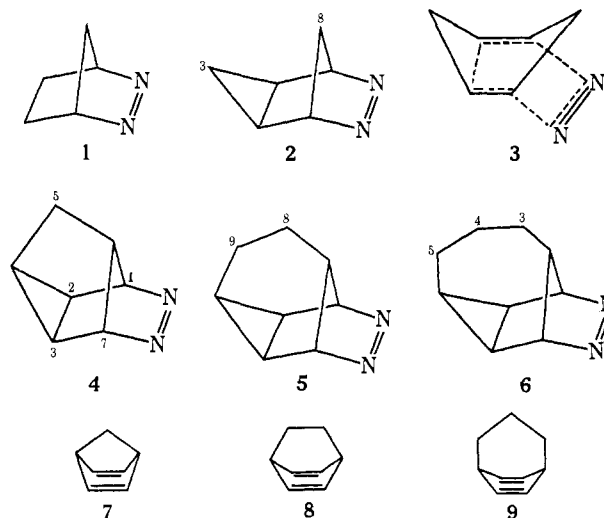
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Received August 4, 1970

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

Sir:

Recent work in this laboratory¹ 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**.



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-dione³ 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.