α,α'-Dichloroazoalkanes. I. Synthesis: Stereospecificity and Side Reactions. The Crystal Structure of 1,1′-Dichloro-1,1′-diphenyl-1,1′-azopropane[1,2]

Donald S. Malament and J. Michael McBride

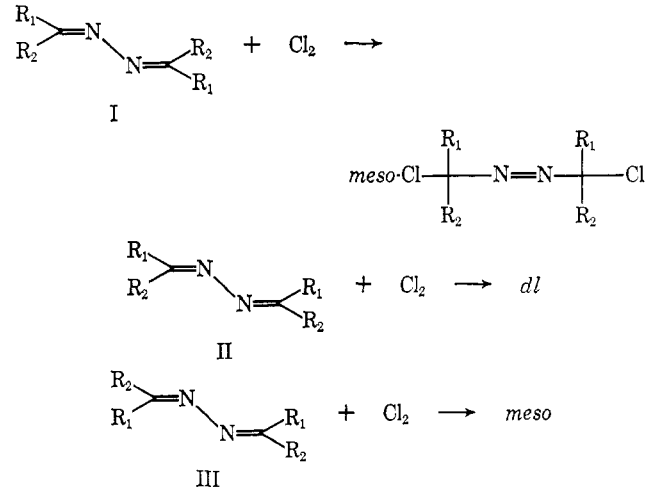
Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520. *Received November 14, 1969*

Abstract: The 1,4 addition of chlorine to ketazines in methylene chloride at −60° is shown by nmr to proceed stereospecifically so that symmetric (*syn,syn* or *anti,anti*) ketazine isomers give *meso*-α,α'-dichloroazoalkanes and unsymmetric (*syn,anti*) ketazine isomers give the *dl* product. Studies on equilibrium and nonequilibrium mixtures of ketazine isomers are reported. At low temperature addition is clean and does not involve radical chains, but at room temperature there is solvent dependent competition from ionic substitution of hindered ketazines and, in the light, from radical-induced decomposition of α-arylazoalkanes. Single crystal X-ray diffraction establishes the chlorine–nitrogen eclipsed conformation for *meso*-1,1′-dichloro-1,1′-diphenyl-1,1′-azopropane in the solid state with C—N and N=N bond distances of 1.46 and 1.24 ± 0.02 Å, respectively. Thermolysis of this azo compound and of its *dl* diastereomer gives cage coupling with ~10% stereospecificity.

As clean thermal and photochemical sources of carbon radical pairs azoalkanes have proven extremely important for radical chain initiation and for the study of free-radical reaction mechanisms. Azoalkanes with tertiary alkyl groups are especially useful because they are not subject to tautomerization to hydrazones. While azobisnitriles and their derivatives have long been readily accessible,[3] general methods for preparation of other "tertiary" azo compounds are relatively recent. They involve moderate yield oxidative coupling of the related amine[4,5] or isocyanate.[6]

The facility with which α,α'-dichloroazoalkanes may be prepared by chlorination of ketazines suggests their potential as intermediates in the synthesis of tertiary azoalkanes. While the initial studies on these compounds showed that chloride could be replaced by a number of nucleophiles,[7,8] efforts to introduce alkyl or aryl groups by coupling with methylmagnesium iodide,[9,10] phenylmagnesium bromide,[7] or phenyllithium[10] led only to ketazine formation. It has recently been found that excess methylmagnesium bromide[9] and methylmagnesium chloride[10] effect the desired transformation in 15–50% yield.

Our need for diastereomerically pure azoalkanes for use in investigating solvent effects on free radical cage reactions prompted us to investigate the stereochemistry of the synthesis of α,α'-dichloroazoalkanes and of their transformation to other azoalkanes. In this paper we discuss evidence for the stereospecific conversion of symmetrical (I, III) ketazines to *meso*-dichloroazoalkanes and of unsymmetrical (II) ketazines to racemic product and for the nature of competing reactions. In the following paper[11] we discuss the mechanism of the reaction in light of evidence on the mechanism for stereospecific conversion of the product to further azoalkanes.



Results and Discussion

Technique of Chlorination. The addition of chlorine to ketazines in a Dry Ice bath (~−60°) is generally insensitive to the nature or even the presence of solvent. Earlier workers have chlorinated both neat crystalline ketazine[7] and solutions or suspensions in petroleum ether[7,8] with quantitative product yields. We find that the reaction proceeds equally well in methylene chloride, sulfur dioxide, or acetyl chloride, at least for ketazine g. We have preferred methylene chloride, since the ketazines remain in solution throughout the reaction, and removal of the solvent under vacuum assures complete removal of excess chlorine leaving pure crystalline product. At higher temperature the reaction often becomes sensitive to solvent and to room light, especially for hindered or aromatic ketazines. The competing reactions involved under these conditions are discussed below.

(1) Based on the Ph.D. dissertation of D. S. M., Yale University, 1969.
(2) Presented in part at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstract ORGN 155.
(3) J. Thiele and K. Heuser, *Ann.*, **290**, 1 (1896).
(4) T. E. Stevens, *J. Org. Chem.*, **26**, 2531 (1961).
(5) (a) R. Ohme and E. Schmitz, *Angew. Chem. Intern. Ed. Engl.*, **5**, 433 (1965); (b) E. Farenhorst and E. C. Kooyman, *Recl. Trav. Chim.*, **72**, 933 (1953).
(6) H. Esser, K. Rastadter, and G. Reuter, *Chem. Ber.*, **89**, 685 (1956).
(7) S. Goldschmidt and B. Acksteiner, *Ann.*, **618**, 173 (1958).
(8) E. Benzing, *ibid.*, **631**, 1 (1960).
(9) J. W. Timberlake and J. C. Martin, *J. Org. Chem.*, **23**, 4054 (1968).
(10) D. S. Malament, Thesis, Yale University, 1969.
(11) D. S. Malament and J. M. McBride, *J. Amer. Chem. Soc.*, **92**, 4593 (1970).

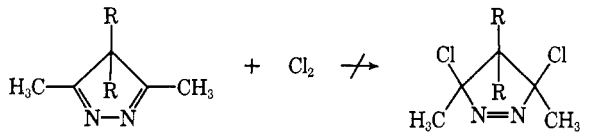
Table I. Isomer Ratios of Ketazine Chlorination in CH_2Cl_2 at −60°

	Ketazine		Isomer, %[b]			Product ratio[a]		
	R_1	R_2	I	II	III	Scheme I	Scheme II	Obsd[c]
			Equilibrium Ketazines					
a	CH_3	C_2H_5	6	41	53	0.70	0.36	0.67
b		i-C_3H_7	0	20	80	0.25	0.11	0.25
c		t-C_4H_9	0	0	100	0	0	*d*
d		β-$C_{10}H_7$	0	0	100	0	0	*e*
e		$CH_2C_6H_5$	10	44	46	0.79	0.47	0.89
f	C_6H_5	CH_3	100	0	0	0	0	*e*
g		C_2H_5	100	0	0	0	0	<0.03
h		i-C_3H_7[f]	16	38	46	0.61	0.54	0.82
i		t-C_4H_7	0	0	100	0	0	*d*
			Nonequilibrium Ketazines					
d	CH_3	β-$C_{10}H_7$	0	60	40	1.5	0.43	*e*
f	C_6H_5	CH_3	50	50	0	1.0	0.33	*e*
g		C_2H_5	58	42	0	0.72	0.27	0.69
h		i-C_3H_7	0	0	100	0	0	<0.05

[a] Isomer which is minor in chlorination of equilibrium ketazine/isomer which is major under these conditions. [b] Percentages determined by nmr are probably accurate to about 10% of their magnitudes. The predicted ratios are also subject to this error. [c] Measured by nmr, accurate to about 15% of the magnitude. [d] There was only evidence for one isomer; by analogy the other should have been easily seen.[16] [e] There was only evidence for one isomer, but the other probably would have been indistinguishable (see text). [f] We are indebted to Mr. Nathan Karch for checking these values.

The ketazines which underwent 1,4-chlorine addition are listed in Table I. The α,α'-dichloroazoalkanes were characterized by combinations of uv, ir, and nmr spectroscopy and elemental analysis. They all decomposed with nitrogen evolution on dissolution in methanol or aqueous acetone. The synthesis was clean and homogeneous for all ketazines in Table I and complete within 5 min after addition of excess chlorine for all but i. After 2.5 hr about one-third of pivalophenone azine remained, but after 5 hr conversion to the product was complete. In crude competition experiments less than 1 equiv of chlorine was added to 1 equiv each of acetone azine and either acetophenone azine in CCl_4 at room temperature or pinacolone azine in methylene chloride at −60°. In both cases all chlorine was consumed by 1,4 addition to 80–90% of the acetone azine, while less than 3% of the other ketazine reacted. Thus acetone azine is at least 40 times[12] as reactive as these others.

The ketazine of *p*-methoxyacetophenone failed to give a dichloroazoalkane. Its reaction solution became turbid with azine–HCl and a mixture of unstable products was isolated. Attempts to establish the presence of a small amount of the azo compound in the solid product mixture by conversion to the acetate in buffered acetic acid[8] led only to ketazine, *p*-methoxyacetophenone, and a substance tentatively identified as 1-*p*-anisylethanol. In the cases of 3,4,4,5-tetramethyl-4H-pyrazole and 3,5-dimethyl-4,4-dibenzyl-4H-pyrazole 1,4-chlorine addition again failed. These reaction solutions also became cloudy and only the hydrochloride salt of the starting material was isolated.



R = CH_3 or CH_2Ph

Ketazine Isomerism. The ketazines which give 1,4 addition are subject to *syn,anti* imine isomerism with the possibility for one unsymmetrical (II) and two symmetrical (I, III) isomers. As Elguero has shown, isomers with bulky groups *anti* to the β-nitrogen are favored at equilibrium.[13] This may result from repulsion between the *syn* substitutents on opposite ends of the molecule as well as from their interaction with the β-nitrogen, since ketazines, unlike dienes, are probably nonplanar in their lowest energy conformation in solution.[11,14] Preferences calculated from our rough nmr determinations of equilibrium isomer ratios (Table I) are consistent with those measured by Karabatsos for dinitrophenylhydrazones and semicarbazones.[15] The second part of Table I lists the nonequilibrium ketazine isomer mixtures which were chlorinated. The first three entries (d, f, g) are for experiments conducted on mixtures enriched in the unsymmetrical isomer by irradiation with a 450-W medium-pressure mercury arc in benzene solution containing benzil sensitizer and a small amount of pyridine. The last entry is for h obtained by slow crystallization from methanol solution. These mixtures are subject to slow thermal equilibration in solution at room temperature,[10] but were chlorinated before a significant amount of reversion had occurred.

Steric Specificity in 1,4 Addition. The most striking feature of our results is that in every case where a single symmetrical ketazine isomer was chlorinated, the nmr spectrum of the crude product gave evidence for only one product diastereomer, while in all but two cases involving a mixture of symmetrical and unsymmetrical ketazine isomers nmr spectra showed a mixture of product diastereomers. The two exceptions (d and f) involve azo compound diastereomers which should be very difficult to distinguish by nmr because of interference by benzil sensitizer in the aromatic region and similarity between the diastereomers in chemical shift of the α-methyl groups.[16] That this steric specificity

(12) Log (A_0/A)/log (B_0/B) > log 5/log 1.03 = 40.

(13) J. Elguero, *et al.*, *Bull. Soc. Chim. Fr.*, 877 (1965); 713 (1968).

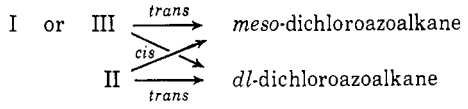
(14) Yu. P. Kitaev, *et al.*, *Dokl. Akad. Nauk SSSR, Ser. Khim.*, **178**, 1328 (1968).

(15) G. J. Karabatsos, J. D. Graham, and F. M. Vane, *J. Amer. Chem. Soc.*, **84**, 753 (1962).

(16) Such α-methyl groups are indistinguishable between diastereo-

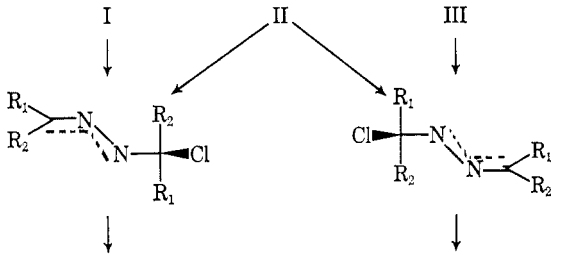
holds for pure isomers and isomer mixtures of the same ketazines (g, h) shows it to be a kinetic rather than a thermodynamic phenomenon. Such specificity could result either from overall stereospecific *cis*- or *trans*-1,4 addition of the chlorine fragments (Scheme I) or

Scheme I. Stereospecific *trans* (or *cis*) Addition



from unusually efficient asymmetric induction in a stepwise mechanism in which chirality at the center generated in addition of the second chlorine is determined by geometrical isomerism at the center to be attacked and by chirality at the first center (Scheme II).

Scheme II. Asymmetric Induction



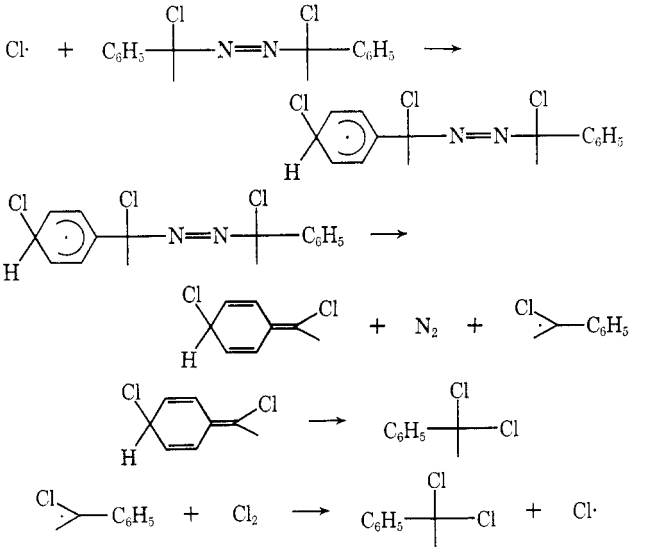
The first possibility predicts that the symmetrical isomers of a given ketazine would both give one product diastereomer, while the unsymmetrical isomer would give the other. The second possibility predicts that the symmetrical isomers would give different diastereomers, while the unsymmetrical isomer could give either or a mixture depending on the ketazine configuration at the site of the initial attack. The choice between these possibilities would be unambiguous if results were available for chlorination of a pure unsymmetrical isomer or of a mixture of symmetrical isomers free of the unsymmetrical isomer. We have been unable to test such an unambiguous case, but comparison of the observed diastereomer ratios with those calculated on the basis of the two possibilities (last three columns of Table I) leaves little doubt that we are dealing with stereospecific *cis* or *trans* addition.

Sense of the Steric Specificity. Our initial prejudice was that the 1,4 addition should be *cis* in conformity with Fukui's predictions for concerted noncyclic additions.[19] Thus a symmetrical *s-trans*-ketazine should give *dl* product, and an unsymmetrical *s-trans*-ketazine should give *meso* product. Our inclination was reinforced by the observation that the new diastereomer from chlorination of the isomer mixture of ketazine g is higher melting (mp 78° dec) than that from chlorination of the pure symmetrical isomer (mp 59°). However, thermolysis of the latter azo compound under conditions which led to significant specificity in formation of the radical cage coupling product gave 3,4-dichloro-3,4-diphenylhexane enriched in its higher melting diastereomer, while the higher melting azo compound gave predominantly the lower melting coupling product. When efforts at resolving the lower melting dichloroazoalkane by partial decomposition with brucine in benzene proved unsuccessful, we undertook the structure determination of the compound by X-ray diffraction. The results reported below show that in fact this diastereomer has the *meso* configuration. Thus it appears that *symmetrical ketazines chlorinate to give meso-dichloroazoalkanes, while unsymmetrical ketazines yield dl-dichloroazoalkanes.* We have found no conditions under which the 1,4 addition is not stereospecific, but competing reactions can become important at higher temperature.

Radical-Induced Decomposition. With 1 equiv of chlorine, addition to most ketazines in methylene chloride solvent is as clean at 0° or room temperature as it is at Dry Ice temperature. The same is true in reaction with excess chlorine both for aliphatic azines and, in the dark, for aromatic azines. However, in ordinary fluorescent room light the α,α'-diphenyldichloroazoalkane from ketazine g is converted to a pungent oil in 15 min by excess chlorine. The radical chain nature of this reaction was confirmed by the finding that addition of excess chlorine to a 1% solution of ketazine g in methylene chloride containing 20% by volume of cyclohexane and removal of excess chlorine all in the dark gave less than 0.1% chlorocyclohexane both at Dry Ice temperature and at room temperature, while reaction with excess chlorine in methylene chloride at room temperature in room light for the same time gave 20% conversion of cyclohexane to chlorocyclohexane. These experiments also show that the 1,4-chlorine addition does not involve radical chains.[20]

The major product from radical chain chlorination of 1,1′-dichloro-1,1′-diphenylazoethane was (1,1-dichloroethyl)benzene. Smaller amounts of (1,1,2-trichloroethyl)benzene and (1,1,2,2-tetrachloroethyl)benzene, presumably derived from the initial product, were also found. The fact that only α-arylazoalkanes are subject to this reaction suggests the induced decomposition chain of Scheme III.

Scheme III



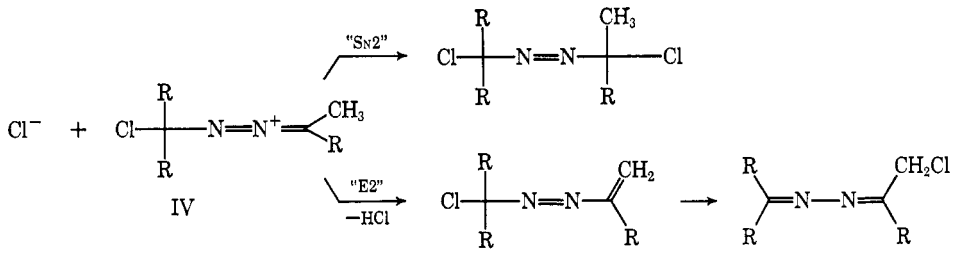
mers of the analogous azo compounds 3,3′-dimethyl-2,2′-diphenyl-2,2′-azobutane[17] and 2,2′-diphenyl-2,2′-azobutane.[18]

(17) P. D. Bartlett and J. M. McBride, *Pure Appl. Chem.*, **15**, 89 (1967).

(18) J. M. McBride, Thesis, Harvard University, 1967.

(19) K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jap.*, **39**, 2116 (1966); **40**, 2018 (1967).

(20) The cyclohexane text for radical chain chlorination has been used extensively by M. L. Poutsma, *J. Amer. Chem. Soc.*, **87**, 2161, 2172, 4285 (1965).



Ionic Substitution. Simple aliphatic ketazines give clean stereospecific 1,4 addition with excess chlorine in CCl_4 at 0° or room temperature with little evolution of heat. However, in this solvent ketazines with bulky substitutents (*e.g.*, pinacolone azine) and alkyl aryl ketazines react exothermically to give ketazines in which protons α to the imine groups in the starting material are replaced by chlorine. The chlorinated azines are inert to 1,4 addition. One equivalent of chlorine converts acetophenone azine to 3 parts of monochlorinated product and 1 part of symmetrically dichlorinated product, showing that the substitution is stepwise. The ionic rather than radical chain character of the reaction is demonstrated by the absence of chlorine substitution at other positions in the ketazines and by the absence (<0.1%) of chlorocyclohexane when the reaction is run in the presence of 20% cyclohexane.

In the following paper[11] we propose intermediate IV for 1,4-chlorine addition to ketazines. IV can add chloride in a slow second step analogous to SN2 substitution, but there can be competition from nucleophilic attack on an α-proton analogous to E2 elimination. The product of the latter sequence should readily undergo ionic isomerization to the observed α-chloro ketazine. Increase in the "E2" component at higher temperatures with increasing hindrance of the carbon center and decreasing solvent polarity is reasonable and consistent with trends observed in other SN2–E2 competitions.[21] A middle ground can be found in the chlorination of pinacolone azine in methylene chloride at room temperature which leads to a mixture of dichloroazoalkane, substitution product, and a small amount of an unidentified product.

Crystal Structure of *meso*-1,1′-Dichloro-1,1′-diphenyl-1,1′-azopropane. Needle crystals of 1,1′-dichloro-1,1′-diphenyl-1,1′-azopropane (mp 56°) were grown from methylene chloride solution and washed with cold hexane. The unit cell was triclinic, a = 10.43 Å, b = 13.98 Å, c = 6.06 Å, α = 84.29°, β = 85.11°, γ = 81.27°, v = 861.99 Å^3, Z = 2, D_c = 1.26 g/cm^3; space group $P\bar{1}$. Using an automated Picker diffractometer with Cu Kα radiation, the 1364 independent reflections within $\sin\theta/\lambda$ = 0.45 were measured with the stationary crystal, stationary counter technique.[22] The crystal yellowed and decomposed during irradiation causing a substantial decrease in intensity due primarily to increasing mosaic spread. This falloff was largest for equatorial reflections of the needle crystal suggesting fragmentation to parallel needles. In addition to the standard intensity corrections a term of the form $A + B\cos\chi$ was applied to correct for the anisotropic mosaic spread. A and B are time dependent and were determined by monitoring standard axial (χ = 90°) and equatorial (χ = 0°) reflections after every 30 measurements.

Chlorine atoms were located from the Patterson map, and a difference synthesis revealed the carbon and nitrogen atoms. Full matrix least squares refinement of three scale factors and of the atomic coordinates and isotropic temperature factors omitting the hydrogen atoms led to an R of 0.124.[23] Final atomic coordinates are presented in Table II. While the calculated root mean square deviations for this level of refinement are about 0.01 Å in bond length and 1° in bond angle, the consistency between symmetrically independent halves of the molecule is 0.02 Å and 2°.

Table II. Fractional Coordinates

Atom[a]	x	y	z
N	0.2331 (8)	−0.2546 (6)	0.3555 (15)
C-1	0.1071 (11)	−0.1950 (8)	0.4053 (19)
C-2	0.1153 (11)	−0.1483 (9)	0.6275 (19)
C-3	0.2209 (11)	−0.0791 (8)	0.6168 (19)
Cl	0.0675 (3)	−0.0945 (2)	0.1923 (5)
C_{ar}-1	0.0058 (11)	−0.2614 (8)	0.4225 (19)
C_{ar}-2	−0.0790 (13)	−0.2648 (10)	0.2584 (22)
C_{ar}-3	−0.1680 (15)	−0.3337 (11)	0.2825 (26)
C_{ar}-4	−0.1739 (14)	−0.3994 (10)	0.4669 (24)
C_{ar}-5	−0.0870 (16)	−0.3983 (12)	0.6341 (27)
C_{ar}-6	0.0037 (14)	−0.3319 (11)	0.6087 (23)
N′	0.2784 (8)	−0.2436 (6)	0.1611 (15)
C-1′	0.4004 (11)	−0.3045 (8)	0.1024 (18)
C-2′	0.3752 (11)	−0.3675 (8)	−0.0837 (19)
C-3′	0.2725 (11)	−0.4366 (8)	−0.0059 (19)
Cl′	0.4646 (3)	−0.3884 (2)	0.3355 (5)
C_{ar}-1′	0.4999 (11)	−0.2346 (8)	0.0344 (19)
C_{ar}-2′	0.5740 (13)	−0.2412 (10)	−0.1748 (22)
C_{ar}-3′	0.6653 (16)	−0.1728 (12)	−0.2263 (27)
C_{ar}-4′	0.6813 (15)	−0.1051 (12)	−0.0852 (26)
C_{ar}-5′	0.6059 (15)	−0.0990 (11)	0.1223 (26)
C_{ar}-6′	0.5148 (12)	−0.1682 (9)	0.1774 (21)

[a] Primed atoms are on the remote half of the molecule in Figure 1.

Bond lengths, angles, and torsional angles of interest are presented in Table III. This was the first crystal structure determination of a pure azoalkane. The C—N and N=N bond lengths and the CN=N bond angle are identical within experimental error to those measured for the copper complex of azomethane by X-ray diffraction.[24] The N=N bond lengths for

(21) See, for example, D. V. Banthorpe, "Elimination Reactions," Elsevier Publishing Co., Amsterdam, 1963, Chapter 2, and the discussion of ref 10, pp 53–57. A referee has pointed out that the contrary effect with respect to solvent polarity is observed for zwitterionic intermediates from electrophilic attack on enamines.

(22) The X-ray equipment was made available to us by Professor Harold Wyckoff of the Department of Molecular Biophysics, Yale University.

(23) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least Squares Program," Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(24) (a) I. D. Brown and J. D. Dunitz, *Acta Cryst.*, 13, 28 (1960). (b) The corresponding values for crystalline azobisisobutyronitrile are 1.47, 1.22, and 115°, respectively.[25]

(25) A. J. Bronkesh, D. S. Malament, K. J. Skinner, and J. M. McBride, Abstracts of Papers, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstract ORGN-118.

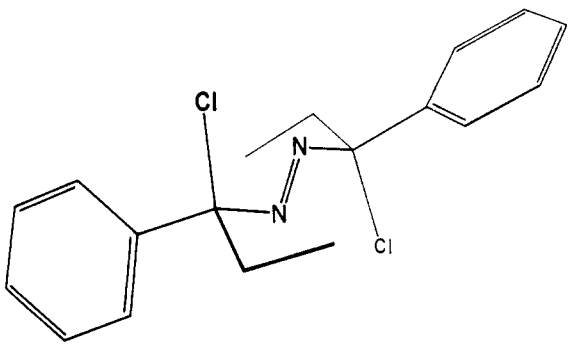


Figure 1. Crystal state conformer of *meso*-1,1′-dichloro-1,1′-diphenyl-1,1′-azopropane.

azomethane in the gas phase[26] and for many azo-aromatics in the crystalline state[27] also agree with our value within the limits of error.

Table III. Selected Bond Distances, Angles, and Torsional Angles for *meso*-1,1′-Dichloro-1,1′-diphenyl-1,1′-azopropane

Atoms	Distance (±0.02 Å)	Atoms	Angle (±2°)
N=N	1.24	CN=N	116
CN	1.47	ClCN	108
CCl	1.84		

Atoms	Torsional angle (±3°)
CN=NC	3
ClCN=N[a]	16
$C_{ar}C_{ar}CCl$[a,c]	19
ClCN=N[b]	0
$C_{ar}C_{ar}CCl$[b,c]	69

[a] Refers to the near end of the molecule in Figure 1. [b] Refers to the far end of the molecule in Figure 1. [c] Torsional angle between the phenyl ring and the C—Cl bond.

The conformation of the molecule in the crystal is shown in Figure 1. It lacks a center of symmetry because of differences in conformation about the bonds joining the central carbon atoms to the aromatic rings and to the nitrogen atoms. The latter difference is not large; the ClCN=N torsional angle at the near end of the molecule in Figure 1 is 16°, while that at the far end is 0°. Complete eclipsing has also been found for the CC≡N and N=N bonds of crystalline azobisisobutyronitrile.[25] Whether this conformational preference results from electrostatic repulsion with the unshared pair of the α-nitrogen, from an attractive interaction with the β-nitrogen, or from some other source is not clear.

The somewhat short intermolecular Cl–Cl distances (3.53, 3.54 Å) and the rather long C–Cl bonds are consistent with crystal stabilization by Cl–Cl non-bonded attraction and have been observed in other cases.[28] The length of the C–Cl bonds may also be related to their facile heterolysis.[7,8,11] The centers of symmetry in the crystal are at the Cl–Cl contacts.

(26) C. H. Chang, R. F. Porter, and S. H. Bauer, *Acta Cryst.*, **A25**, S152 (1969).

(27) See, for example, those in L. E. Sutton, Ed., "Tables of Interatomic Distances, and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

(28) F. Mo and H. Sorum, *Acta Cryst.*, **B24**, 605 (1968); D. Mootz, *ibid.*, **B24**, 839 (1968); I. L. Karle and J. Karle, *ibid.*, **B25**, 1097, (1969).

Experimental Section

Proton nmr spectra were measured using Varian A-60, A60-A, and HA-100 spectrometers. Ir and uv spectra were taken on Perkin Elmer 421 and Bausch and Lomb Spectronic 505 instruments. Mass spectra were recorded on an AEI-MS9 mass spectrometer. Elemental analyses were by Galbraith Laboratories, Knoxville, Tenn. Chemicals were reagent grade and used without further purification except as noted.

Ketazines were prepared (except as noted below) by refluxing 2 mol of ketone with one of 97% hydrazine in ethanol containing 2–3 ml of concentrated hydrochloric acid for about 1 hr.[29] Solid ketazines were recrystallized from methanol to literature melting point and showed no impurities (<5%) in pmr. Liquid ketazines were distilled and shown by pmr to be of a similar degree of purity.

Addition of Chlorine to Equilibrium Ketazines. General Procedure. A 10% solution (w/v) of the ketazine was prepared in methylene chloride and cooled to *ca.* −70° in Dry Ice–acetone. Chlorine was bubbled in until excess chlorine was observed. (This is somewhat difficult in the case of aryl ketazines because these azines and chlorine have a similar color in solution.) The solution was allowed to stand for 5 min, and then excess chlorine and solvent were removed using a flash evaporator and warming the flask containing the mixture with a pan of water at ambient temperature.

Chlorine Addition to 2-Butanone Azine (a). A sample of 2,2′-dichloro-2,2′-azobutane was prepared from 2-butanone azine according to the general procedure. The yellow liquid sample appeared identical with that prepared by Benzing.[8] A 100-MHz nmr spectrum in benzene showed methyl singlets separated by 2.4 Hz for the two isomers of 2,2′-dichloro-2,2′-azobutane.

Chlorine addition to 3-methyl-2-butanone azine (b), which 100-MHz nmr showed to be a 4:1 mixture of symmetrical and unsymmetrical isomers,[30] gave a mixture of diastereomers of 2,2′-dichloro-3,3′-dimethyl-2,2′-azobutane in the ratio 4:1 as shown by 100-MHz nmr in benzene by methyl singlets at τ 5.53 and 5.60, respectively, and by pairs of methyl doublets centered at τ 6.17, 6.13, and τ 6.15, 6.26, respectively.

Addition of Chlorine to Pinacolone Azine (c). Pinacolone azine was prepared according to the procedure of Overberger.[31] A sample of 2,2′-dichloro-3,3,3′,3′-tetramethyl-2,2′-azobutane was prepared from the azine according to the general procedure. The crystalline product (mp 93°) was obtained as light tan cubes in quantitative yield: nmr (10% carbon tetrachloride) τ 8.25 (singlet, 6 H), 8.82 (singlet, 18 H); ir (10% carbon tetrachloride) 2975, 2920, 2880, 1485, 1465, 1395, 1375, 1240, 1131, 1071, 840, 625 cm^{-1}; uv (in hexane) λ_{max} 3710 Å (log ϵ_{max} 1.39).

Anal. Calcd for $C_{12}H_{24}N_2Cl_2$: C, 53.93; H, 9.05; N, 10.48; Cl, 26.54. Found: C, 53.78; H, 9.18; N, 10.60; Cl, 26.73.

Chlorine Addition to 2-Acetonaphthone Azine (d). A sample of 1,1′-dichloro-1,1′-bis(2-naphthyl)-1,1′-azoethane (mp 137° dec) was prepared from 2-acetonaphthone azine according to the general procedure. The nmr spectrum of the crude product in benzene and 50/50 benzene–pyridine showed only one methyl singlet.

Addition of Chlorine to Phenylacetone Azine (e). A sample of 2,2′-dichloro-1,1′-diphenyl-2,2′-azopropane was prepared from phenylacetone azine according to the general procedure. The product was obtained as a brown semisolid. The nmr spectrum (10% in carbon tetrachloride) shows that two isomers of 2,2′-dichloro-1,1′-diphenyl-2,2′-azopropane are present (B/A = 53/47): nmr (A) τ 2.86 (apparent singlet, 10 H), 6.63 (AB pattern observed as apparent doublet split by 3.5 cps, 4 H), 8.35 (singlet, 6 H); (B) τ 2.86 (apparent singlet, 10 H), 6.69 (AB pattern observed as apparent singlet, 4 H), τ 8.28 (singlet, 6 H).

Isomer A (mp 91°) could be isolated upon recrystallization from hexane: ir (A) (10% in carbon tetrachloride) 3092, 3070, 3038, 2990, 2939, 1948, 1872, 1805, 1608, 1499, 1458, 1450, 1375, 1220, 1170, 1110, 1080, 1055, 1030, 920, 832, 693, 660, 630 cm^{-1}.

Anal. (A) Calcd for $C_{18}H_{20}N_2Cl_2$: C, 64.48; H, 6.02; N, 8.36; Cl, 21.15. Found: C, 64.70; H, 6.11; N, 8.52; Cl, 21.36.

Addition of Chlorine to Acetophenone Azine (f). Samples of 1,1′-dichloro-1,1′-diphenyl-1,1′-azoethane were prepared according to the general procedure. Highly crystalline, slightly yellow product

(29) W. A. Schulze and H. L. Lochte, *J. Amer. Chem. Soc.*, **48**, 1030 (1926).

(30) Elguero has mistakenly assigned a 9:1 ratio to this equilibrium by neglecting superposition of three of the six methyl peaks of unsymmetrical b on the three methyl singlets of symmetrical b.[13]

(31) C. G. Overberger and M. B. Berenbaum, *J. Amer. Chem. Soc.*, 73, 2618 (1951).

was obtained (mp 110° dec). The samples appeared to be identical with those prepared by Goldschmidt:[7] uv (in hexane) λ_{max} 2070, 3640 Å (log ϵ_{max} 1.72); nmr (10% carbon tetrachloride) τ 2.25 (multiplet, 4 H), 2.80 (multiplet, 6 H), 7.84 (singlet, 6 H).

The nmr spectra in chloroform, benzene, acetonitrile, benzonitrile, pyridine, nitrobenzene, and carbon disulfide showed only a single nmr upfield singlet. The same product was obtained when the addition was effected in sulfur dioxide or acetyl chloride solvent at −70°.

Addition of 1 Equiv of Chlorine to Acetophenone Azine at Room Temperature. One equivalent of chlorine was obtained as a 19% (w/w) saturated solution in carbon tetrachloride at 0°.[32]

A solution containing 1.0 g of acetophenone azine (3.2 mmol) in 20 ml of methylene chloride was prepared at room temperature and 1.35 g of the saturated chlorine–carbon tetrachloride solution (3.2 mmol of chlorine) was added. The reaction solution was allowed to stand for 5 min, and the solvent was removed.

The nmr spectrum of the crude product in carbon tetrachloride, methylene chloride, dioxane, benzonitrile, and pyridine indicated only one methyl signal arising from 1,1′-dichloro-1,1′-diphenyl-1,1′-azoethane, and no other products were formed.

Addition of Chlorine to *trans,trans*-Propiophenone Azine (g). *meso*-1,1′-Dichloro-1,1′-diphenyl-1,1′-azopropane (mp 56°) was prepared from *trans,trans*-propiophenone azine according to the general procedure: nmr (10% in carbon tetrachloride) τ 2.37 (multiplet, 4 H), 2.75 (multiplet, 6 H), 7.55 (*AB*X$_3$, 4 H), 9.16 (triplet, J = 7 cps, 6 H); ir (10% in carbon tetrachloride) 3098, 3070, 3040, 3034, 2986, 2948, 2888, 1969, 1955, 1900, 1885, 1812, 1603, 1492, 1465, 1447, 1382, 1330, 1285, 1215, 1188, 1078, 1032, 935, 912, 841, 740, 685, 645, 590 cm^{-1}; uv (in hexane) λ_{max} 3600 Å (log ϵ_{max} 1.62).

Anal. Calcd for $C_{18}H_{20}N_2Cl_2$: C, 64.48; H, 6.02; N, 8.36; Cl, 21.15. Found: C, 64.43; H, 5.90; N, 8.43; Cl, 21.05.

Addition of Chlorine to Isobutyrophenone Azine (h). Precise quantitative estimation of the equilibrium proportion of the geometric isomers of isobutyrophenone azine was complicated by the substantial overlap of methyl resonances of isomers I and II.[13] Chlorine addition by the general procedure to a mixture of I, II, and III (~16:38:46) gave a 55:45 mixture of diastereomers of 1,1′-dichloro-2,2′-dimethyl-1,1′-diphenyl-1,1′-azopropane: nmr (chemical shift in parts per million from benzene solvent) major isomer 6.32 (doublet, J = 7 Hz, 6 H), 4.3 (septet, 2 H); minor isomer 6.13 (doublet, J = 7 Hz, 6 H), 6.04 (doublet, J = 7 Hz, 6 H), 4.3 (septet, 2 H). Both isomers showed broad phenyl multiplets (10 H) in CCl_4.

Addition of Chlorine to Pivalophenone Azine (i). Pivalophenone azine was prepared according to the procedure of Overberger.[31] A solution of 42.4 g of pivalophenone (0.26 mol) and 3.0 g of 97% hydrazine (0.10 mol) in a 100-ml round-bottom flask with condenser was heated at *ca.* 70° with magnetic stirring. The reaction was monitored for the disappearance of pivalophenone hydrazone by nmr. After 50 hr, the colorless ketazine was obtained in quantitative yield based on hydrazine (mp 79° from methanol): nmr (10% carbon tetrachloride) 2.71 (multiplet, 10 H), 3.08 (multiplet, 6 H), 9.10 (singlet, 18 H); ir (10% carbon tetrachloride) 3088, 3065, 3025, 2962, 2950, 2930, 2901, 2870, 1957, 1900, 1880, 1815, 1615, 1600, 1580, 1497, 1478, 1463, 1445, 1392, 1361, 1292, 1220, 1200, 1075, 1045, 1030, 1005, 990, 960, 910, 708, 695 cm^{-1}; uv (in hexane) λ_{max} 2340 Å (log ϵ_{max} 3.90).

Anal. Calcd for $C_{22}H_{28}N_2$: C, 82.45; H, 8.81; N, 8.74. Found: C, 82.61; H, 8.83; N, 8.56.

A sample of 1,1′-dichloro-1,1′-diphenyl-2,2,2′,2′-tetramethyl-1,1′-azopropane was prepared from pivalophenone azine according to the general procedure except that the reaction was allowed to proceed for 5 hr, at −70°. The crystalline product (mp 122°, from hexane) was obtained in quantitative yield: nmr (10% carbon tetrachloride) τ 2.20 (multiplet, 4 H), 2.70 (multiplet, 6 H), 8.99 (singlet, 18 H); uv (in hexane) λ_{max} 3600 Å (log ϵ_{max} 1.28), 2350, 2580, 2642, 2710.

Chlorine Addition to Nonequilibrium Ketazine Mixtures. Addition of Chlorine to Mixed Isomers of 2-Acetonaphthone Azine (d) and to Mixed Isomers of Acetophenone Azine (f). A solution of 1.0 g of acetophenone azine (isomer I), 0.3 g of benzil, and 1 ml of pyridine in 10 ml of benzene was cooled and irradiated through Pyrex with a 450-W medium-pressure Hg arc. After 100 min a pair of methyl singlets were observed in the nmr spectrum 0.04 and 0.13 ppm downfield from isomer I corresponding to 68% of the total ketazines. Assignment of these peaks to isomer II was confirmed by the clean thermal reversal of the photoisomerization.

Removal of solvent and pyridine from a 50/50 photomixture of IIf and If and chlorination by the general procedure gave 1,1′-dichloro-1,1′-diphenyl-1,1′-azoethane showing only one methyl singlet for 100 MHz; nmr in CCl_4, benzene, and pyridine solvents.

Similar results were obtained for chlorine addition to a 60/40 photomixture of isomers II and III of ketazine d (CH_3 singlets at τ 7.32 and 7.37 and at 7.44, respectively).

Addition of Chlorine to Mixed Isomers of Propiophenone Azine (g). A 58/42 mixture of isomers I and II of ketazine g (CH_3 triplets at τ 8.75 and at 8.58 and 8.63, respectively) containing ~30 wt % benzil was prepared by removing benzene and pyridine after photoisomerization.

The chlorine addition product mixture was a light tan semisolid. Nmr analysis clearly showed the presence of two isomers of 1,1′-dichloro-1,1′-diphenyl-1,1′-azopropane.

The *dl* isomer (mp 79° dec) was isolated by recrystallizing the product mixtures three times at 0° from hexane: nmr (10% carbon tetrachloride) τ 2.51 (multiplet, 4 H), 2.79 (multiplet, 6 H), 7.52 (*AB*X$_3$, 4 H), 9.03 (triplet, J = 7 cps, 6 H); ir (10% carbon tetrachloride) 3094, 3064, 3035, 3028, 2980, 2944, 2885, 1970, 1953, 1895, 1880, 1805, 1600, 1492, 1448, 1380, 1330, 1280, 1208, 1182, 1073, 1030, 999, 910, 840, 731, 690, 645 cm^{-1}; uv (in hexane) λ_{max} 3640 Å (log ϵ_{max} 1.66).

Chlorination was performed on a sample of *anti,anti*-propiophenone azine which had been obtained from a benzene–pyridine solution with added benzil without irradiation. This sample of ketazine was contaminated with benzil and traces of benzene and pyridine. The nmr spectrum of the crude chlorine addition product showed that only *meso*-1,1′-dichloro-1,1′-diphenyl-1,1′-azopropane was formed.

Addition of Chlorine to *syn,syn*-Isobutyrophenone Azine (IIIh). The colorless *syn,syn* isomer (mp 78°, lit.[13] mp 76°) was isolated by slow crystallization from a methanol solution of the mixed isomers. Addition of chlorine by the general procedure gave 1,1′-dichloro-1,1′-dimethyl-1,1′-diphenyl-1,1′-azopropane (mp 79° dec) with the nmr spectrum of the major isomer from chlorination of the equilibrated ketazine. None of the alternate isomer was detected.

Competitive Chlorination. Chlorination of Acetone Azine and Pinacolone Azine at −70° in Methylene Chloride. A solution was prepared containing 0.56 g (0.005 mol) of acetone azine and 1.00 g (0.005 mol) of pinacolone azine in 25 ml of methylene chloride at *ca.* −70° and 0.30 g (0.0042 mol) of chlorine (dissolved in carbon tetrachloride) was added. The reaction solution was allowed to stand in a Dry Ice–acetone bath for *ca.* 15 min, and then solvent was removed under vacuum. Nmr analysis revealed that ~85% of the acetone azine had reacted to form 2,2′-dichloro-2,2′-azopropane but no reaction product of pinacolone azine was detected.

Chlorination of Acetone Azine and Acetophenone Azine in Carbon Tetrachloride. A solution was prepared containing 0.56 g (0.005 mol) of acetone azine and 1.18 g (0.005 mol) of acetophenone azine in 25 ml of carbon tetrachloride, and 0.30 g (0.0042 mol) of chlorine (dissolved in carbon tetrachloride) was added at room temperature. The reaction solution was allowed to stand for *ca.* 5 min, and excess solvent was then removed under vacuum. Nmr analysis of the product mixture showed that ~85% of the acetone azine had reacted to form 2,2′-dichloro-2,2′-azopropane and no reaction product of acetophenone azine was observed.

Reaction of *p*-Methoxyacetophenone Azine with Chlorine. A sample of 1.0 g of *p*-methoxyacetophenone azine was placed in 40 ml of methylene chloride at −70°. A slow stream of chlorine was bubbled in. The solution became turbid. Excess chlorine and solvent were removed under vacuum. The product was a pungent yellow semisolid, partially soluble in methylene chloride. The nmr spectrum of the portion soluble in methylene chloride was complex and changed with time. Gas evolution was noted.

After one run the crude product (*ca.* 1.0 g) was added to 50 ml of acetic acid saturated with sodium acetate at room temperature, and stirred for 3 hr.[8] The solid material was then removed by filtration and washed twice with water. This material was shown to be *p*-methoxyacetophenone azine by mixture melting point. The liquid fraction was diluted with 100 ml of water and extracted twice with 50 ml of ether. Sufficient 10% aqueous sodium hydroxide was added to make the ether fraction basic. The ether was washed once with 50 ml of water and once with 50 ml of saturated sodium chloride and removed under vacuum. The nmr spectrum (10% in methylene chloride) of the liquid product showed that the major product was *p*-methoxyacetophenone (equal singlets at 1.49 ppm and 2.83 ppm upfield from methylene chloride) and

(32) "International Critical Tables," Vol. III, E. W. Washburn, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p 261.

the minor product was 1-methoxy-4-(1-acetoxyethyl)benzene (CH_3CO– at 3.32 ppm upfield and CH_3CHOAc– at 3.89 ppm upfield from methylene chloride, doublet, $J = 7$ Hz).

Reaction of 3,4,4,5-Tetramethyl-4H-pyrazole with Chlorine. 4H-Pyrazoles were prepared by the method of Grandberg.[33] A slow stream of chlorine was bubbled into a solution containing 1.0 g of 3,4,4,5-tetramethyl-4H-pyrazole in 40 ml of methylene chloride at −70°. The solution became turbid and a yellowish precipitate was observed. Excess chlorine and solvent were removed under vacuum leaving a pungent yellow semisolid. The nmr spectrum of the portion of the product soluble in methylene chloride showed numerous singlets between τ 4 and 7. Recrystallization from acetone led to the recovery of a crystalline substance (mp 120–160°). The nmr spectrum of the portion of this material soluble in methylene chloride showed only two upfield singlets (2.80 and 3.89 ppm upfield from methylene chloride).

The addition of the starting pyrazole to a methylene chloride solution of the product did not lead to the appearance of additional nmr peaks but rather the "migration" of the observed product peaks (arising from the hydrochloride salt) upfield.

Reaction of 3,5-Dimethyl-4,4-dibenzyl-4H-pyrazole and Chlorine. When a slow stream of chlorine was bubbled into 1.0 g of 3,5-dimethyl-4,4-dibenzyl-4H-pyrazole in 40 ml of methylene chloride, the solution became turbid as above. The product was a yellow semisolid which was partially soluble in methylene chloride. The nmr spectrum in methylene chloride showed that the product was a complex mixture. A crystalline material (mp 120–140°) was obtained by crystallization from acetone and was partially soluble in methylene chloride. The nmr spectrum in methylene chloride displayed two upfield singlets at 1.71 (4 H) and 2.64 ppm (6 H) upfield from methylene chloride. The starting pyrazole gave rise to singlets at 2.17 and 3.07 ppm upfield from methylene chloride.

Reaction of Acetophenone Azine and Excess Chlorine in Methylene Chloride at Room Temperature. A solution of 1.0 g of acetophenone azine in 100 ml of methylene chloride was prepared at room temperature and a steady stream of chlorine was bubbled in for ~15 min in ordinary fluorescent light. Excess chlorine and solvent were then removed under vacuum leaving a light soluble oil. The nmr spectrum (carbon tetrachloride) of the product showed a mixture of compounds. Bulb-to-bulb distillation at 10^{-2} mm and room temperature led to the isolation of (1,1-dichloroethyl)benzene contaminated by a trace of acetophenone: nmr (19% carbon tetrachloride) τ 2.34 (multiplet, 2 H), 2.70 (multiplet, 3 H), 7.54 (singlet, 3 H); ir (10% carbon tetrachloride) 3050, 3020, 2998, 2990, 2890, 1981, 1960, 1891, 1811, 1692, 1603, 1497, 1450, 1380, 1337, 1318, 1240, 1220, 1191, 1112, 1062, 1042, 1030, 1000, 980, 952, 918, 878, 710, 700, 689, 668, 620 cm^{-1}. The product was identical with an authentic sample prepared by the procedure of Taylor.[34]

Identical chlorine addition to acetophenone azine in methylene chloride at room temperature in a flask wrapped in aluminum foil and kept in the dark led only to 1,1′-dichloro-1,1′-diphenyl-1,1′-azoethane.

Identical chlorine addition to 1,1′-dichloro-1,1′-diphenyl-1,1′-azoethane in methylene chloride and in carbon tetrachloride at room temperature in ordinary fluorescent lighting led to the same mixture of products observed above for the addition to acetophenone azine in the light.

Chlorine Addition to Propiophenone Azine in Methylene Chloride in the Presence of Cyclohexane. To a solution containing 2.5 g (0.010 mol) of propiophenone azine in 80 ml of methylene chloride–20 ml of cyclohexane in a flask covered with aluminum foil in a darkened room, 1.0 g of chlorine (0.014 mol, dissolved in carbon tetrachloride) was added at room temperature and the reaction solution was allowed to stand for ~15 min. Excess chlorine and some solvent were removed at reduced pressure for 5 min. Then solvent and volatile products were distilled under vacuum into a trap cooled by Dry Ice–acetone. About 80 ml of liquid was collected. Vpc analysis showed that this liquid contained less than 0.1% chlorocyclohexane (w/v).

Chlorine Addition to Propiophenone Azine in Methylene Chloride in the Presence of Cyclohexane at −70°. A solution was prepared containing 1.0 g (0.0038 mol) of propiophenone azine in 80 ml of methylene chloride–20 ml of cyclohexane at *ca.* −70° in a flask covered with aluminum foil in a darkened room. Then 2.0 g (0.027 mol) of chlorine was added (dissolved in carbon tetrachloride) and the reaction solution was allowed to stand for 3 hr. Work-up and analysis were performed as above. Vpc analysis indicated the presence of a small amount of material which may correspond to *ca.* 0.1% chlorocyclohexane.

Chlorination of Cyclohexane in Methylene Chloride. A solution containing 80 ml of methylene chloride–20 ml of cyclohexane was prepared and a stream of chlorine was bubbled in for 15 min in the presence of ordinary fluorescent room lighting. Substantial warming of the reaction was noted. Work-up and analysis were performed as above. At least 20% of the cyclohexane had been converted to chlorocyclohexane.

Reaction of Acetophenone Azine and Chlorine in Carbon Tetrachloride and in Cyclohexane at Room Temperature. A 1% solution of 1.0 g of acetophenone azine in carbon tetrachloride was prepared, and 10 equiv of chlorine (in carbon tetrachloride) was added at room temperature. A yellowish precipitate was formed almost immediately. If the solution was rapidly filtered at this point, the yellow material was obtained and shown by mixture melting point and nmr to be acetophenone azine·xHCl, where $x \ll 1$. After a few minutes, this precipitate disappeared and the reaction solution became warm. The reaction was allowed to proceed in the dark for 1 hr at room temperature and then excess chlorine and solvent were removed under vacuum leaving a clear oil which rapidly crystallized to form long white needles (mp 100°). The product, 2,2,2-trichloroacetophenone azine, which may be recrystallized from methanol, was obtained quantitatively: nmr (10% carbon tetrachloride and 10% carbon disulfide) 3081, 3063, 3038, 1974, 1953, 1885, 1810, 1610, 1600, 1579, 1490, 1448, 1279, 1255, 1230, 1180, 1155, 1095, 1070, 1027, 1000, 915, 860, 815, 742, 702, 690, 648, 610 cm^{-1}; uv (in hexane) λ_{max} 2190 Å (log ϵ_{max} 4.01), 2460 (3.82); mass spectrum, parent at 440, 442, 444, 446, ratio 1.0/2.0/1.7/0.7; calcd for Cl_6 1.0/2.0/1.6/0.7).

Anal. Calcd for $C_{16}H_{10}N_2Cl_6$: C, 43.38; H, 2.28; N, 6.32; Cl, 48.02. Found: C, 43.43; H, 2.06; N, 6.27; Cl, 47.96.

When only 1 equiv of chlorine (in carbon tetrachloride) was added under these conditions to a 1% solution of acetophenone azine in carbon tetrachloride, a yellow semisolid was obtained. The nmr spectrum of this material (10% in carbon tetrachloride) showed two singlets at τ 7.96 and 5.51 (in a ratio of 3/2) tentatively assigned to 1-chloro-2,5-diphenyl-3,4-diaza-2,4-hexadiene and another singlet at 5.46 tentatively assigned to 2-chloroacetophenone azine. The ratio of these two products was *ca.* 3/1.

When 10 equiv of chlorine was added at room temperature to 0.1 g of acetophenone azine in 90 ml of carbon tetrachloride and 10 ml of cyclohexane in a flask wrapped with aluminum foil and kept in the dark for 1 hr, the product, 2,2,2-trichloroacetophenone azine, obtained upon evaporation of excess chlorine and solvent in the dark was identical with that previous obtained. No chlorocyclohexane was found in the nmr spectrum of the crude product. An identical addition of chlorine in the dark to 1.0 g of acetophenone azine in 100 ml of cyclohexane also led exclusively to the formation of 2,2,2-trichloroacetophenone azine.

A solution was prepared containing 1.0 g (0.04 mol) of acetophenone azine in 80 ml of carbon tetrachloride–20 ml of cyclohexane in a flask covered with aluminum foil in a darkened room, and 0.4 g of chlorine (0.055 mol, 0.5 equiv) was added (dissolved in carbon tetrachloride). The reaction was allowed to stand at room temperature for 1 hr. Work-up and vpc analysis as above showed no chlorocyclohexane (<0.1%).

A blank solution containing 0.20% chlorocyclohexane in 40 ml of carbon tetrachloride–10 ml of cyclohexane was prepared and added to the solid product of the above chlorination of acetophenone azine in carbon tetrachloride. Work-up as above gave 35 ml of liquid shown by vpc to contain 0.15% chlorocyclohexane.

Reaction of Propiophenone Azine and Chlorine in Carbon Tetrachloride at Room Temperature. Ten equivalents of chlorine (in carbon tetrachloride) was added to a solution of 1.0 g of propiophenone azine in 100 ml of carbon tetrachloride at room temperature. The crystalline product, 2,2-dichloropropiophenone azine (mp 101° from methanol), was obtained in quantitative yield: nmr (10% carbon tetrachloride) τ 2.68 (apparent singlet, 10 H), 7.75 (singlet, 6 H); ir (10% carbon tetrachloride) 3088, 3062, 3038, 3025, 3005, 2945, 1948, 1872, 1805, 1612, 1598, 1495, 1450, 1445, 1385, 1282, 1150, 1079, 1000, 990, 960, 725, 700, 635 cm^{-1}; uv (in hexane) λ_{max} 2250 Å (log ϵ_{max} 4.17), shoulder 2380 sh (log ϵ 3.97).

Reaction of Pinacolone Azine and Chlorine in Carbon Tetrachloride at Room Temperature. To a solution of 1.0 g of pinacolone azine (0.005 mol) and 50 ml of carbon tetrachloride, chlorine (1.5 equiv) dissolved in carbon tetrachloride was added in the dark at room

(33) I. I. Grandberg, A. P. Krasnoshcek, A. N. Kost, and G. K. Faizova, *Zh. Obshch. Khim.*, **33**, 2586 (1963).

(34) W. Taylor, *J. Chem. Soc.*, 343 (1947).

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]

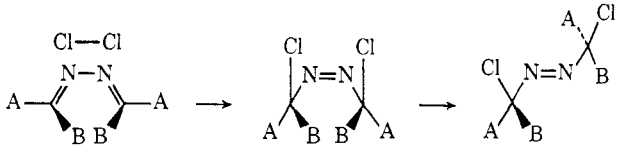
Donald S. Malament and J. Michael McBride

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

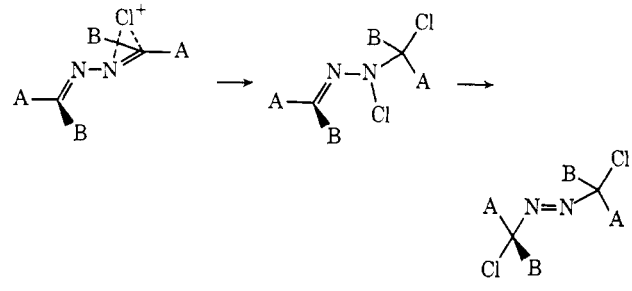
Abstract: Five mechanisms are proposed to explain stereospecific 1,4-chlorine addition to ketazines. Three of these are shown to be consistent with experimental observations on the reaction and with theory. Factors favoring nucleophilic attack *trans* to an emerging lone pair are discussed. The true 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.

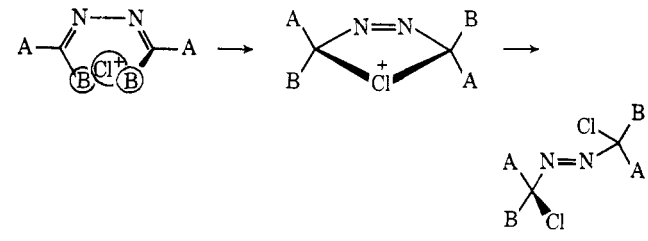
(a) Concerted [2 + 4] addition to the *s-cis* ketazine conformer followed by product isomerization to the *trans*-azo geometry.



(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).