temperature. The reaction solution was allowed to stand for 1 hr and excess chlorine and solvent were removed under vacuum. The crystalline product, 3,3-dimethyl-1,1-dichloro-2-butanone azine (mp 56°, from hexane at −70°), was obtained in almost quantitative yield: nmr τ 3.54 (singlet, 2 H), 8.64 (singlet, 18 H).

Anal. Calcd for $C_{12}H_{20}N_2Cl_4$: C, 43.14; H, 6.03; N, 8.38; Cl, 42.45. Found: C, 43.26; H, 5.95; N, 8.43; Cl, 42.56.

A similar reaction of pinacolone azine with excess chlorine at room temperature in the dark in methylene chloride led to the same tetrachlorinated ketazine (~10%), 1,1′-dichloro-1,1′-diphenyl-1,1′-azoethane (~70%), and an unidentified product (~20%).

Thermal Decomposition of *meso*- and *dl*-1,1′-Dichloro-1,1′-diphenyl-1,1′-azopropane (Neat). Samples (100 mg) of *meso*- and *dl*-1,1′-dichloro-1,1′-diphenyl-1,1′-azopropane were placed in nmr tubes and heated at 80° for 75 min in an oil bath. Then 0.4 ml of carbon tetrachloride was added to each tube. The *meso*-azo compound (mp 56°) gave rise to a mixture of isomers of 3,4-dichloro-3,4-diphenylhexane in which the more crystalline isomer (mp 148–158°) predominated by 55/46 as shown by nmr. Similarly, the *dl*-azo compound (mp 79° dec) gave rise to a mixture of isomers in which the noncrystalline isomer of 3,4-dichloro-3,4-diphenylhexane predominated by 57/43.

Acknowledgments. We are especially grateful to Professor Harold W. Wyckoff and Dr. G. E. Schulz of the Department of Molecular Biophysics, Yale University, for their hospitality, encouragement, and help during the X-ray work. The mass spectrum was kindly measured by Dr. Walter McMurray of Yale Medical School. The 60- and 100-MHz nmr spectrometers were provided by institutional grants from the National Science Foundation to Yale University. D. S. M. thanks the National Institutes of Health for predoctoral fellowship support (1967–1969). This work was supported in part by Grant GM-15166 from the U. S. Public Health Service, National Institute of General Medical Sciences.

α,α'-Dichloroazoalkanes. II. The Mechanism of Stereospecific Synthesis and Substitution[1]

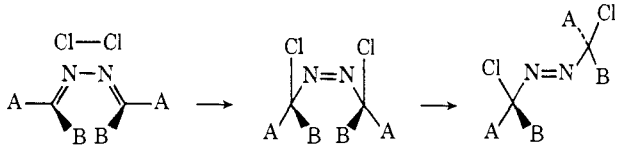
Donald S. Malament and J. Michael McBride

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520. *Received November 14, 1969*

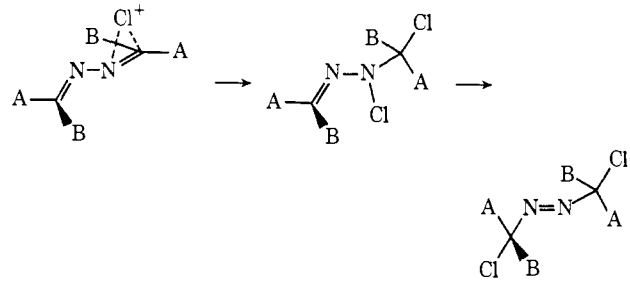
Abstract: Five mechanisms are proposed to explain stereospecific 1,4-chlorine addition to ketazines. Three of these are shown to be consistent with experimental observations on the reaction and with theory. Factors favoring nucleophilic attack *trans* to an emerging lone pair are discussed. The true cationic intermediate is expected to be identical with that formed in the rate-determining step in unimolecular nucleophilic chloride displacement from α,α'-dichloroazoalkanes. Apparent retention of stereochemistry in both steps of this displacement is consistent with both diazirinium and allene-like cation intermediates. The latter is preferred on the basis of a fourfold acceleration in hydrolysis rate accompanying replacement of an α-methyl group by *t*-butyl. Hydrolysis product distribution supports this choice.

The 1,4 addition of chlorine to ketazines is a nonradical-chain process which stereospecifically converts symmetrical ketazine isomers to *meso*-α,α'-dichloroazoalkanes and unsymmetrical ketazines to the *dl* product.[1c] With the help of studies on substitution reactions of the products we now attempt to choose among the following five mechanisms for this stereospecific addition.

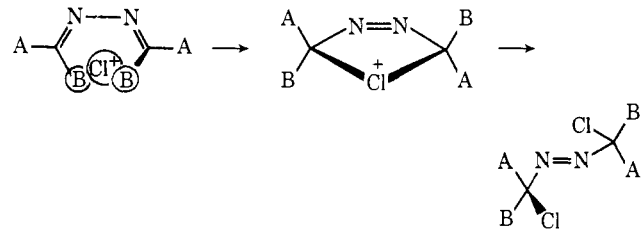
(a) Concerted [2 + 4] addition to the *s-cis* ketazine conformer followed by product isomerization to the *trans*-azo geometry.



(b) *trans*-1,2 addition to the *s-trans* ketazine conformer followed by *cis*-SN2′ displacement or by suprafacial 1,3-chloride shift.



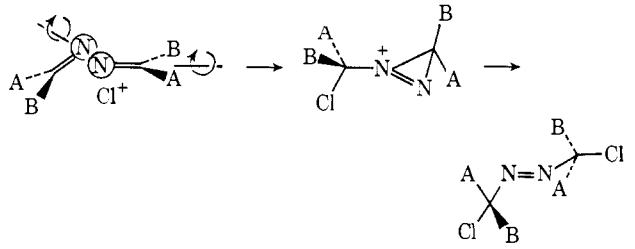
(c) Antarafacial [4 + 1] addition of the chlorine electrophile to cisoid ketazine followed by backside nucleophilic ring opening and *cis–trans* azo isomerization as in a.



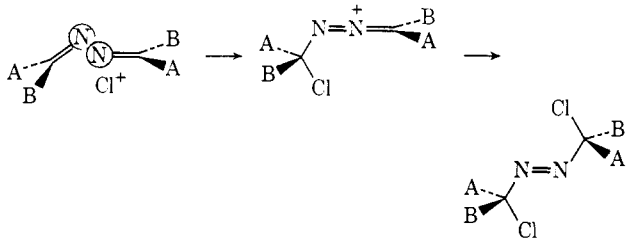
(d) Attack by a chlorine electrophile complexed within the smaller dihedral angle of a skew ketazine

(1) (a) Presented in part at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstract ORGN 155. (b) Based on the Ph.D. Thesis of D. S. M., Yale University, 1969. (c) Part I: D. S. Malament and J. M. McBride, *J. Amer. Chem. Soc.*, **92**, 4586 (1970).

conformer with simultaneous conrotatory ring closure to form a "diazirinium" intermediate subject to backside nucleophilic ring opening.



(e) Attack as in d with concerted formation of a nitrogen-stabilized carbonium ion subject to nucleophilic attack only on the face opposite the tetrahedral carbon.[2]



Results and Discussion

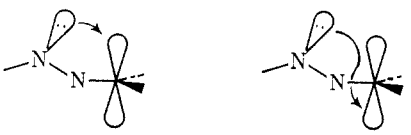
Preliminary Consideration of Mechanisms a–e. (**a**) While concerted [2 + 4] addition provides a simple rationale for the observed stereospecifity, it is difficult to conceive a suitable transition state geometry for addition to such hindered ketazines as those of pivalophenone and isobutyrophenone.[1c] Much less hindrance completely suppresses the Diels–Alder reaction of dienes.[3] If hindered ketazines do react by this mechanism, it is equally difficult to understand the failure of 4H-pyrazoles to react,[1c] since they do undergo the Diels–Alder reaction.[4] Although cyclic dienes can give *cis*-1,4-halogenation, the mechanism is stepwise,[5] and 1,4-halogen addition to acyclic butadiene involves *s-trans*-diene.[6] On the basis of these objections we exclude mechanism a.

(**b**) The addition–displacement mechanism also fails to rationalize the behavior of 4H-pyrazoles. Stereospecificity in this mechanism requires the second step (SN2′ displacement or allylic migration) to occur prior to inversion of the intermediate's pyramidal nitrogen. Such inversions may be slow,[7] but so should the second step. Together with its failure to explain the steric course of SN1 reactions of the dichloroazo compounds (see below), these considerations lead us to reject mechanism b.

Mechanisms c, d, and e are consistent with the results of chlorination experiments, since each involves an intermediate which would be prohibitively strained in the reaction of 4H-pyrazoles. These mechanisms share the requirement that at some stage of reaction the chlorine electrophile be "sandwiched" within the smaller dihedral angle of a skew conformer of the ketazine. Preference of ketazines for the skew conformation is likely in light of their considerable dipole moments.[8] Values of the CNNC dihedral angle calculated from these moments vary from 90 to 135° depending on the magnitude and direction chosen for the $R_2C{=}N-$ group moment.[8,9] The ability of chlorine to form charge-transfer complexes with olefins is well known.[10]

(**c**) The cyclic chloronium ion of mechanism c is analogous to recently observed tetramethylenechloronium ions.[11] However, the latter are much less stable when chlorine bridges secondary centers than primary,[11] and in our case the centers are tertiary and often benzylic. It is not clear whether one would expect the strained *cis*-azo product to decompose spontaneously or to isomerize to give the *trans*-azo linkage.[12]

(**d**) The diazirinium ion intermediate of mechanism d could be generated by conrotatory or disrotatory closure. Neglecting the influence of orbital symmetry one might predict disrotatory closure, since by this path the unshared electron pair of the terminal nitrogen attacks the nearer lobe of the carbon p_z orbital. This prediction was tested by a series of CNDO/2 semi-



disrotatory conrotatory

empirical molecular orbital calculations on a conrotatory and a disrotatory sequence of geometries for the addition of a proton (H5) to formaldazine as shown.[13,16] The limiting geometries (0 and 100% reaction) were calculated using Wiberg's atomic coordinates program[17] for the bond lengths, angles, and torsional angles given in the Appendix. The reaction coordinate was arbitrarily chosen by making proportional changes in all these parameters to lead smoothly from the 0 to the 100% geometry. The paths differed only in the sense of rotation about the

(2) While the intermediates of mechanisms a–d owe their diastereoisomerism to possession of two chiral centers, this intermediate possesses one center and one axis of chirality. Because of the latter symmetry property, we refer to the intermediate as "allene-like."

(3) J. Sauer, *Angew. Chem. Intern. Ed., Engl.*, 6, 16 (1967).

(4) A. B. Evnin and D. R. Arnold, *J. Amer. Chem. Soc.*, 90, 5330 (1968).

(5) W. G. Young, L. K. Hall, Jr., and S. Winstein, *ibid.*, 78, 4338 (1956); K. H. Büchl, A. E. Ginsburg, and A. Fischer, *Chem. Ber.*, 99, 421 (1966); *cf.* ref 1b, pp 18–28.

(6) K. Mislow and H. M. Hellman, *J. Amer. Chem. Soc.*, 73, 244 (1951).

(7) S. M. Brois, *ibid.*, 90, 508 (1968).

(8) B. A. Arbuzov, Yu. Yu. Samitov, and Y. P. Kitaev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 55 (1966); Yu. P. Kitaev, L. E. Nivorozhkin, S. A. Plegontov, O. A. Raevskii, and S. Z. Titova, *Dokl. Akad. Nauk SSSR, Ser. Khim.*, 178, 1328 (1968).

(9) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p 245.

(10) J. E. Dubois and F. Garnier, *Spectrochim. Acta, A*, 23, 2279 (1967).

(11) G. A. Olah and P. E. Peterson, *J. Amer. Chem. Soc.*, 90, 4675 (1968).

(12) T. Mill and R. S. Stringham, *Tetrahedron Lett.*, 1853 (1969); J. M. Lehn and B. Munsch, *Theor. Chim. Acta*, 12, 91 (1969); M. S. Gordon and H. Fischer, *J. Amer. Chem. Soc.*, 90, 2471 (1968).

(13) We used the Pople–Santry–Segal program[14] as modified by Wiberg[15] but kept the original parameterization.

(14) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, 43, S129 (1965); J. A. Pople and G. A. Segal, *ibid.*, 43, S236 (1965); 44, 3289 (1965).

(15) K. B. Wiberg, *Tetrahedron*, 24, 1083 (1968).

(16) The calculations were performed for proton attack from outside the fold of the azine. The hydrogen orbital plays a negligible role in the orbitals which disfavor disrotatory closure, so the results should apply for attack within the fold as well.

(17) K. B. Wiberg, personal communication.

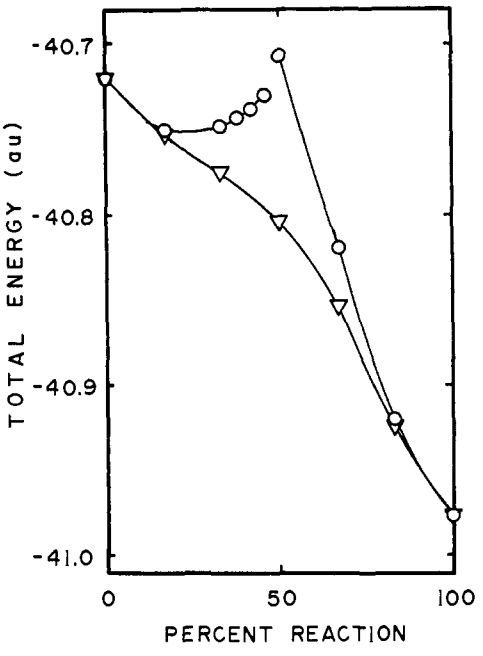
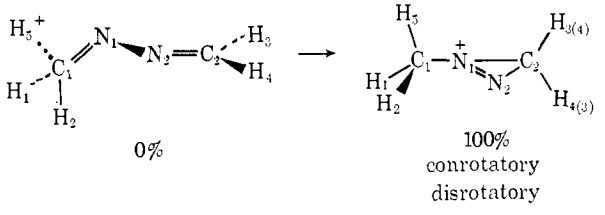


Figure 1. CNDO/2 energy along the reaction coordinate for electrocyclic formation of N-methyldiazirinium cation: O, disrotatory path; ▽, conrotatory path.

N_2–C_2 bond. Figure 1 shows the variation of the sum of valence electron and nuclear repulsive energies with per cent reaction for the conrotatory and disrotatory paths. While the conrotatory transformation



is smooth, the disrotatory path shows a discontinuity in energy which is mirrored by discontinuities in the Wiberg bond indices[15] (see Figure 2). Such discontinuities are symptomatic of "forbidden" reaction paths involving crossing between filled and vacant orbitals. Figure 3 traces the energies of the tenth through thirteenth valence shell molecular orbitals during the disrotatory reaction. The eigenfunction tables clearly show that the initial tenth orbital crosses first with the filled eleventh and then with the vacant twelfth. Near 70% reaction it mixes severely with the thirteenth orbital and its ultimate fate is unclear. This tenth orbital initially has 84% of its electron density in the p_z (π) orbitals of atoms N_1, N_2, and C_2 with a node between the nitrogens. It is thus analogous to the filled antisymmetric allylic π orbital which inhibits disrotatory closure of the allyl anion.[18] In simple terms one can consider the unshared pair of N_1 with the electron pair of the N_2–C_2 π bond to constitute a four-electron allylic system for which thermal disrotatory closure is forbidden.

Alkylated diazirinium ions have not been reported, although diazirines can be recovered from concentrated acid.[19]

(18) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

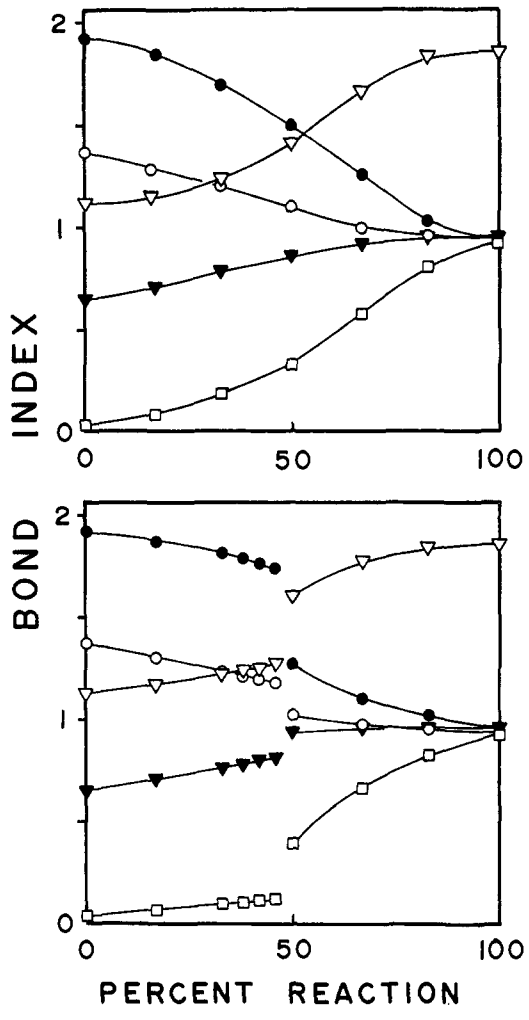


Figure 2. Variation in bond indices along reaction coordinate for electrocyclic formation of N-methyldiazirinium cation: top, conrotatory path; bottom, disrotatory path; ●, N_2–C_2; O, C_1–N_1; ▽, N_1–N_2; ▼, H_5–C_1; □, N_1–C_2.

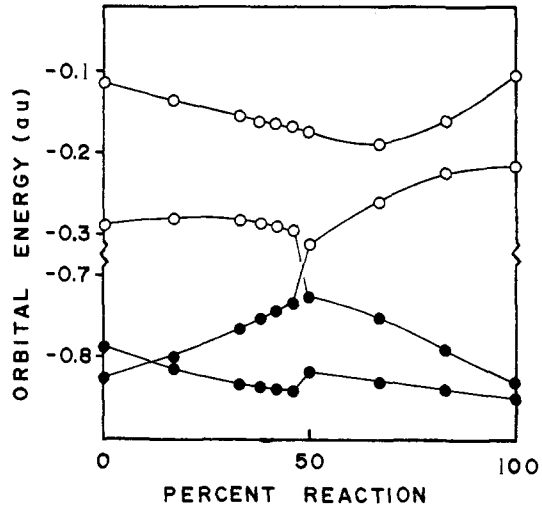
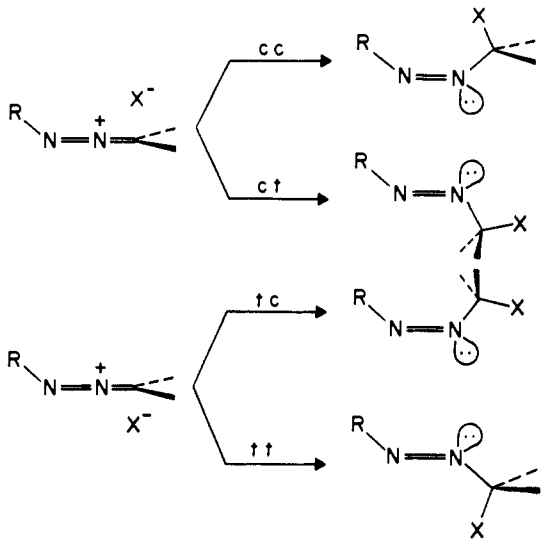


Figure 3. Calculated energies of highest filled and lowest vacant molecular orbitals along reaction coordinate for disrotatory formation of N-methyldiazirinium cation: ●, filled orbital; O, vacant orbital.

(19) E. Schmitz in "Advances in Heterocyclic Chemistry," A. R. Katritzky, Ed., Academic Press, New York, N. Y., 1963, p 125 ff.

(e) Although the allene-like intermediate of mechanism e is reasonable in terms of accessibility and stabilization, it seems unlikely at first glance that the remote chloroalkyl group should exert so dramatic an influence on the relative reactivity of the two faces of the trigonal electrophilic carbon. Four geometrical paths can be envisioned for bond formation to this center: *cis* or *trans* attack to give either *cis*- or *trans*-azo linkages (see Scheme I).

Scheme I. Paths for Nucleophilic Attack on an Allene-like Intermediate



It is probable that steric hindrance from the R group becomes quite unfavorable in the transition states leading to *cis*-azo products (*cc* and *tc*), but the difference in hindrance between the other transition states (*ct* and *tt*) should not be large when R is relatively small (*e.g.*, 2-chloro-2-butyl). The latter transition states differ primarily in that *ct* generates the unshared pair on the adjacent nitrogen *cis* to the entering nucleophile, while *tt* generates the *trans* electron pair. Preference for the latter path is predicted on the basis of three considerations: (i) electrostatic repulsion between the emerging electron pair and the entering chloride should be lower for *tt* than for *ct;* (ii) there may be an attractive interaction between chlorine and the β-nitrogen, since these atoms are eclipsed in the crystalline state conformer of an α,α'-dichloroazoalkane;[1c] (iii) from the orbital symmetry viewpoint of Fukui[20] generation of the electron pair *trans* to the entering nucleophile is a concerted *trans*-1,2 addition with an imaginary electrophile. This case may provide an unusually clear example of symmetry control in noncyclic additions, since concertedness in this "1,2 addition" is assured. We have attempted to confirm this prediction by performing CNDO/2 calculations[13] on seven sequential geometries along each of the paths in Scheme I for addition of H^- to the carbon atom of $HN{=}N^+{=}CH_2$ (see Appendix). As expected, none of the paths showed changes in orbital occupancy during "reaction." The small differences in path energies are of questionable significance because of uncertain parametrization,[21] but in total electronic energy paths *cc* and *tt* were favored over *ct* and *tc*, respectively, by about 0.1 atomic unit.[22] While this is in conformity with the prediction of "*trans*-1,2 addition," the calculated preferences are reversed by a similar margin when nuclear repulsion is included.

Solvolytic Route to the Cationic Intermediate. None of our observations on the chlorination reaction itself permit a clear choice among mechanisms c, d, and e. However, each of these mechanisms involves a cationic intermediate which is in principle accessible by reversal of the second step in the addition, that is, by ionization of the α,α'-dichloroazoalkane. Goldschmidt and Acksteiner[23] and Benzing[24] have shown that chloride in these azo compounds is subject to replacement by such nucleophiles as cyanide, azide, thiols, and carboxylates. Benzing's demonstration of common ion rate suppression in the hydrolysis of 2,2′-dichloro-2,2′-azopropane in 85% aqueous acetone confirms the expectation that nucleophilic displacement at these tertiary centers should involve rate-determining ionization.[24] Although there is a difference in solvent, it is a reasonable hypothesis that the cation formed by ionization of the dichloroazoalkane during nucleophilic substitution is the same as that which adds chloride to generate the azo compound in the ionic chlorination of ketazines.

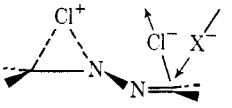
Stereospecificity in Nucleophilic Substitution. If these cationic intermediates were identical, one would expect nucleophilic displacement to proceed with retention of configuration. In sequential displacement of both chlorines one would expect double retention if the intermediate involves nitrogen participation as in mechanisms d and e. Retention in the second displacement would not generally be expected if specificity depends on chlorine participation as in mechanism c.

Although the dichloroazoalkanes were not resolved, it could be shown indirectly that at least the first displacement involves retention of configuration. First-order plots of nitrogen evolution during the hydrolysis of 0.03 *M meso*-1,1′-dichloro-1,1′-diphenyl-1,1′-azopropane in 85% aqueous acetone at 0° showed an apparent rate constant which decreased from 8.2×10^{-4} to 5.8×10^{-4} sec^{-1} during the reaction. As in the work of Benzing[24] this attenuation was assigned to common ion rate suppression on the basis of an invariant rate constant of 2.7×10^{-4} sec^{-1} measured in the presence of 0.1 *M* LiCl. When hydrolysis in the presence of 0.1 *M* LiCl was interrupted after about two half-lives (5100 sec), recovered starting material showed no trace of the *dl*-diastereomer, although 3% of this isomer would have been readily detected by nmr. The first-order rate constant for epimerization of the starting material is thus less than 3×10^{-6} sec^{-1}. The total rate of ionization with return by external chloride must be at least equal to the decrease in rate due to added chloride ($8.2 \times 10^{-4} - 2.7 \times 10^{-4} = 5.5 \times 10^{-4}$ sec^{-1}) and is perhaps as much as three times this large, since Benzing found rate enhancement for hydrolysis by a factor of 2.6 from addition of 0.1 *M* $LiClO_4$.[24] The nucleophilic displacement of chloride by chloride must proceed with greater than $1 - [(3 \times 10^{-6})/(5.5 \times 10^{-4})] = 99.5\%$ retention of configuration.

(20) K. Fukui, *Tetrahedron Lett.*, 2427 (1965); K. Fukui and H. Fujimoto, *ibid.*, 4303 (1965); *Bull. Chem. Soc. Jap.*, **39**, 2116 (1966); **40**, 2018 (1967).
(21) K. B. Wiberg, *J. Amer. Chem. Soc.*, **90**, 59 (1968).
(22) The difference is probably exaggerated; see ref 21.
(23) S. Goldschmidt and B. Acksteiner, *Ann.*, **618**, 173 (1958).
(24) E. Benzing, *ibid.*, **631**, 1, 10 (1960).

Overall stereospecificity through both displacement steps was shown for acetolysis in buffered acetic acid and for displacement by cyanide in acetone–methanol–water (40/40/20 by volume).[25] The *meso* and *dl* diastereomers of 1,1′-dichloro-1,1′-diphenyl-1,1′-azopropane were solvolyzed separately to single diastereomers of the diacetoxyazoalkane in 70% yield with no detectable crossover (<10%). Similarly, a single diastereomer of 2,2′-dichloro-1,1′-diphenyl-2,2′-azopropane was converted to a single azodinitrile under conditions which converted a mixture of dichloroazo diastereomers to a mixture of azodinitrile diastereomers.

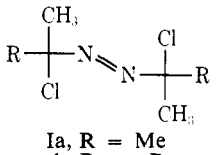
Although these reaction mixtures are heterogeneous, the fact that unreacted starting material and the products of one and two displacements can be observed simultaneously leads us to believe that the two displacements are similar in rate and mechanism. Given the implausibility of bridging by both acetate or phenyl and cyanide to an adjacent nitrogen,[26] or to a



tertiary benzylic carbon, we can exclude the intermediates of mechanisms b and c as sources of stereospecificity in the second displacement.

Hydrolysis Rates. A choice between mechanisms d and e can be attempted on the basis of steric effects on reaction rates. The 1,4-chlorine addition itself is not well suited for such a study since the first step is probably rate limiting and its transition state geometry is uncertain. However, since the intermediates for 1,4-chlorine addition and for hydrolysis are very likely identical, the mechanistic distinction can be based on rates for the latter process. Our failure to observe any chloro alcohol along with starting material when hydrolysis of 1,1′-dichloro-1,1′-diphenyl-1,1′-azopropane was interrupted after two half-lives shows that here initial ionization is rate determining.

A bulky substitutent, R, would be expected to retard ionization of I to a diazirinium ion (mechanism d)

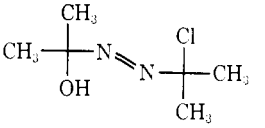


Ia, R = Me
b, R = *t*-Bu

because of increasing repulsion with the β-nitrogen and its substitutent. This repulsion should outweigh the small relief in B strain from opening the $RCCH_3$ angle from tetrahedral to trigonal. Relief of B strain would be the primary consideration in ionization to the allene-like intermediate (mechanism e), and some acceleration of hydrolysis would be expected for bulky R.

Hydrolyses of Ia and Ib at 20° in 85% aqueous acetone were monitored by nitrogen evolution. Initial first-order rate constants for these compounds were estimated to be 8.6×10^{-4} sec^{-1} and 37.4×10^{-4} sec^{-1}, respectively.[27] The rate increase by a factor of about 4 for the more hindered compound is consistent with ionization to the allene-like intermediate. The analogous ionization of 2-chloro-2,3,3-trimethylbutane is usually about twice as fast as that of *t*-butyl chloride in a variety of solvents.[28]

Hydrolysis Products. The products from hydrolysis of Ia are acetone, nitrogen, isopropyl alcohol, HCl, isopropyl chloride, and propylene.[24] Benzing rationalized formation of these products in terms of intermediate II which can undergo stepwise or concerted



II

cleavage to acetone, diazoisopropane, and HCl.[24] The colors of diazoalkanes can be observed during solvolysis in anhydrous alcohol.[23] If a diazirinium ion were an intermediate in the second step of the hydrolysis, one would not expect to observe the diazoalkane products since loss of (protonated) ketone would leave a diazirine which is known to be stable even in strong acid.[19]

All lines of evidence suggest that the allene-like cation is an intermediate both in the synthesis and in the nucleophilic displacement reactions of α,α′-dichloroazoalkanes.

Experimental Section[29]

Hydrolysis rates were followed by nitrogen evolution on an apparatus similar to that of Benzing.[24] Solvent and an acetone solution of α,α′-dichloroazoalkane were allowed to equilibrate in the constant-temperature bath (±0.1°) for 10 min before mixing to give 50 ml of a solution 85% acetone–15% water by volume. Substrate concentration was in the range 0.03–0.1 *M*. Rate constants were estimated from the early slopes of first-order plots. An excess gas evolution of 2–10% over theoretical nitrogen was noted, but not investigated further. This excess cannot be due to elimination products in all cases.[24]

Epimerization of *meso*-1,1′-dichloro-1,1′-diphenyl-1,1′-azopropane during hydrolysis was tested by dissolving 5.0 g of the azoalkane in 550 ml of 85% aqueous acetone (0.10 *M* LiCl) at 0°. After stirring for 5100 sec (~2 half-lives) the organic material was extracted into 1000 ml of pentane, washed with saturated aqueous soldium chloride, and dried over magnesium sulfate. The solvent was stripped off, and volatile products were removed by pumping at 10^{-3} mm at room temperature. The remaining crystalline solid (1.1 g, mp 48–50°) was shown by nmr (CCl_4) to consist of starting material and a trace of propiophenone with none of the *dl* diastereomer of the starting material and no peaks attributable to 1-chloro-1′-hydroxy-1,1′-diphenyl-1,1′-azopropane.

Acetolysis of *meso*- and of *dl*-1,1′-dichloro-1,1′-dipheny-1,1′-azopropane was conducted according to the procedure of Benzing.[24] The *meso* compound (1.86 g, 5.5 mmol) was added to 15 ml of glacial acetic acid containing 1.18 g (22.2 mmol) of sodium acetate at room temperature. A chalky white precipitate formed immediately. After 3 hr of stirring, 100 ml of water was added, and the mixture was extracted with 200 ml of ether. The ether layer was washed with 10% aqueous sodium hydroxide and water and dried. Removal of the ether left a white semisolid containing 70% diacetate, 30% decomposition products (by nmr). Removal of the volatile decomposition products (10^{-3} mm, room temperature) left *meso*-1,1′-diacetoxy-1,1′-diphenyl-1,1′-azopropane (mp 146° dec, from chloroform) free of the *dl* isomer by nmr: nmr (10% in CH_2Cl_2) τ 2.6 (m, 10), 7.87 (s, 6), 7.99 (ABX_3, 4), 9.25 (t, 6); ir (10% in $CHCl_3$) 3108, 3079, 3045, 3024, 2995, 2958, 2899, 1965, 1897, 1768, 1618, 1600, 1512, 1480, 1468, 1400, 1387, 1349, 1310,

(25) Such overall specificity has also been observed for coupling with Grignard reagents.[1b,c]

(26) Such an intermediate could maintain stereochemistry during displacement by a mechanism related to b and involving *cis*-SNi′ and SN2′ displacements.

(27) The former value is within experimental error of Benzing's rate constant for Ia under the same conditions, 7.2×10^{-4} sec^{-1}.[24]

(28) E. Spinner, *J. Chem. Soc.*, 1590 (1956).

(29) Spectrometers, analyses, and materials were as described in ref 1c.

1250, 1198, 1160, 1125, 1095, 1035, 990, 931, 901, 712, 640, 628 cm^{-1}; uv $\lambda_{max}^{CHCl_3}$ 359 nm (ϵ 33).

Anal. Calcd for $C_{22}H_{26}N_2O_4$: C, 69.09; H, 6.85; N, 7.32. Found: C, 69.31; H, 6.83; N, 7.44.

Identical treatment of the *dl*-dichloride gave the *dl*-diacetate as a yellow oil: nmr (10% in CH_2Cl_2) τ 2.6 (m, 10), 7.89 (s, 6), 7.72 (*AB*X_3, 4), 9.24 (t, 6), no peaks for the *meso* isomer.

Cyanide displacement on 2,2′-dichloro-1,1′-diphenyl-1,1′-azopropane followed a procedure similar to that of Benzing.[24] Pure isomer A[1c] (6.7 g, 20 mmol) was added to 100 ml of acetone–methanol–water (40/40/20 by volume) containing 4.0 g (80 mmol) of sodium cyanide. A chalky precipitate formed immediately. After stirring for 3 hr at room temperature, 100 ml of water was added and the dinitrile was collected by filtration (3 g, 45% yield; mp 144° dec, from chloroform). The product was a single diastereomer of 2,2′-dicyano-1,1′-diphenyl-2,2′-azopropane: nmr (10% in $CDCl_3$) τ 2.75 (s, 10), 6.70 (AB, J = 14 Hz, δ = 0.11 ppm, 4), 8.49 (s, 6); ir (10% in $CHCl_3$) 3110, 3089, 3050, 3015, 2951, 2155, 1990, 1975, 1905, 1832, 1769, 1625, 1607, 1519, 1472, 1399, 1268, 1250, 1185, 1140, 1050, 932, 719, 658 cm^{-1}; uv $\lambda_{max}^{CHCl_3}$ 348 nm (ϵ 39).

Anal. Calcd for $C_{20}H_{20}N_4$: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.79; H, 6.50; N, 17.49.

Identical treatment of the 53/47 mixture of isomers B and A gave a mixture of dinitriles in roughly equal amounts (by nmr): nmr (isomer B, $CDCl_3$) τ 2.76 (s, 10), 6.76 (*AB*, 4), 8.39 (s, 6).

Acknowledgments. We thank Professor K. B. Wiberg for copies of the programs used and for use of the PDP-8 computer. The 60- and 100-MHz nmr spectrometers were provided by institutional grants from the National Science Foundation to Yale University. D. S. M. thanks the National Institutes of Health for predoctoral fellowship support (1967–1969). This work was supported in part by Grant GM-15166 from the U. S. Public Health Service, National Institute of General Medical Sciences.

Appendix

Geometries for MO Calculations. Atomic coordinates for input to the CNDO/2 program were calculated from bond lengths, angles, and torsional angles using Wiberg's program.[17] The reaction coordinate was simulated by changing these parameters between chosen initial and final values by increments proportional to the fraction of reaction. For example, in calculating the electrocyclic closure to a diazirinium ion, the N_1–N_2 bond lengths for 0, 33, 67, and 100% reaction were 1.39, 1.34, 1.28, and 1.23 Å, respectively. The angle of incidence between an N–C bond and an HCH plane was similarly varied from 90° to a value appropriate to the product so that the hydrogens would fold back as the new bond was formed. The extent of concertedness suggested by these proportional changes is probably exaggerated, but should not affect the qualitative interpretation of the results.

Parameters for the electrocyclic closure were chosen as follows: N_1–N_2 [1.39 Å (0%), chosen 0.06 Å shorter than in hydrazine (1.45 Å)[30] to allow for attenuation by hybridization change (0.08 Å for C–C[31]) and partial positive charge (1.41 Å for $N_2H_6^{2+}$ [30]); 1.23 Å (100%) from microwave spectrum of diazirine];[32] C_1–N_1 [1.30 Å (0%), lengthened by 0.03 Å from C=N distance of dimethylglyoxime (1.27 Å[33]); 1.48 Å (100%), from $CH_3NH_3^+$, etc.[34]]; N_2–C_2 [1.30 Å (0%), as for C_1–N_1; 1.48 Å (100%), from diazirine[32]]; C_1–H_5 [1.45 Å (0%), chosen arbitrarily to give half the overlap of a bonded hydrogen; 1.09 Å (100%), standard CH bond length[35]]; other C–H [1.09 Å throughout]; C_1–N_1–N_2 [116° (0%), from azoalkane crystal structures;[1c,36] 148° (100%), to bisect C_2–N_1–N_2]; N_1–N_2–C_2 [116° (0%), as for C_1–N_1–N_2; 65° (100%), from diazirine[32]]; N_1–C_1–H_5 [90° (0%), arbitrary; 109.5° (100%), tetrahedral]; H_1–C_1–H_2 [120° (0%), trigonal; 110° (100%), ~tetrahedral]; H_3–C_2–H_4 [120° (0%), trigonal; 117° (100%), from diazirine[32]]; C_1–N_1–N_2–C_2 [110° (0%), estimated from dipole moment of ketazines;[8] 180° (100%), planar].

Parameters for addition of hydride to an allene-like cation intermediate were as follows: CN [1.27 Å (0%), from dimethylglyoxime;[33] 1.48 Å (100%), from azoalkanes[1c,36]]; NN [1.25 Å throughout, from azoalkanes[1c,36]]; NH [1.02 Å throughout, from N_3H[37]]; CH^- [1.45 Å (0%), 1.09 Å (100%), as above for C_1–H_5]; CH [1.09 Å throughout, as above]; H–CN [90° (0%); 109.5° (100%), as above for H_5–C_1–N_1]; HCH [122° (0%), as in ketene;[38] 109.5° (100%), tetrahedral]; NNH [116° throughout, from NNC of azoalkanes]; CNN [180° (0%), linear; 116° (100%), as for NNH].

(30) L. E. Sutton, Ed., "Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement," Special Publication No. 18, The Chemical Society, London, 1965, p S7s.
(31) M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962, p 54.
(32) L. Pierce and V. Dobyns, *J. Amer. Chem. Soc.*, **84**, 2651 (1962).
(33) See ref 30, p S20s.
(34) See ref 30, p S19s.
(35) See ref 30, p S18s.
(36) See ref 1c, footnote 24.
(37) See ref 30, p S7s.
(38) H. R. Johnson and M. W. P. Strandberg, *J. Chem. Phys.*, **20**, 687 (1952).