

not at all as arbitrary as would be a unitary transformation in the closed-shell case. In heteronuclear molecules and complex ions, the valence-bond hypothesis is not of much use. The opinion that N orbitals and $2N$ electrons are needed for the covalent bonding in MX_N is, on the whole, an illusion.⁴⁹

It should be realized that the d-like or f-like character of the partly filled shell of transition group compounds does not depend on the approximate numerical validity of the electrostatic "ligand field" model which was so

(49) C. K. Jørgensen, *Struct. Bonding (Berlin)*, **6**, 94 (1969); *Chimia*, **25**, 109 (1971).

popular among chemists between 1952 and 1956. The important point here is that while energy levels are correctly classified by a distribution of symmetry types which is identical with that predicted by the "ligand field" model (a weak perturbation by V_{res} of eq 9), this model is otherwise inappropriate. In fact, the induction from the observed absorption spectra^{14,50} has allowed a consistent description of energy levels by careful selection of the relevant symmetry and including a definition of spectroscopic oxidation states⁴ based on the preponderant one-electron configuration point of view.

(50) C. K. Jørgensen, *Advan. Chem. Phys.*, **5**, 33 (1963).

Reactions of Primary Aliphatic Amines with Nitrous Acid¹

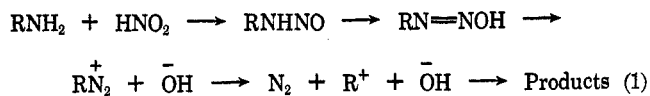
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Received September 8, 1970

Of all reactions which are presumed to go through carbonium ion intermediates, the decomposition of aliphatic diazonium ions is one of the most puzzling. A common method for carrying out the reaction is to treat primary² aliphatic amines with nitrous acid, the latter being generated *in situ* by the reaction between an organic or mineral acid and sodium or potassium nitrite. Although we shall avoid the term "deamination," since it is probably best employed to mean the replacement of an amino group with hydrogen, the term has been loosely applied not only to the amine-nitrous acid reaction but also to many other reactions³ which involve amino or substituted-amino groups.

In this Account I shall be concerned with the processes shown in eq 1. When the reactant is a primary



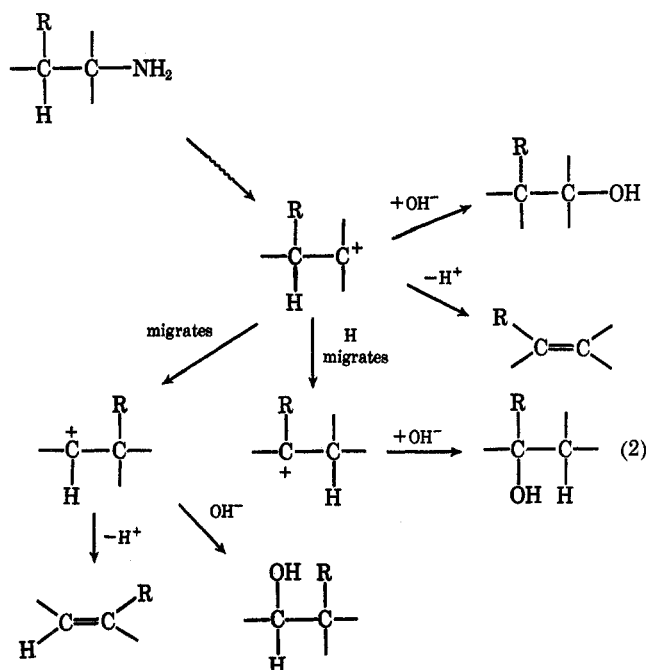
amine or amine hydrochloride, and the solvent is

(1) Work supported by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(2) The word primary here means monosubstituted ammonia, RNH_2 , and does not refer to the number of substituents on the carbon attached to nitrogen.

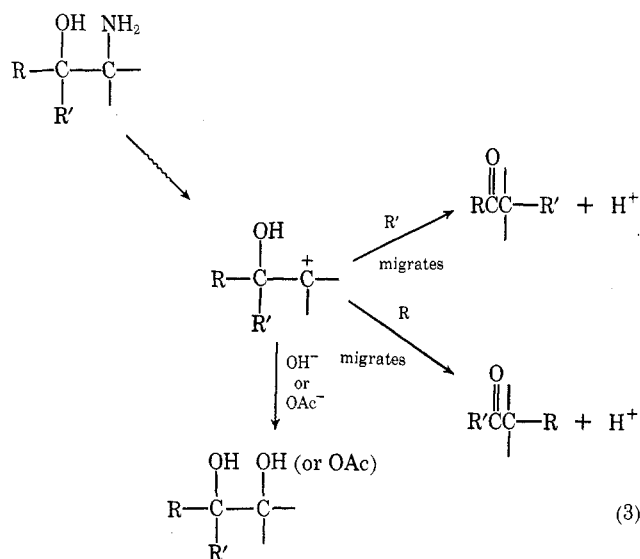
(3) See, for example, A. Nickon and A. S. Hill, *J. Amer. Chem. Soc.*, **86**, 1152 (1964); C. L. Bumgardner, K. J. Martin, and J. P. Freeman, *ibid.*, **85**, 97 (1963); G. A. Olah, N. Friedman, J. M. Bollinger, and J. Lukas, *ibid.*, **88**, 5328 (1966); R. A. Moss and S. M. Lane, *ibid.*, **89**, 5655 (1967); E. H. White, H. P. Tiwari, and M. J. Todd, *ibid.*, **90**, 4734 (1968); J. L. Bada and S. L. Miller, *ibid.*, **91**, 3946 (1969); W. Kirmse and G. Wächterhäuser, *Justus Liebig's Ann. Chem.*, **707**, 44 (1967); P. J. DeChristopher, J. P. Adamek, G. D. Lyon, J. J. Galante, H. E. Haffner, R. J. Boggio, and R. J. Baumgarten, *J. Amer. Chem. Soc.*, **91**, 2384 (1969); K. Ebisu, L. B. Batty, J. H. Higaki, and H. O. Larson, *ibid.*, **87**, 1399 (1965); T. Cohen and A. R. Daniewski, *ibid.*, **91**, 533 (1969); H. W. Heine, J. D. Meyers, and E. T. Pelzer, III, *Angew. Chem.*, **82**, 395 (1970); E. H. White, H. Maskill, D. J. Woodcock, and M. A. Schraeder, *Tetrahedron Lett.*, **21**, 1713 (1969); R. A. Moss and G. H. Temme, III, *ibid.*, 3219 (1968).

aqueous mineral acid, the carbonium ion formed on decomposition of the diazonium hydroxide can theoretically follow the pathways shown in eq 2, and the



products are carbinols and olefins. When (for example) acetic acid is used as the solvent, there is an exchange of acetate for hydroxyl ion, and much or all of the potential carbinol may be converted to ester. The use of a common ion (sodium acetate in acetic acid) assists the exchange.

When α -hydroxy amines are treated with sodium or potassium nitrite in aqueous mineral acid solution, or in organic acids such as acetic, the reaction can, in principle, proceed as shown in eq 3, and the product is



usually a ketone or mixture of ketones, although it is sometimes possible to isolate glycols or glycol acetates as well.

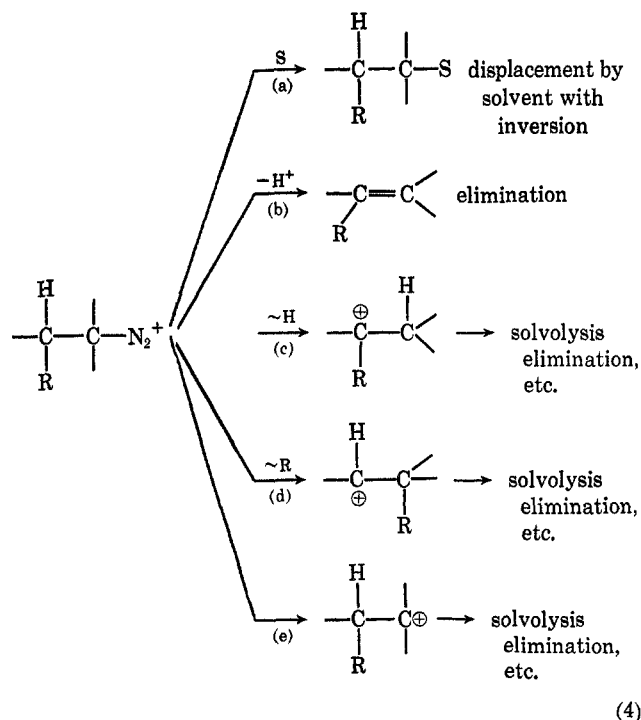
There is an excellent review of the literature through the first half of 1957 by Söll,⁴ and the experimental bases for eq 1 have been exhaustively reviewed by Ridd,⁵ who sums up the evidence that the rate-determining step of the reaction is formation, from nitrous acid, of the nitrosating agent (N_2O_3 , $NOCl$, etc.).

The most serious problem in understanding reaction 1 has been that the postulated carbonium ion intermediates do not behave the same as when they are generated in other ways. By comparison with related solvolytic reactions, the decomposition of aliphatic diazonium ions often yields additional products, some of which are unprecedented in solvolyses.⁶ In addition, the migratory aptitude⁷ of the *p*-tolyl group (for example) during solvolytic reactions is in the range 3–15, yet in the reaction of 2-phenyl-2-*p*-tolyl-1-ethyl-1-¹⁴C-amine⁸ with nitrous acid it is only 1.2. A similar situation exists for the migratory aptitude of the *p*-anisyl group, which can be as high as 500,⁷ yet in the action of nitrous acid on 1-*p*-anisyl-1-phenyl-2-aminoethanol it is only 1.6.^{8b}

An early attempt was made to explain these peculiarities in terms of "hot" carbonium ions⁹ of extremely

high energy which were therefore lacking in discrimination. Another theory which is also widely accepted was originally proposed by Huisgen,¹⁰ who suggested that in the decomposition of diazo esters there is a compression of the energy profile, relative to solvolyses, leading to smaller differences in the activation energies for the several processes which are possible.

In two widely quoted papers,^{11,12} Streitwieser expanded upon Huisgen's suggestion, proposing "that the diazonium ion rather than a carbonium ion is the branching point of the competing reactions." He combined the scheme shown in eq 4 with Huisgen's con-



cept of the transition-state energy profile¹⁰ to explain the multiplicity of products and the near-unity of migratory aptitudes. Thus solvent displacement (eq 4a), elimination (eq 4b), and solvolyses with hydride shift (eq 4c) or with alkyl or aryl shifts (eq 4d) all were postulated to take place with concurrent elimination of nitrogen, whereas reaction 4e was believed to produce a "normal" (contrasted with the "hot"⁹) carbonium ion. Streitwieser^{11,12} and Cram and McCarty¹³ agreed that processes 4c and 4d occur with *inversion* at the migration terminus and are more or less controlled by the ground-state conformations of the reactant amine or of the diazonium compound.

In spite of the long-standing interest^{4,5} in these reactions, the mechanism for the decomposition is therefore still not well understood. This is due, in part, to the special kinetic situation for which it has been cal-

(4) H. Söll in Houben-Weyl, "Methoden der Organische Chemie," E. Müller, Ed., Georg Thieme, Stuttgart XI/2, 1958, pp 133–181.

(5) J. H. Ridd, *Quart. Rev., Chem. Soc.*, **15**, 418 (1961).

(6) W. Hüchel and F. Nerdel, *Justus Liebig's Ann. Chem.*, **528**, 57 (1937); W. Hüchel and U. Ströle, *ibid.*, **585**, 182 (1954); W. Hüchel, *ibid.*, **533**, 1 (1938); W. Hüchel and K.-D. Thomas, *ibid.*, **645**, 177 (1961); W. Hüchel and G. Ude, *Chem. Ber.*, **94**, 1028 (1961); W. Hüchel and K. Heyder, *ibid.*, **96**, 220 (1963); H. Feltkamp, F. Koch, and T. N. Thanh, *Justus Liebig's Ann. Chem.*, **707**, 95 (1967); W. Kraus and P. Schmutte, *Chem. Ber.*, **99**, 2259 (1966); J. G. Traynham and M. T. Yang, *J. Amer. Chem. Soc.*, **87**, 2394 (1965); W. Hüchel and H. J. Kern, *Justus Liebig's Ann. Chem.*, **728**, 49 (1969).

(7) W. E. Bachmann and J. W. Ferguson, *J. Amer. Chem. Soc.*, **56**, 2081 (1934); J. G. Burr, Jr., and L. S. Ciereszko, *ibid.*, **74**, 5426 (1952); L. S. Ciereszko and J. G. Burr, Jr., *ibid.*, **74**, 5431 (1952); P. S. Bailey and J. G. Burr, Jr., *ibid.*, **75**, 2951 (1953); C. J. Collins, W. T. Rainey, W. B. Smith, and I. A. Kaye, *ibid.*, **81**, 460 (1959); B. M. Benjamin and C. J. Collins, *ibid.*, **78**, 4332 (1956).

(8) (a) B. M. Benjamin and C. J. Collins, *ibid.*, **78**, 4932 (1956); (b) D. Y. Curtin and M. C. Crew, *ibid.*, **76**, 3719 (1954).

(9) D. Semenov, C. H. Shih, and W. G. Young, *ibid.*, **80**, 5472 (1958).

(10) R. Huisgen and Ch. Rüdhardt, *Justus Liebig's Ann. Chem.*, **601**, 1 (1956).

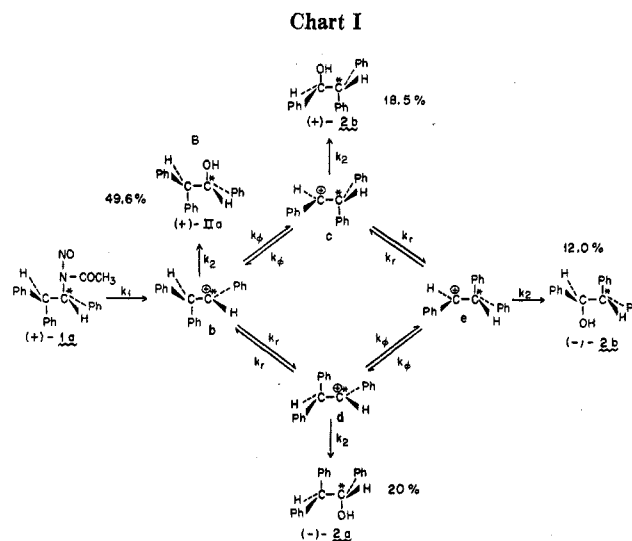
(11) A. Streitwieser, Jr., and W. D. Schaeffer, *J. Amer. Chem. Soc.*, **79**, 2888 (1957).

(12) A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957).

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

culated⁵ that the rate of reaction of primary amine with nitrosating agent must approach that of diffusion control. It has therefore not been possible, by kinetic techniques, to differentiate SN1- (eq 4e) from SN2-like (eq 4a) inversion, and the problem of whether SN2-like processes ever take place during such reactions remains largely unresolved¹⁴ (see, however, discussion later in this Account). The kinetic situation⁵ also makes it difficult to identify neighboring group participation and anchimeric assistance,¹⁵ although some early work of Roberts¹⁶ and more recent work by Hanack¹⁷ on homoallylic ring closures during the amine-nitrous acid reaction certainly imply that such participation is possible.¹⁸

Hückel⁶ has explained some of the peculiar stereochemistry of the amine-nitrous acid reaction by postulating that the intermediate carbonium ion does not reach planarity before reaction with entering group, and White¹⁹ discussed the thermal decomposition of the *N*-nitrocarbamate of 1-norbornylamine, which is presumed also to proceed through diazonium ion intermediates, in terms of oriented, noninterceptable ion pairs, similar to an earlier proposal of Huisgen.²⁰ The effect of changing solvent upon the stereochemistry²¹ and the observations that in mixed aqueous-acetic acid solutions the carbinol produced often exhibits more rearrangement^{22,23} than the acetate have recently received renewed attention²⁴ and have been explained by specific solvation of the cation,²³ or of the ion pair,²⁴ or in terms of micelle formation.²⁵ The role of the counterion in controlling stereochemistry has been studied,^{26,27} and White²⁸ includes a discussion of this subject in his review. In a recent summary²⁹ of the evidence for protonated cyclopropanes as cationic intermediates, I discussed their importance to decompositions of aliphatic diazonium ions, and Kirmse and Arold³⁰ have added important new evidence for these



intermediates by showing that optically active 1-amino-2-methylbutane, on treatment with nitrous acid, yields—among other products—partially racemic 2-methyl-1-butanol.

Finally, the concept of “transference of unusual behavior” to the carbonium ions formed during decompositions of aliphatic diazonium ions was first mentioned by Silver³¹ and later called a “memory effect” by Berson.³²

Results of Raaen, Benjamin, Collins, and Coworkers

Our own results on the amine-nitrous acid reaction were obtained over a period of about 15 years and are in accord with Huisgen's concept¹⁰ of the compression of transition-state energies and with Streitwieser's^{11,12} formulation of the solvolytic displacement process (reaction 4a). Our results, however, do not agree with Streitwieser's postulate that the diazonium ion “is the branching point of the competing reactions,”^{11,12} at least for the *secondary* systems studied.

We began our investigation with a determination for several amine-nitrous acid reactions of the *p*-tolyl/phenyl (1.18)⁸ and *o*-tolyl/phenyl (0.75)³³ migration ratios, values much closer to unity than those observed³⁴ for solvolytic and pinacolic rearrangements. We then studied the stereochemistry of the reaction of (+)-1,2,2-triphenylethyl-1-¹⁴C-amine (1a)³⁵ and showed, by a determination of the carbon-14 distributions in the resolved products [(+)- and (-)-2ab], that the reaction most likely proceeds by the mechanism shown in Charts I and II. In Chart I the yields of each product are shown for a typical run. (Chart II shows the processes giving k_2 , k_ϕ , and k_r in more detail, with the help of Newman projection formulas. The

(14) E. J. Corey, J. Casanova, Jr., P. A. Vatakencherry, and R. Winter, *J. Amer. Chem. Soc.*, **85**, 169 (1953); J. A. Berson and A. Remanick, *ibid.*, **86**, 1749 (1964).

(15) P. D. Bartlett, “Nonclassical Ions,” W. A. Benjamin, New York, N. Y., 1965, p 65.

(16) J. D. Roberts and R. H. Mazur, *J. Amer. Chem. Soc.*, **73**, 2509 (1951).

(17) M. Hanack and W. Keberle, *Chem. Ber.*, **96**, 2937 (1963); M. Hanack and H. J. Schneider, *Angew. Chem.*, **76**, 783 (1964).

(18) See, however, E. J. Corey, and R. L. Dawson, *J. Amer. Chem. Soc.*, **85**, 1782 (1963), who fail to find evidence for homoallylic participation in a system (3-bicyclo[3.1.0]hexyl) which exhibits such participation during solvolysis.

(19) E. H. White, H. P. Tiwari, and M. J. Todd, *ibid.*, **90**, 4734 (1968).

(20) R. Huisgen and H. Reimlinger, *Justus Liebigs Ann. Chem.*, **599**, 161, 183 (1956); R. Huisgen and Ch. Rütchardt, *ibid.*, **601**, 21 (1956).

(21) E. Ott, *ibid.*, **488**, 186 (1931).

(22) C. J. Collins, W. A. Bonner, and C. T. Lester, *J. Amer. Chem. Soc.*, **81**, 466 (1959).

(23) M. Silver, *ibid.*, **83**, 3482 (1961).

(24) T. E. Cohen and E. Jankowski, *ibid.*, **86**, 4217 (1964); R. A. Moss, *J. Org. Chem.*, **31**, 1032 (1966).

(25) R. A. Moss and S. M. Lane, *J. Amer. Chem. Soc.*, **89**, 5655 (1967); R. A. Moss and D. W. Reger, *ibid.*, **91**, 7539 (1969).

(26) E. H. White, *ibid.*, **77**, 6011, 6014 (1955); E. H. White and C. A. Aufdermarsh, *ibid.*, **80**, 2597 (1958).

(27) C. J. Collins, J. B. Christie, and V. F. Raaen, *ibid.*, **83**, 4267 (1961); C. J. Collins and J. B. Christie, *ibid.*, **82**, 1255 (1960).

(28) E. H. White in “The Chemistry of the Amino Group,” S. Patai, Ed., Interscience, New York, N. Y., 1968, Chapter 8.

(29) C. J. Collins, *Chem. Rev.*, **69**, 543 (1969).

(30) W. Kirmse and H. Arold, *Chem. Ber.*, **103**, 23 (1970).

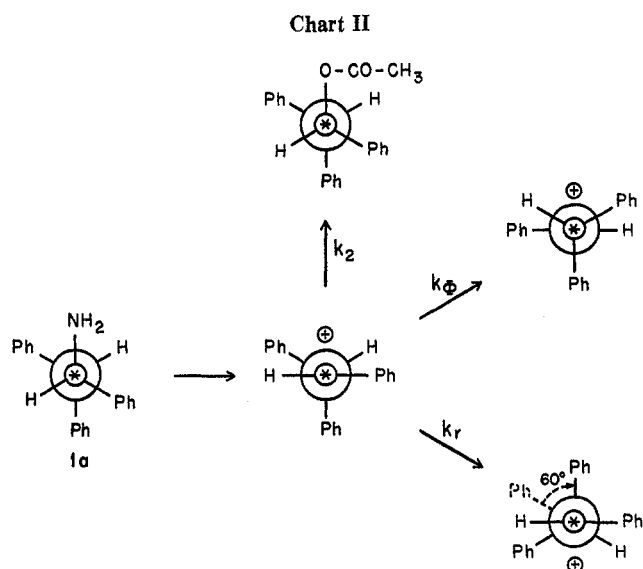
(31) M. Silver, *J. Amer. Chem. Soc.*, **83**, 3483 (1961); **82**, 2971 (1960).

(32) J. A. Berson, *Angew. Chem.*, **80**, 765 (1968).

(33) V. F. Raaen and C. J. Collins, *J. Amer. Chem. Soc.*, **80**, 1409 (1958).

(34) C. J. Collins, *Quart. Rev., Chem. Soc.*, **14**, 357 (1960). See particularly references given on pp 360–361.

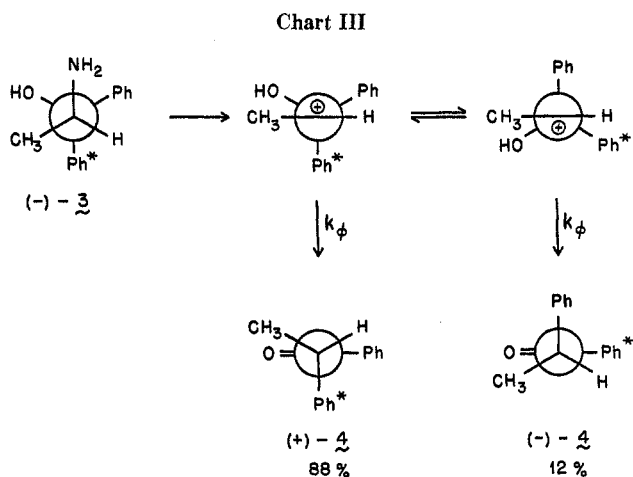
(35) W. A. Bonner and C. J. Collins, *J. Amer. Chem. Soc.*, **78**, 5587 (1956); C. J. Collins and B. M. Benjamin, *ibid.*, **85**, 2519 (1963); C. J. Collins, W. A. Bonner, and C. T. Lester, *ibid.*, **81**, 466 (1959).



asterisk (*) in Chart II signifies carbon-14 labeling in the "front" carbon.) The specific reaction rate constant, k_ϕ , denotes phenyl migration, whereas k_r signifies a rotation of 60° . The pathway $b \rightarrow d \rightarrow e$ (Chart I) for formation of (-)-2b is in conflict with Streitwieser's concept^{11,12} (reaction 4d) that aryl migration must occur with *inversion* of configuration at the migration terminus.

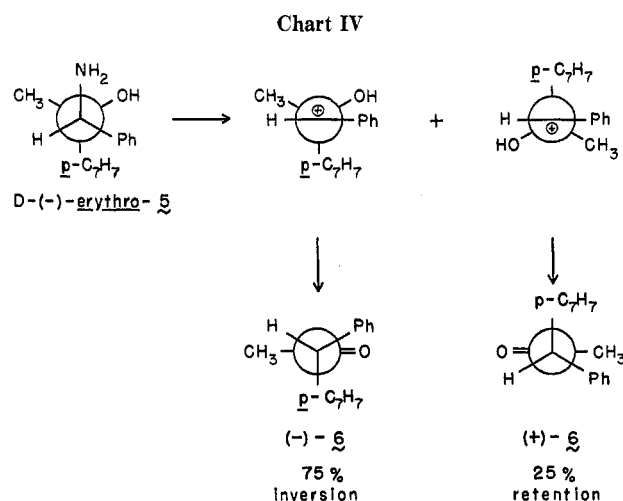
Equations describing the mechanism of Chart I were derived³⁵ and shown to be compatible with the experimental data which could not be explained, however, by nonclassical ions. The thermal decomposition of (-)-N-acetyl-¹⁴C-N-nitroso-1,2-triphenylethyl-¹⁴C-amine was also shown²⁷ to be compatible with the mechanism in Chart I (see later discussion on counterion control of product formation). The ratios k_r/k_ϕ and k_2/k_ϕ were calculated from the experimental data and shown to be in the range 0.9-2.3.

We next examined³⁶ the classic reaction with nitrous acid³⁷ of 1,1-diphenyl-2-amino-1-propanol [(-)-3, Chart



(36) B. M. Benjamin, H. J. Schaeffer, and C. J. Collins, *J. Amer. Chem. Soc.*, **79**, 6160 (1957).

(37) A. McKenzie, R. Roger, and G. D. Wills, *J. Chem. Soc.*, 779 (1926); H. I. Bernstein and F. C. Whitmore, *J. Amer. Chem. Soc.*, **61**, 1324 (1939).



III] and demonstrated that the 12% retention of configuration leading to (-)-4 results from *migration of the unlabeled phenyl with retention to the migration terminus*, a result also incompatible with Streitwieser's reaction (eq 4d).^{11,12} That portion of the reaction leading to (+)-4 (88%) took place through migration of the *labeled* phenyl with inversion at the migration terminus. Both the labeled and the unlabeled phenyls migrated through *trans* transition states, in which the methyl and nonmigrating phenyl are *trans* to each other, whereas the minor component of the reaction had previously been supposed³⁸ to occur through a *cis* transition state, in which the methyl and nonmigrating phenyl are *cis* to each other.

These studies were expanded³⁹⁻⁴¹ to include the reactions shown in Chart IV in which the migrating group can undergo 1,2 shift with inversion (75%) or with retention (25%) at the migration terminus. In the reaction shown in Chart IV, inversion predominates because it results from the migration of a *p*-tolyl group through a *trans* transition state,³⁸ whereas retention at the migration terminus must occur through a *cis* transition state,³⁸ a situation less conducive to migration. When it can occur through a *trans* transition state, retention predominates, as is demonstrated by the results⁴⁰ outlined in Chart V, in which the migrating group is *p*-tolyl. Replacement of the *p*-tolyl group in *threo*-5 with *p*-anisyl⁴¹ and subjection of the compound so obtained to similar reaction conditions resulted in 60% retention of configuration *vs.* 40% inversion in the product. The *o*-tolyl group, when replacing the *p*-tolyl in *D-threo*-5, could not be induced⁴¹ to migrate with predominant retention.

Since the papers of Bartlett and Pöckel,^{42a} Hückel,^{42b}

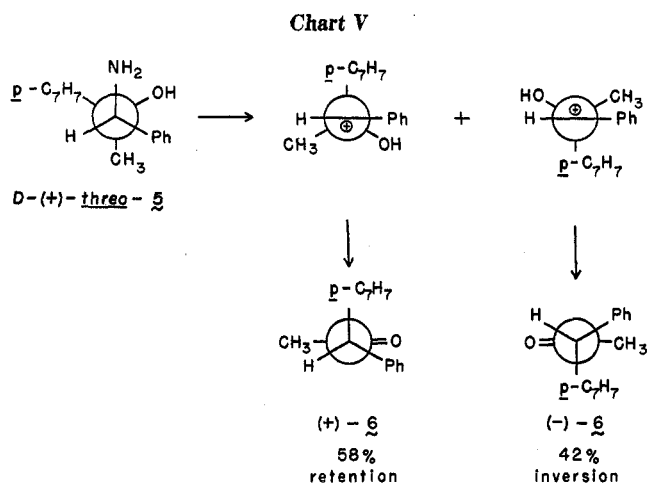
(38) P. I. Pollak and D. Y. Curtin, *ibid.*, **72**, 961 (1950); D. Y. Curtin, E. E. Harris, and E. K. Meislich, *ibid.*, **74**, 2901 (1952); D. Y. Curtin and E. K. Meislich, *ibid.*, **74**, 5518 (1952); D. Y. Curtin and P. I. Pollak, *ibid.*, **73**, 992 (1951); D. Y. Curtin and E. K. Meislich, *ibid.*, **74**, 5905 (1952).

(39) B. M. Benjamin, P. Wilder, Jr., and C. J. Collins, *ibid.*, **83**, 3654 (1961).

(40) B. M. Benjamin and C. J. Collins, *ibid.*, **83**, 3362 (1961).

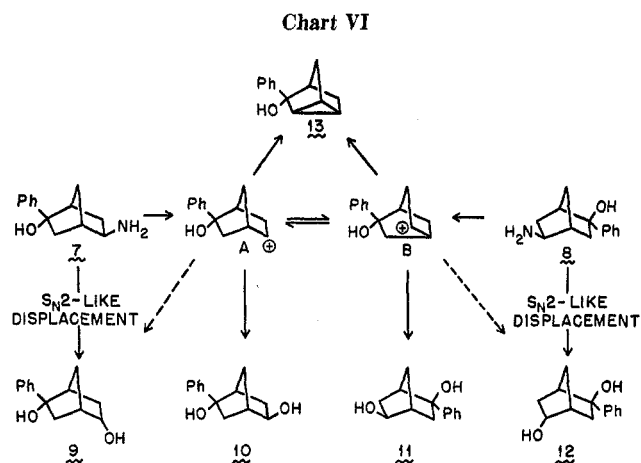
(41) C. J. Collins, M. M. Staum, and B. M. Benjamin, *J. Org. Chem.*, **27**, 3525 (1962).

(42) (a) P. D. Bartlett and I. Pöckel, *J. Amer. Chem. Soc.*, **59**, 820 (1937); **60**, 1585 (1938); (b) W. Hückel, *Nachr. Akad. Wiss. Goettin-*



and Bernstein and Whitmore,³⁷ it has been generally assumed^{11,12,42c} that inversion is the predominant (if not the exclusive!) stereochemical result both at the migration origin and at the migration terminus during 1,2 shifts. The experiments³⁹⁻⁴¹ just reviewed show that the foregoing assumption *at least for 1,2 shifts occurring during the amine-nitrous acid reaction is unwarranted*. It seemed expedient, therefore, to turn our attention to the amine-nitrous acid reactions of substituted 2-*exo*- and 2-*endo*-norbornylamines, concerning which there has been some controversy.^{14,43}

In the reactions with nitrous acid⁴⁴ (in acetic acid-sodium acetate) of the two *exo* amines **7** and **8** (Chart VI) the *exo/endo* stereospecificities for attack on cations A and B were measured by determining the yields (after reduction with lithium aluminum hydride) of compounds **9**, **10**, **11**, and **12** using the isotope-dilution method.⁴⁵ Since rearranged ion B (from **7**) and rearranged ion A (from **8**) exhibit very high *exo/endo* stereospecificities (220:1 and 650:1, respectively), whereas when B is formed directly from **8** and A from **7** the ratios are much smaller (19:1 and (11-18):1, respec-

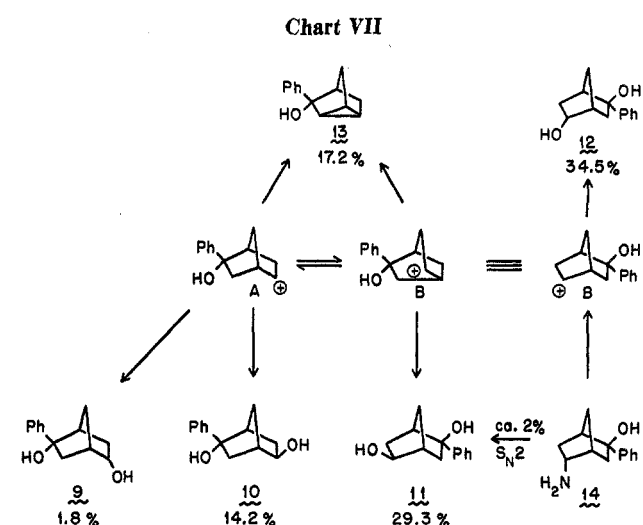


gen, *Math.-Phys. Kl.*, **2A**, 59 (1941); (c) see, for example, R. T. Morrison and R. N. Boyd, "Organic Chemistry," 2d ed, Allyn and Bacon, Boston, Mass., 1966, p 883.

(43) P. D. Bartlett "Nonclassical Ions," W. A. Benjamin, New York, N. Y., 1965, p 463.

(44) C. J. Collins and B. M. Benjamin, *J. Amer. Chem. Soc.*, **92**, 3182 (1970).

(45) V. F. Raaen, G. A. Ropp, and H. P. Raaen, "Carbon-14," McGraw-Hill, New York, N. Y., 1968, Chapter 2.



tively), we concluded that both **7** and **8** undergo the amine-nitrous acid reaction with 2-3% S_N2-like processes. Further, since **7** and **8** do not give the same ratio of **10**:**11** under like conditions,⁴⁶ **7** yielding more **10** than **11** (2.3:1) and **8** yielding more **11** than **10** (1.7:1), we conclude that the intermediates are best formulated as the classical ions A and B.

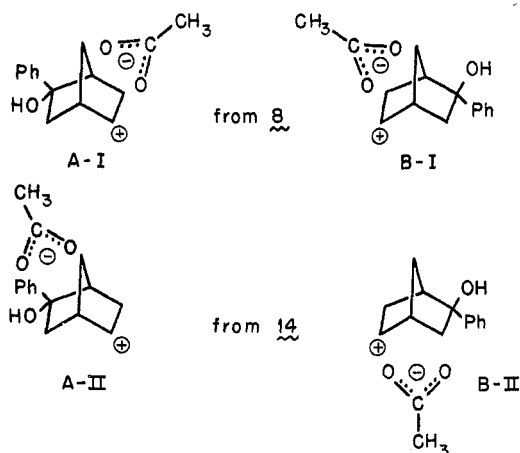
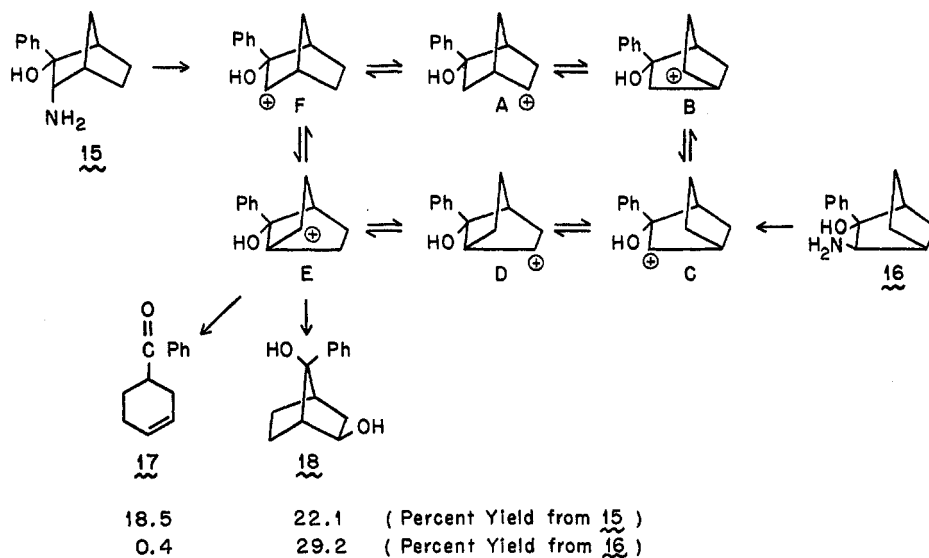
Further evidence for the classical character of A and B was obtained by carrying out the reaction with nitrous acid, in acetic acid-sodium acetate, of the *endo* amine **14**.⁴⁷ The results are illustrated in Chart VII. Here we were able to isolate in 1.8% yield the product, **9**-acetate, of *endo* attack on ion A after it had been formed from B through a Wagner-Meerwein rearrangement, thus illustrating⁴⁷ that, at least to the extent (1.8%) that **9**-acetate is produced, A could be considered to be a classical ion. Once again **11**-acetate was formed in greater yield than **10**-acetate, whereas we know from solvolytic studies⁴⁶ that **10** predominates in a ratio of 1.4:1 in the situation where nonclassical ions might be expected.

The high yield (34.5%) of unrearranged **12**-acetate from the deamination of **14** compared with that (29.3%) of **11**-acetate is evidence, we think, for the configuration-holding ability of the counterion in B-II, for when cation B is generated from the *exo* amine **8** (Chart VI) the relative yields of *endo*-**12**-acetate (2.2%) and *exo*-**11**-acetate (42.6%) are now reversed. That is to say, from *endo* amine **14** the *exo/endo* ratio of unrearranged product is 0.9:1 whereas from *exo* amine **8** this same ratio is 19:1. Since the acetate counterion formed (eq 1) on decomposition of the diazonium acetates from **8** and **14** should assume the approximate positions shown in B-I and B-II, respectively, it seems possible to us that the *endo* acetate in B-II could control formation of *endo* product, whereas the *exo* product should be preferred from ion pair B-I. The surprisingly large yield (1.8%) of *endo*-**9**-acetate obtained from deamina-

(46) The two tosylates corresponding to **7** and **8** both yield **10** and **11** in the same ratio of 1.4:1 (B. S. Benjaminov and V. F. Raaen, unpublished work).

(47) B. M. Benjamin and C. J. Collins, *J. Amer. Chem. Soc.*, **92**, 3183 (1970).

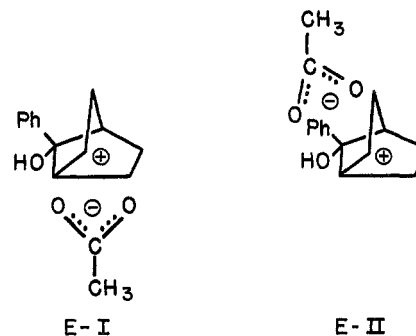
Chart VIII



tion of **14** can also be formulated as resulting from counterion control by the acetate in A-II, even after Wagner–Meerwein rearrangement of B-II to A-II, for from **8**, where the counterion must be exo, as in A-I, the yield of *endo*-9-acetate is only 0.04%.⁴⁴ Hückel and Kern⁶ have also observed *endo* product after Wagner–Meerwein rearrangement during deamination of *both* *exo*- and *endo*-fenchylamines, for the tertiary carbinol fractions of α -fenchene hydrate consisted of *both* *exo* and *endo* isomers in the ratios, respectively, of 17:1 and 12:1.

The foregoing results are reminiscent of our earlier work²⁷ on the thermal decomposition, in acetic acid–sodium acetate, of optically active (–)-*N*-acetyl-¹⁴C-*N*-nitroso-1,2,2-triphenylethyl-¹⁴C-amine. Here we showed that product of retained configuration—(+)-1,2,2-triphenylethyl-¹⁴C acetate-¹⁴C—still contained 40 mole % of the acetate-¹⁴C radioactivity (28% of the overall reaction), whereas the inverted product contained only 10 mole % (3% overall reaction). Since there was common acetate ion present—as in the reactions of Charts VI and VII—it appears that the initially formed ion pair can hold its configuration. In support of this conclusion, we established²⁹ that *rearranged* 1,2,2-triphenylethyl-²-¹⁴C acetate-¹⁴C was produced.

We have additional data concerning the product-controlling ability of the counterion. The reaction with nitrous acid^{48–51} of the *endo* amines **15** and **16** in acetic acid–sodium acetate led to several products, among which are the ketone **17** and the monoacetate of diol **18** (Chart VIII). Among the products from **15**, in about equal yields, were both Δ^3 -cyclohexenyl phenyl ketone (**17**), produced by ring opening of cation E (this was demonstrated by deuterium labeling;⁵⁰ there was no observable ketone **17** formed from ion D), and 18-acetate, produced by collapse of E with acetate. During reaction of **16**, however, only a trace (0.4%) of ketone **17** was observed, whereas 18-acetate was formed in nearly 30% yield. If we assume the counterions from **15** and **16** maintain their same relative positions with respect to cation E as in the original diazonium acetates, then **15** should yield ion pair E-I, whereas **16** should give E-II. Since E-I is not well situated for



collapse to product, cation E can undergo ring opening to yield the ketone **17**. Any 18-acetate produced must arise through reaction with acetate from the solvent.

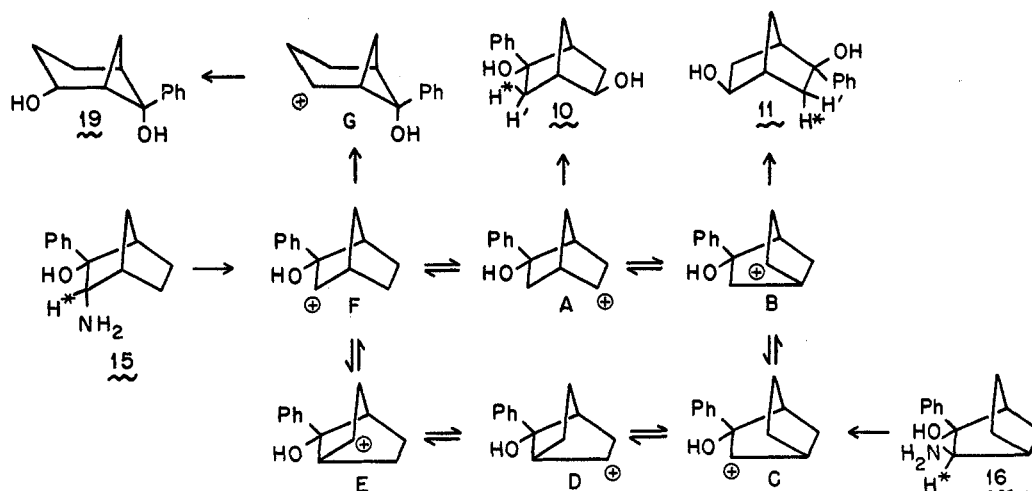
(48) C. J. Collins, V. F. Raaen, B. M. Benjamin, and I. T. Glover, *J. Amer. Chem. Soc.*, **89**, 3940 (1967).

(49) C. J. Collins, V. F. Raaen, and M. D. Eckart, *ibid.*, **92**, 1787 (1970).

(50) C. J. Collins, B. M. Benjamin, V. F. Raaen, I. T. Glover, and M. D. Eckart, *Justus Liebig's Ann. Chem.*, **739**, 7 (1970).

(51) V. F. Raaen, B. M. Benjamin, and C. J. Collins, *Tetrahedron Lett.*, submitted for publication.

Chart IX



Ion pair E-II from **16**, however, is well situated for collapse, and, if our proposal is correct, apparently does so to the near exclusion of ring opening.⁵⁰

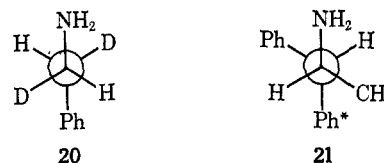
In the reactions just discussed of **15** and **16** the monoacetates of the two diols **10** and **11** are also produced in low yields (3–6%) (Chart IX). Using the isotope-dilution method⁴⁵ we were able to show⁵¹ that from either **15** or **16** the ratio of **10**:**11** was 1.65:1. Here the capture ratio for the Wagner–Meerwein pair $A \rightleftharpoons B$ —in contrast to our other observations^{44,47,50}—is very close to that (1.4:1) observed when these same ions are formed on solvolyses.⁴⁶ It is thus tempting to conclude that both ions are nonclassical ($A \leftrightarrow B$) and have been formed by the short routes $15 \rightarrow F \rightarrow A$ and $16 \rightarrow C \rightarrow B$.

That the foregoing conclusion is incorrect, however, was demonstrated by carrying out the reactions of deuterated **15** and **16** (H^* and $H' = D$, Chart IX). By a determination of the deuterium distributions in **10** and **11** from both reactants we were able to show that **10**-acetate (and thus **A**) are formed predominantly (85–89%) by clockwise routes. That is, **15** goes to **A** predominantly by the short route ($15 \rightarrow F \rightarrow A$) whereas **16** prefers the long route ($16 \rightarrow C \rightarrow D \rightarrow E \rightarrow F \rightarrow A$). (H^* results from clockwise pathways in both reactions, H^1 from counterclockwise pathways.) Thus, since in both reactions **A** is predominantly formed before **B**, the similar capture ratio (1.65:1) of $A \rightleftharpoons B$ from the two reactants is not indicative of nonclassical character. Further, if $A \rightleftharpoons B$ were, in fact, one nonclassical ion, the deuterium distribution in **10** and **11** (H^*/H^1) should be the same. That the H^*/H^1 ratios for **10** and **11** were significantly different⁵¹ from both reactant **15** and **16** means either that the ions **A** and **B** cannot be one single, nonclassical ion, or that some extra route to **9** or **10** is possible. The tendency⁵⁰ of the endo amine **15** to undergo 1,2 shift of C-7 ($F \rightarrow G$) resulting in the formation of **19**-acetate (Chart IX) might also be considered a consequence of counterion control of product formation, for neither **7** nor **8** yielded measurable quantities of **19**, and **16** produced, at best, a trace.

Conclusions

The results of our experiments (Charts I–V) on the amine–nitrous acid reactions of 1,2,2-triphenylethylamine,^{22,27,35} of 1,1-diphenyl-2-amino-1-propanol,^{36,37} and of the 1,2-diaryl-1-amino-2-propanols^{39–41} are not in accord with Streitwieser's proposal "that the diazonium ion rather than a carbonium ion is the branching point of the competing reactions."^{11,12} Our repeated observations that aryl shift to the migration terminus can take place with partial or with predominant retention of configuration mean that the diazonium ion must already have decomposed before this can occur. Therefore aryl shift with retention of configuration at the migration terminus must take place after process 4e, and not concurrently with process 4d.

Our results^{44,47–51} with substituted 2-*exo*- and -*endo*-norbornylamines (Charts VI–IX) also indicate that hydrogen and aryl migrations do not necessarily occur by processes 4c and 4d, but in most cases *after* the decomposition of the diazonium ion (process 4e). These conclusions are quite in contrast to those of Snyder⁵² for the reaction with nitrous acid of optically active *erythro*-2-phenylethyl-1,2-*d*₂-amine (**20**). Here 52% retention of configuration and 25–27% carbon-14 re-



arrangement were observed, results nicely rationalized through competing phenonium ion and SN_2 pathways.

The latter mechanism is not necessarily incompatible with our conclusions, however, since the primary cations from **20** should show more tendency for nonclassical formation than any of the ions depicted in Charts I–IX. It is possible, therefore, that the primary amine **20** does in fact undergo aryl migration by process

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4d. In this connection our data³⁹ for the reaction of **21** with nitrous acid revealed only backside migration of Ph* (the asterisk denotes that the phenyl is labeled with carbon-14) with inversion at the migration terminus, a result we explained³⁹ by invoking ground-state control of product formation and restricted rotation about the C-C⁺ bond.

The cations formed during reaction of nitrous acid with the various substituted norbornylamines we investigated⁴⁷⁻⁵¹ undergo reactions which are not observed when cations of presumably identical structures are formed on solvolyses.⁵³ Further, their unusual character is preserved through one or several Wagner-Meerwein rearrangements or 6,2-hydride shifts. For example, endo attack by anion can occur *after* Wagner-Meerwein rearrangement (Charts VI and VII); even after five or six such consecutive shifts (Chart IX, cations A and B) complete nonclassical character has not yet been attained. Since a "hot" carbonium ion

(53) C. J. Collins and B. M. Benjamin, *J. Amer. Chem. Soc.*, **89**, 1652 (1967); **88**, 1558 (1966).

by definition⁹ undergoes no charge delocalization and *directly* produces only unrearranged product, then none of the cations designated in Charts VI-IX—except possibly those formed *directly* on decomposition of the diazonium ion—can be "hot" carbonium ions.

If these cations are neither "hot" nor nonclassical, the question as to how best to describe them still remains. We believe the answer to this question is to be found in ion-pairing phenomena, for the anion directly formed on decomposition of an aliphatic diazonium hydroxide (or acetate) not only is part of an ion pair but predominantly collapses²⁷ with the cation to yield product, quite in contrast to the situation which exists during solvolyses.⁵⁴ The "memory effects"³² observed in our work (Charts VII-IX) are explainable through ion pairs in which the two partners are differently oriented, depending upon the structure of the starting material.

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Narcissistic Reactions: Synchronism vs. Nonsynchronism in Automerizations and Enantiomerizations

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Received March 1, 1971

Reactions Which Are Equivalent to Pure Reflection

The year 1970 may mark the beginning of an era in which the very concept of organic reaction will undergo a profound change. There are indications that the beautiful mechanistic schemes used by organic chemists to interpret organic reactions will slowly be supplemented and may eventually be replaced by a detailed picture of the dynamic behavior of the reacting species on a complex potential energy surface. Extremely small, but often highly instructive, fragments of potential energy surfaces for some elementary organic reactions have already been calculated both by semi-empirical¹ and by *ab initio*² methods. In the coming

years one can confidently predict the total resolution of several organic transition states and of the potential surfaces surrounding them as well as preliminary calculations of the dynamical pathways on these surfaces.

Major difficulties in these quantum-mechanical calculations are the many dimensions of the potential surface (30 for as small a molecule as cyclobutane) and the awkward fact that, unlike reactant or product, the transition state is not an absolute energy minimum on the surface. Thus *any* simplifying feature in the search for the transition state—even for a restricted class of reactions—should be extremely precious. We shall investigate a family of reactions where two types of pathways, synchronous and nonsynchronous, can be distinguished, and where for one of these (synchronous) an extremely useful constraint is imposed on the reaction midpoint. This family includes all reactions which are equivalent to pure reflection.

Organic chemists have long been aware—probably

† The Laboratoire de Chimie Théorique is also part of the Laboratoire de Physico-Chimie des Rayonnements associated with the CNRS.

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