Oxymercuration of Norbornadiene.—Whereas the reaction of mercuric chloride with norbornadiene in acetic acid[32a] or in methanol[32b] produces oxymercuration products and no metallic mercury, the reaction of mercuric trifluoroacetate (0.05 mole) with norbornadiene (0.1 mole) in 35 ml. of water produced a

large quantity of metallic mercury and an oil which was not identified. Similar treatment with mercuric acetate also yielded mercury, but at a slower rate.

(32) (a) S. Winstein and M. Shatavsky, *Chem. Ind.* (London), 56 (1956); (b) R. A. Alexander, N. C. Baenziger, C. Carpenter, and J. R. Doyle, *J. Am. Chem. Soc.*, **82**, 535 (1960). We have repeated their reaction with similar results.


Azo Compounds.[1] Dipole Moments and Spectral Data

BY C. G. OVERBERGER, JEAN-PIERRE ANSELME,[2] AND J. R. HALL

The dipole moments, the ultraviolet, infrared, and n.m.r. spectra of 1-azo-bis-1-phenylpropane and of cyclic azo compounds (I, $n = 1, 3, 4$) have been determined. It is concluded that the cyclic compounds I have a *cis*-azo linkage and that the 3,5-substituents of the 1-pyrazolines are *trans* to each other.

Introduction

The study of the rates of the thermal decomposition of cyclic azo compounds of types I and II have indicated that they can be classified in two groups: *trans*-azo compounds, including the large cyclic compounds (II, $n = 6, 8, 10$) and the acyclic compounds such as 1-azo-bis-1-phenylpropane, and *cis*-azo compounds such as I ($n = 1, 2, 3$)[3–6] which were found to decompose considerably faster than the *trans* compounds. Surprisingly, 3,8-diphenyl-1,2-diaza-1-cyclooctene(I, $n = 4$) proved to be much more stable than either the *cis* or *trans* compounds[7]; the rate of decomposition was one-

I, $n = 1$–4
Ar = C₆H₅, p-C₆H₄

II, $n = 6, 8, 10$
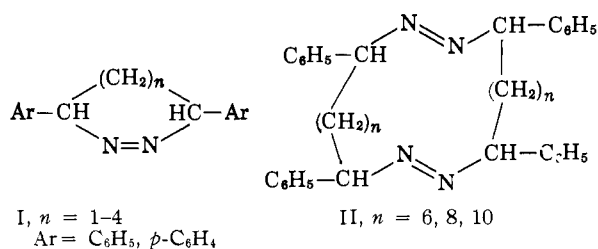
thousandth that of the six- and seven-membered rings (I, $n = 2, 3$) and one-one hundred eightieth that of 1-azo-bis-1-phenylpropane. It was concluded that the eight-membered ring had a *cis*-azo linkage but that steric effects prevented the phenyl groups from being coplanar with the C—N=N—C system in the transition state, thereby reducing the labilizing effect of the phenyl substituents on the C–N bonds.[7] The *trans* structure could not be ruled out completely, however, in view of its anomalous ultraviolet spectrum, λ_{max} 368 mμ; the *trans*-azo compounds had maxima at 359–360 mμ while the six- and seven-membered rings absorbed at 387 and 390 mμ, respectively. Furthermore, it was possible that the eight-membered ring could accommodate a

trans —N=N— bond since the *trans* isomer of cyclooctene had been isolated.[8]

While the decomposition of the seven- and eight-membered rings (I, $n = 3, 4$) had resulted in the formation of a mixture of the *cis* and *trans* isomers of the corresponding cycloalkane and olefin, it was found that 3,5-diphenyl-1-pyrazoline (I, $n = 1$, Ar = C₆H₅) decomposed stereoselectively to *trans*-1,2-diphenylcyclopropane.[3] No trace of the *cis* isomer or of the corresponding olefin could be detected. This was the first authenticated case of the thermal decomposition of a pyrazoline resulting in the formation of only one isomer of the coupled product. Subsequently, 3,5-bis-(*p*-chlorophenyl)-1-pyrazoline (I, $n = 1$, Ar = *p*-ClC₆H₄) was synthesized and again *trans*-1,2-bis-(*p*-chlorophenyl)-cyclopropane was the sole product of decomposition.[9] The mode of formation of 1-pyrazolines from diazoalkanes and activated olefins has been viewed as a *cis* addition.[10] Therefore it was assumed that the present pyrazolines were the *trans* isomers. However, since these were the first and only cases of thermal stereoselective decomposition, more evidence was necessary to support our claim.

In order to shed some light on the configuration of those cyclic azo compounds, we have determined their dipole moments, their ultraviolet, infrared, and n.m.r. spectra.

Results and Discussion

The dipole moments were calculated from the dielectric constants measured in benzene solutions at 25° and are shown in Table I with the ultraviolet maxima. The

TABLE I
DIPOLE MOMENTS AND ULTRAVIOLET MAXIMA

	μ, D.[a]	λ_{max}, mμ[b]
1-Azo-bis-1-phenylpropane	0.50	359
I, $n = 1$, Ar = C₆H₅	2.23	329[c]
I, $n = 1$, Ar = p-ClC₆H₄	2.32	327[c]
I, $n = 3$, Ar = C₆H₅	2.42	390
I, $n = 4$, Ar = C₆H₅	2.33	368
II, $n = 8$	. .	360

[a] Probable error ±0.05 D. [b] In chloroform unless otherwise noted. [c] In ethanol.

n.m.r. spectra were taken in deuteriochloroform with tetramethylsilane as an internal standard. The τ-values, along with the infrared frequency of the —N=N— bond, are given in Table II.

(1) This is the 42nd in a series of papers concerned with the preparation and decomposition of azo compounds. For the previous paper in this series, see C. G. Overberger, M. Tobkes, and A. Zweig, *J. Org. Chem.*, **28**, 620 (1963).

(2) This paper comprises a portion of a thesis submitted by Jean-Pierre Anselme in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

(3) C. G. Overberger and J-P. Anselme, *J. Am. Chem. Soc.*, **84**, 869 (1962).

(4) C. G. Overberger and J. G. Lombardino, *ibid.*, **80**, 2317 (1958).

(5) C. G. Overberger, I. Tashlick, M. Bernstein, and R. G. Hiskey, *ibid.*, **80**, 6556 (1958).

(6) S. G. Cohen, S. Hsiao, E. Saklad, and C. H. Wang, *ibid.*, **79**, 4400 (1957).

(7) C. G. Overberger and I. Tashlick, *ibid.*, **81**, 217 (1959).

(8) A. C. Cope, R. A. Pike, and C. F. Spencer, *ibid.*, **75**, 3212 (1953).

(9) C. G. Overberger and J-P. Anselme, unpublished results.

(10) For an excellent discussion, see T. V. Van Auken and K. L. Rinehart, *J. Am. Chem. Soc.*, **84**, 3736 (1962).

TABLE II

N.M.R.[a] AND INFRARED DATA

	Aromatic protons	Benzylic protons	β-Protons	Other protons	—N= N—, cm.[-1]
1-Azo-bis-1-phenylpropane	2.86	5.79[b]	8.03[b]	9.33[b]	..
I, n = 1, Ar = C₆H₅	2.78	4.19[c]	7.89[c]	..	1548
I, n = 1, Ar = p-ClC₆H₄	2.83[d]	4.30[c]	7.97[c]	..	1543
I, n = 3, Ar = C₆H₅	2.60[d]	5.06[e]	Broad unresolved		1542
I, n = 4, Ar = C₆H₅	2.56[d]	5.21[e]	Broad unresolved		1537

[a] Given in τ-values.   [b] J = 7.0 c.p.s.   [c] J = 8.5 c.p.s.   [d] Center of multiplet.   [e] Triplet.

TABLE III

DIELECTRIC CONSTANT DATA

	w_2	e_{12}	d (25°)
1-Azo-bis-1-phenylpropane	0.00000	2.2725	0.87378
	.00747	2.2741	.87462
	.02911	2.2776	.87729
	.04494	2.2803	.87831
	.05515	2.2818	.87950
I, n = 1, Ar = C₆H₅	.00000	2.2725	.87378
	.00029	2.2743	.87403
	.00055	2.2749	.87426
	.00085	2.2765	.87452
	.00114	2.2777	.87478
I, n = 1, Ar = p-ClC₆H₄	.00000	2.2725	.87378
	.00115	2.2777	.87478
	.00146	2.2786	.87506
	.00188	2.2798	.87542
	.00332	2.2851	.87669
I, n = 3, Ar = C₆H₅	.00000	2.2725	.87378
	.00044	2.2756	.87416
	.00055	2.2772	.87426
	.00158	2.2804	.87516
	.00207	2.2825	.87560
	.00222	2.2841	.87572
I, n = 4, Ar = C₆H₅	.00000	2.2725	.87378
	.00042	2.2746	.87415
	.00121	2.2799	.87484
	.00224	2.2830	.87575
	.00275	2.2836	.87619

Fig. 1.—A, 3,5-diphenyl-1-pyrazoline;   B, 3,5-bis-(p-chlorophenyl)-1-pyrazoline;   C, 1-azo-bis-1-phenylpropane.

Azomethane[11] and trans-azobenzene[12] have been reported to have a zero dipole moment while cis-azobenzene had a dipole moment of 3.0 D.[12] The cis configuration of the seven-membered ring azo compound was then confirmed by its dipole moment of 2.42 D. The 2.2–2.3 D. for the two five-membered rings (1-pyrazolines) supported this assignment. The eight-membered ring exhibited a dipole moment of 2.33 D. This strongly suggested that it had the cis configuration and that the explanation put forward[7] for its slower rate of decomposition was reasonable. The hypsochromic shift in its ultraviolet spectrum could also be ascribed to the same steric effects. In comparison, the dipole moment of 1-azo-bis-1-phenylpropane, 0.50 D., was in agreement with its assigned trans structure.

According to Bellamy,[13] the weak intensity and the position of the absorption of the —N=N— group usually prevent any useful correlation for this system. However, in the strained compounds at hand, a sharp peak of moderate intensity between 1530–1550 cm.[-1] was assigned to the azo grouping,[10,14] while the trans compounds such as 1-azo-bis-1-phenylpropane and II did not show any absorption in this region.[15] The fact

that the —N=N— bond can be seen in the infrared spectra confirms the dipole moment data. Thus the evidence accumulated suggests the cis configuration for the azo linkage in all the medium-sized cyclic compounds.

While there was no question that the two pyrazolines had a cis-azo bond, the configuration of the 3,5-substituents with respect to the ring became important in view of their stereoselective decomposition. Their sharp melting points suggested the presence of only one isomer. The nearly identical dipole moments of 3,5-diphenyl-1-pyrazoline and of 3,5-bis-(p-chlorophenyl)-1-pyrazoline lead to the conclusion that the two compounds had the same configuration and that the substituents were trans with respect to each other. Indeed, if they were cis, then the substitution of the two para hydrogens with chlorine would be expected to cause a sizable difference in the dipole moments.

The n.m.r. spectra (Fig. 1) further confirmed that the two pyrazolines were both trans isomers. The only difference, which was expected, occurred in the aromatic region where the p-chlorophenyl compound exhibited a complex absorption (typical A_2B_2 spectrum). However, the chemical shifts were almost the same. The benzylic protons and the remaining two ring protons appeared as symmetrical triplets at almost the same position in both spectra. The coupling constant, J, in both cases, was about 8.5 c.p.s. The striking similarity and the simplicity of the two spectra need no discussion; suffice it to say that if either or both pyrazolines were the cis isomer, one would expect more complex spectra. The spectra of the other azo compounds were consistent with their structures; the chemical shifts are given in Table II.

(11) W. West and R. B. Killingsworth, J. Chem. Phys., 6, 1 (1938).

(12) G. S. Hartley and R. J. W. LeFevre, J. Chem. Soc., 531 (1939).

(13) L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 272.

(14) (a) J. A. Moore, J. Org. Chem., 20, 1067 (1955); (b) J. A. Moore and R. W. Medeiros, J. Am. Chem. Soc., 81, 6026 (1959); (c) J. A. Moore, W. F. Holton, and E. L. Little, ibid., 84, 390 (1962); (d) R. Wiechert and and E. Kaspar, Chem. Ber., 93, 1710 (1960).

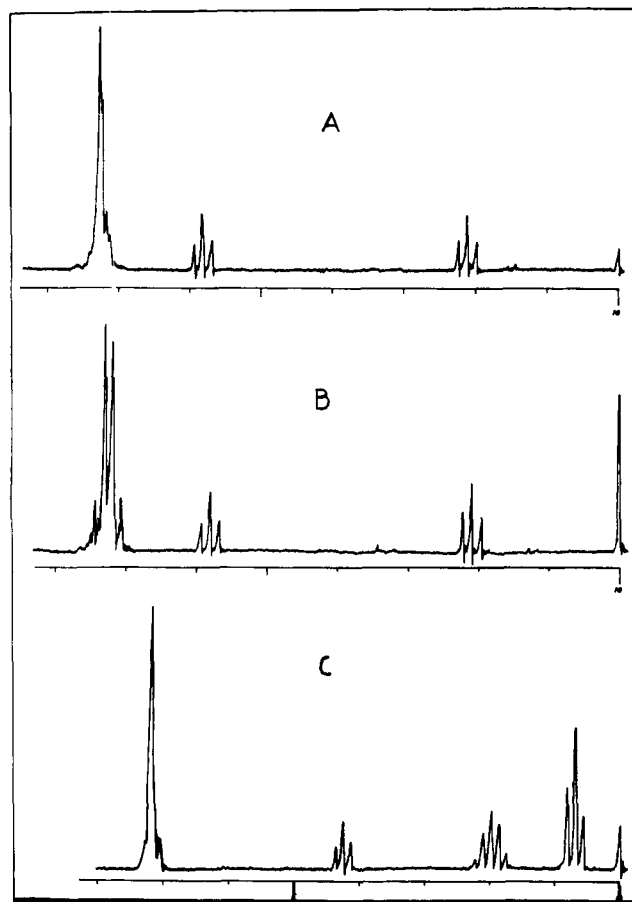(15) I. Tashlick, Ph.D. Thesis, Polytechnic Institute of Brooklyn, 1958.

Experimental[16]

Dipole Moment Measurements.—The dielectric constants were measured in benzene solutions at 25° with a heterodyne beat type apparatus[17] similar to that described by Chien,[18] modified by the addition of a 1000-cycle filter. The dipole moments were calculated as described by Halverstadt and Kumler.[19] The molecular refractivities were obtained by summation of the bond refractivities values given by Vogel, *et al.*[20] The infrared spectra were run as potassium bromide pellets and n.m.r. spectra were carried out as saturated solutions in deuteriochloroform with tetramethylsilane as an internal standard.

(16) The authors wish to thank Mr. H. Talts for running the infrared and n.m.r. spectra.

(17) L. F. Reed, M.S. Thesis, Polytechnic Institute of Brooklyn, 1960.

(18) J. Y. Chien, *J. Chem. Educ.*, **24**, 494 (1947).

(19) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2933 (1942).

(20) A. I. Vogel, W. T. Cresswell, G. J. Jeffery, and J. Leicester, *Chem. Ind.* (London), 358 (1950).

[Contribution from the Department of Chemistry, University of Florida, Gainesville, Florida]

The Cyclopropylidene[1]: Generation and Reactions

By W. M. Jones,[2] Michael H. Grasley, and Wallace S. Brey, Jr.

Received May 2, 1963

A study of the reaction of N-nitroso-N-(2,2-diphenylcyclopropyl)-urea with various bases has been carried out. The most effective base was found to be lithium ethoxide (presumably as its alcoholate). In the absence of carbene acceptors the reaction leads to a high yield (up to 96%) of 1,1-diphenylallene. Reaction of the nitrosourea with base in the presence of acceptor olefins leads to a mixture of 1,1-diphenylallene and the spiropentane (*ca.* 20%) that would be expected to result from addition of 2,2-diphenylcyclopropylidene to the olefin. The spiropentane structures were proved by their spectral properties and, in one case, by alternate synthesis. Evidence is presented for initial formation of 2,2-diphenyldiazocyclopropane followed by its spontaneous collapse to 1,1-diphenylallene and 2,2-diphenylcyclopropylidene. The carbene can apparently either collapse to give the allene or react with the olefin to give the spiropentane. Competition reactions were run with various olefins and it was found that the results could be accommodated by an electrophilic carbene in which the two aryl groups create a dominating steric effect when opposed to alkyl groups on the acceptor olefin. Reaction of the cyclopropylidene with *cis*- and *trans*-2-butene is stereospecific.

Unsuccessful attempts to capture the cyclopropylidene have been reported by several investigators. For example, Moore and Ward[3] first reported the fact that the reaction of 1,1-dibromocyclopropanes with methyl- or butyllithium in cyclohexene gives allenes, but none of the spiropentanes that would result from addition of the anticipated[4] cyclopropylidene to the carbon–carbon double bond. Similar failures to trap this intermediate have also been reported by Logan,[5] who examined the reaction of 1,1-dichloro-2-alkylcyclopropanes with magnesium metal in the presence of alkyl or aryl halides, and by Skattebol,[6] who studied the reaction of a variety of dihalocyclopropanes with alkyllithiums. Again, both of these investigators found the predominant products to be allenes.

The production of allenes in reactions of this type is certainly not surprising in view of the fact that as early as 1958, Doering and LaFlamme[7] reported that the reaction of dibromocyclopropanes with magnesium or sodium yielded allenes as the predominant products. Furthermore, Doering and LaFlamme suggested a variety of possible intermediates from which allene formation might occur in these reactions and convincingly narrowed the possibilities down to collapse of either the bromocarbanion or the carbene. However, they were not able to assess the relative importance of these two modes of reaction. The problem of preventing the collapse to allene of either the halo carbanion or the cyclopropylidene was very cleverly solved by Moore and Ward,[3] who examined the reaction of 7,7-dibromonorcarane with methyllithium. In this system, the cyclopropane is fused to a six-membered ring which would certainly inhibit formation of the allene (1,2-cycloheptadiene) and, indeed, Moore and Ward have isolated a variety of products which are typical of carbene intermediates. For example, reaction with isobutylene gave spiropentane (I).[8]
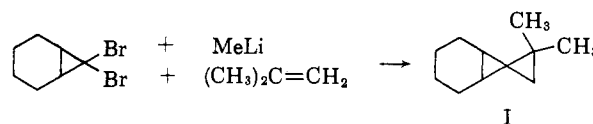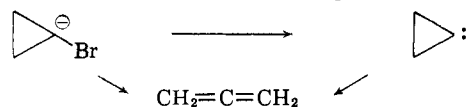
At the same time that Moore and Ward were examining the dibromonorcarane system, we began a study of the generation and decomposition of selected diazocyclopropanes. The purpose of this paper is to report some of the results of our investigations on 2,2-diphenyldiazocyclopropane.

As a convenient starting material we selected 2,2-diphenylcyclopropanecarboxylic acid, a compound which can be readily obtained from the reaction of diphenyldiazomethane with methyl acrylate.[9] Conversion of this acid to the corresponding nitrosourea was cleanly effected by the reactions shown in the flow sheet.

The nitrosourea was then treated with a variety of bases in attempts to generate 2,2-diphenyldiazocyclopropane. However, under all conditions where any reaction occurred, spontaneous nitrogen evolution was observed and, except for transient yellow colors, in no case was a solution obtained that had the typical color of a diazoalkane. When the reaction was effected in saturated hydrocarbon solvents, it was found that the

(1) For the preliminary communication on this work, see W. M. Jones, *J. Am. Chem. Soc.*, **82**, 6200 (1960).

(2) Alfred P. Sloan Fellow, 1963–1965.

(3) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **26**, 2073 (1960); **27**, 4179 (1962).

(4) For references related to the production of carbenes from the reaction of polyhalomethylenes with alkyllithium reagents, see: G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **81**, 4996 (1959); W. T. Miller, Jr., and C. S. Y. Kim, *ibid.*, **81**, 5008 (1959).

(5) T. J. Logan, *Tetrahedron Letters*, 173 (1961).

(6) L. Skattebol, *ibid.*, 167 (1961).

(7) W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958).

(8) For another example of the formation of a spiropentane from reaction of a *gem*-dibromocyclopropane with methyllithium, see L. Skattebol, *Chem. Ind.* (London), 2146 (1962).

(9) H. M. Walborsky and F. M. Hornyak, *J. Am. Chem. Soc.*, **77**, 6026 (1955).