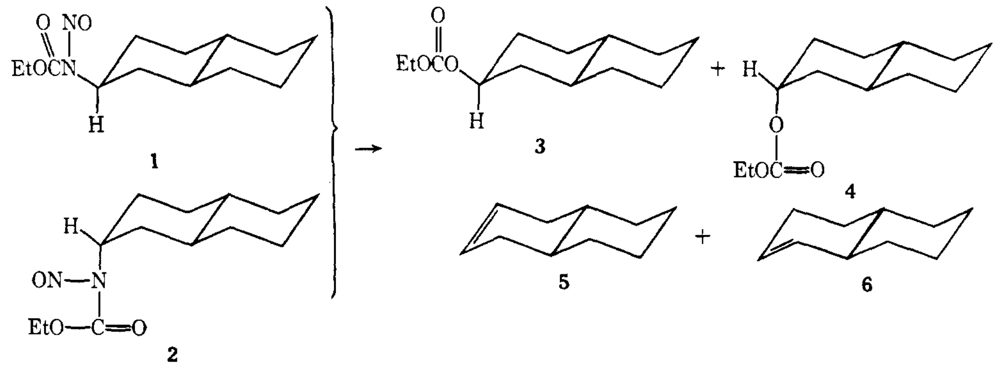
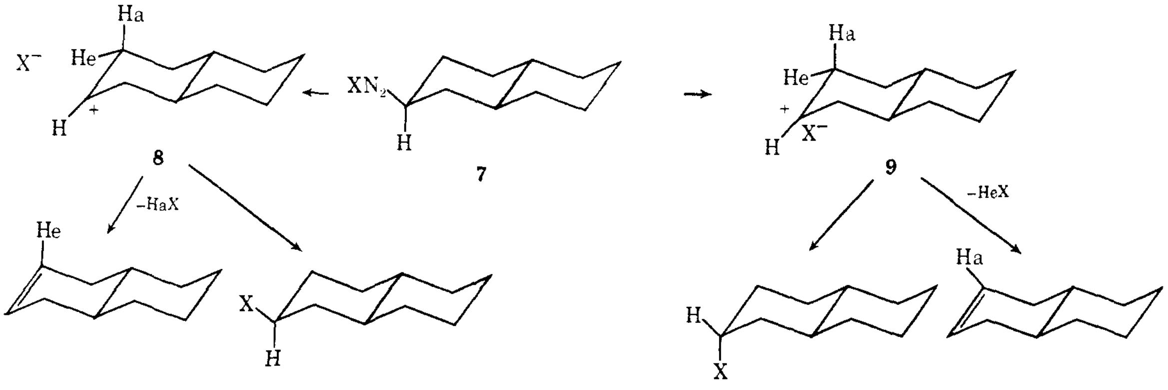
Relationship between Substitution and Elimination in *N*-Nitrosoamide Deaminations. An Application of Isotope Effects Manifested after the Rate-Determining Step[1]

Sir:

It has recently been reported that in the formation of 2-octalin (**5**) by β elimination in the decomposition of the *N*-nitrosocarbamates **1** and **2** derived from the epimeric *trans*-2-decalylamines the cis proton is lost predominantly.[2] We now report data which reveal a novel α elimination and which throw new light on the relationship of the substitution, elimination, and inversion processes in this system.





X = EtOCO$_2$

The α elimination was detected by the loss of deuterium in the olefinic products, but not in the substitution products, from the decomposition of the α-deuterio analogs of **1** and **2** (Table I, entries 2 and 6). This reaction presumably results from the rearrangement of a carbene-like intermediate which may arise by (a) formation of a diazoalkane by irreversible loss of the α proton of a diazonium ion followed by nitrogen loss or (b) loss of the carbinyl proton from a carbonium ion.[3] When the α elimination and some rearrangement by hydride transfer[4] (occurring only in the axial case **2**) are taken into account, approximately 84 and 94% of cis β elimination, respectively, occur in the unlabeled equatorial (**1**) and axial (**2**) epimers. A somewhat similar degree of stereoselectivity is exhibited in the ester-forming reaction (Table I), substantial retention of configuration being observed in both cases.[5]

Substitution of a cis-3 proton by a deuteron causes a decrease in the yield of 2-octalin (**5**), an increase in that of retained ester, and an unchanged yield of inverted ester (Table I);[6] replacement of a trans-3 proton, of which very little is lost during elimination, by a deuteron has a negligible effect. Such a distribution of isotope effects[7] indicates that cis-3 proton removal is competitive with formation of retained but not of inverted ester. It is clear that the act which determines whether inverted ester formation on the one hand or retained ester formation and cis elimination on the other will occur must precede the competition which determines which of the latter two processes will occur. This apparently precludes a concerted elimination from the diazotic ester by way of a quasi eight-membered ring transition state since a cis-3 deuterium isotope effect

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(1) Supported by Grants GP-22955 and GU-3184 from the National Science Foundation and AM 06419 from the National Institutes of Health.

(2) T. Cohen and A. R. Daniewski, *J. Amer. Chem. Soc.*, 91, 533 (1969).

(3) R. A. Olofson, S. W. Walinsky, J. P. Marino, and J. L. Jernow, *ibid.*, 90, 6554 (1968).

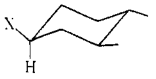
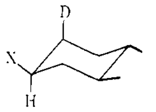
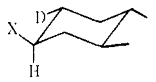
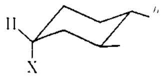
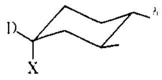
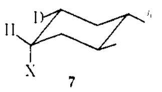
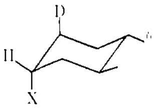
(4) A. D. C. Botelho, Ph.D. Thesis, University of Pittsburgh, 1970.

(5) E. H. White and F. W. Bachelor, *Tetrahedron Lett.*, 77 (1965).

(6) The significance of the yield changes upon deuteration is attested to by the fact that in the case of either nitrosoamide, every run using cis-deuterated material gave less 2-octalin and more retained ester than *any* of the runs using the corresponding undeuterated analog.

(7) Isotope effects in fast steps have been very informative in sorting out competitive and noncompetitive paths when hydrogen transfers are involved: T. Cohen, K. W. Smith, and M. D. Swerdloff, *J. Amer. Chem. Soc.*, 93, 4303 (1971); T. Cohen, C. H. McMullen, and K. Smith, *ibid.*, 90, 6866 (1968); J. M. McBride, *ibid.*, 93, 6302 (1971); T. J. Katz and S. A. Cerefice, *ibid.*, 91, 6519 (1969); T. Cohen and J. Z. Tarino, manuscript in preparation.

Table I. Decomposition of Labeled *N*-Nitrosocarbamates in Boiling Cyclohexane

Reactant[a]	No. of runs	Product composition (% D loss if determined[c]) 1-Octalin	2-Octalin	Axial ester	Equatorial ester
 1	6	19.1 ± 0.4	30.3 ± 0.4	19.2 ± 0.3	31.3 ± 0.3
 2	6	16.7 ± 0.7 (14)	26.6 ± 1.1 (24)	21.9 ± 0.6 (0)	34.7 ± 1.3 (0)
 3	6	20.2 ± 0.4 (0)	27.0 ± 1.2 (70)	19.5 ± 0.5	33.3 ± 1.1
 4	3	20.3 ± 0.9 (0)	29.4 ± 1.2 (10)	19.5 ± 0.3	30.8 ± 1.3
 5	3	38.6 ± 0.2	37.5 ± 0.3	15.5 ± 0.2	3.2 ± 0.2
 6	3	37.3 ± 0.1 (4)	38.0 ± 0.5 (7)	16.3 ± 0.4 (0)	2.9 ± 0.1 (0)
 7	3	38.0 ± 0.4 (0)	35.5 ± 0.9 (77)	17.4 ± 0.9	3.4 ± 0.3
 8	3	36.8 ± 0.7 (0)	38.4 ± 0.7 (4.4)	16.2 ± 0.7	3.0 ± 0.4

[a] $X = N(NO)CO_2Et$. [b] In addition, the rearranged olefin, $\Delta^{1,9}$-octalin, was formed (5.3–5.7% of product) from the axial *N*-nitrosocarbamate. [c] Determined by combined glpc–mass spectrometry on the LKB-9000 at 15 eV.

would then lead to an increase in yield of both ester products.

The concept enunciated by White and Aufdermarsh[8,9] that the rotation of the carbonium ion which constitutes intramolecular inversion occurs as a recoil from the loss of nitrogen by the diazonium carboxylate appears particularly appealing for the explanation of our results. The loss of nitrogen (using the equatorial reactant as an example) from the diazonium carboxylate ion pair or its diazotic ester precursor 7[9] would lead to the retained ion pair **8** and an inverted ion pair **9**.[10] The former undergoes either cis elimination[2] or substitution to give retained ester. The inverted ion pair gives mainly substitution product and possibly a small quantity of olefin by overall trans elimination. A similar scheme would hold for the axial reactant.[10] The suggestion that the axial and equatorial diazonium ions decompose by substantially different mechanisms[11] is rendered doubtful by the striking similarity in their stereochemistry of elimination and in their isotope effect behavior.

Since cis elimination is directly competitive with retained ester formation, it is evident that any explanation of the greater elimination/substitution ratio for the axial reactant **2** than for the equatorial reactant **1** must take into account not only the relative ease of elimination but also that of substitution in the retained ion pairs. The controlling factor may well be the difficulty, due to steric compression, of the collapse of the retained ion pair from the axial reactant to form axial ester.

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(8) E. H. White and C. A. Aufdermarsh, *J. Amer. Chem. Soc.*, **83**, 1179 (1961).

(9) E. H. White and D. J. Woodcock, "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N. Y., 1968, p 440.

(10) There is no reason to expect that inverted ion pair **9** from the equatorial reactant would be identical in every way with the retained ion pair from axial reactant and *vice versa* and the results in Table I indicate that the two do indeed behave differently. In addition to a possible difference in the juxtaposition of the ions, the retained ion pairs may still include a nitrogen molecule.

(11) L. Friedman in "Carbonium Ions," Vol. II, G. A. Olah and P. von R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, Chapter 16.

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