material was recrystallized twice from cyclohexane and had m.p. 162–163° (60% yield); ν_{max}^{KBr} 1700 cm.$^{-1}$; λ_{max}^{EtOH} 245 mμ (log ε 4.4). Recrystallization from ethyl acetate gave a polymorph of m.p. 172–173°.

Anal. Calcd. for $C_{20}H_{20}N_2O$: C, 78.92; H, 6.62; N, 9.20. Found: C, 78.69; H, 6.62; N, 9.19.

The n.m.r. spectrum of the product in deuteriochloroform showed absorptions at τ 2.4–3.4 (10 H), 4.7 (1 H), 6.0 (1 H), 7.2–7.6 (2 H), and 8.0–8.8 (6 H).

Double resonance n.m.r. experiments run with field-sweep operation were employed to study the nature of the coupling of the protons with peaks at τ 4.7 and 6.0.

When ($\omega_1 - \omega_2$) was 150 c.p.s., the peak at τ 4.7 became a doublet with a coupling constant of 2.3 c.p.s., while the peak at 6.0 remained a quartet. When ($\omega_1 - \omega_2$) was 82 c.p.s., the peak at τ 4.7 was observed as a doublet with a coupling constant of 5.4 c.p.s. and the peak at 6.0 became a doublet with a coupling constant of 2.3 c.p.s.

The over-all result of the double resonance n.m.r. work was that the protons at τ 4.7 and 6.0 are coupled with each other (J = 2.3 c.p.s.) and that they are each coupled to a proton at 7.2–7.6 with J = 5.4 and 6.0 c.p.s.

The n.m.r. spectrum of this adduct in chloroform–trifluoroacetic acid and its mass spectrum are reported above.

Attempted catalytic hydrogenation of 0.38 g. of the $C_{20}H_{20}N_2O$ product with 34 mg. of platinum oxide in glacial acetic acid at atmospheric pressure for 4 hr. resulted in no consumption of hydrogen.

Ethanolysis of Adduct **22**. Compound **22** (0.444 g.) was dissolved in 40 ml. of 10% potassium hydroxide–95% ethanol solution and refluxed for 2 hr. The cooled reaction mixture was diluted with water and extracted with ether. The ethereal extract was dried and concentrated to give a crystalline residue which was recrystallized twice from ethanol–water; the product had m.p. 150–152° (0.204 g., 40% of theory).

Anal. Calcd. for $C_{22}H_{26}N_2O_2$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.43; H, 7.48; N, 7.99.

This colorless solid had $\nu_{max}^{CHCl_3}$ 3300, 3070 (w), 2955, 1665, 1600, 1550, 1450, 1270 (m), 1250 (m), and 1055 cm.$^{-1}$.

Its n.m.r. spectrum showed absorptions at τ 0.01 (1 H), 2.3–3.4 (10 H), 5.1 (1 H), 5.8 (1 H), 6.3 (2 H), and 7.0–7.9 (11 H).

Lithium Aluminum Hydride Reduction of **22**. To a magnetically stirred solution of 0.496 g. of lithium aluminum hydride in 30 ml. of dry tetrahydrofuran under an argon atmosphere was added a solution of the $C_{20}H_{20}N_2O$ adduct (**22**) (0.281 g.) in 20 ml. of tetrahydrofuran over a 20-min. period. The reaction mixture was refluxed for 3.5 hr., cooled, and decomposed by cautious addition of water and 15% aqueous sodium hydroxide. Filtration, ether extraction of the filtrate, and drying, filtration, and concentration of the ethereal solution gave a residue which was purified by g.l.p.c. on a 0.6-m. SE-30 silicone rubber column at 230°. The major component was collected as a colorless oil.

Anal. Calcd. for $C_{20}H_{22}N_2$: C, 82.76; H, 7.59. Found: C, 82.10; H, 7.71.

The oil had $\nu_{max}^{CHCl_3}$ 3100–2800 (m), 1600 (s), 1500 (s), 1060 (w), and 990 cm.$^{-1}$ (w); its n.m.r. spectrum showed absorptions at τ 2.8–3.65 (10 H), 4.86 (1 H), 6.1 (1 H), 6.8 (2 H), and 7.3–9.0 (8 H).

A minor product was isolated by g.l.p.c. on a 1-m. XF-1150 column at 150° as a colorless oil; ν_{max}^{neat} (selected) 3430, 3100–2800, 1610, 1510, 1470, 1445, 1420, 1315, 1260, 1145, and 1170 cm.$^{-1}$ (all s or m).

The Synthesis and the Decomposition of *cis*- and *trans*-3,5-Bis(*p*-anisyl)-1-pyrazolines[1]

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Contribution from the Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, New York. *Received May 5, 1965*

The isolation and the characterization of cis- and trans-3,5-bis(p-anisyl)-1-pyrazolines are reported and their n.m.r. spectra are interpreted. A mechanism for the formation of the two isomers is suggested. Their thermolysis and their photolysis have been studied, and the possible pathways of these decompositions are discussed.

Introduction

As part of our general interest in aliphatic azo compounds, the chemistry of medium-sized cyclic azo compounds has been investigated over a number of years. In the latest papers in the series,[3a-c] the synthesis and the stereospecific decomposition of *trans*-3,5-diaryl-1-pyrazolines (I) were described. More recently, a preliminary communication from this laboratory[4] reported the isolation and the characteriza-

(1) This is the 44th paper in a series of papers concerned with the preparation and decomposition of azo compounds. For the previous paper, see C. G. Overberger and J-P. Anselme, *J. Am. Chem. Soc.*, **86**, 658 (1964).

(2) This paper comprises a portion of a thesis submitted by N. Weinshenker in partial fulfillment of the requirements for the B.S. degree, 1964.

(3) (a) C. G. Overberger and J-P. Anselme, *J. Am. Chem. Soc.*, **84**, 869 (1962); (b) C. G. Overberger, J-P. Anselme, and J. R. Hall, *ibid.*, **85**, 2752 (1963); (c) C. G. Overberger and J-P. Anselme, *ibid.*, **86**, 658 (1964).

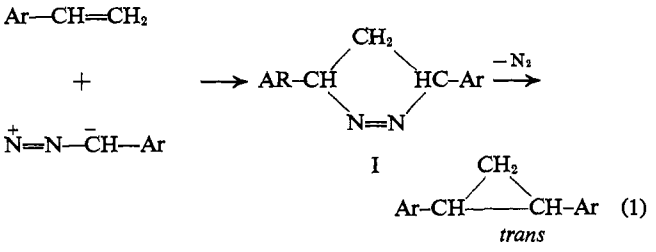
(4) C. G. Overberger, N. Weinshenker, and J-P. Anselme, *ibid.*, **86**, 5364 (1964).

Table I. N.m.r. Data of 3,5-Diaryl-1-pyrazolines (I)[a]

Aryl group	Aromatic protons		Benzylic protons		Methylenic protons				Ref.
	cis	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	
C_6H_5	...	2.78	...	4.19[b]	...	7.89[b]	...	...	3b, 3c
p-ClC_6H_4	...	2.83[c]	...	4.30[b]	...	7.97[b]	...	...	3b, 3c
p-$CH_3OC_6H_4$	2.92[c]	2.98[c]	4.80[c]	4.25[d]	7.66[e] 8.63[f]	7.95[d]	6.19	6.26	This work

[a] Given in τ-values and determined as saturated solutions in $CDCl_3$ ar 60 Mc. with tetramethylsilane as internal standard. [b] Triplet, J = 8.5 c.p.s. [c] Quartet. [d] Triplet, J = 8.0 c.p.s. [e] Sextet, *trans* to aryl groups. [f] Sextet, *cis* to aryl groups.

tion of a *cis–trans* pair of 3,5-diaryl-1-pyrazolines of type I (Ar = *p*-methoxyphenyl). It is the purpose of this paper to report in detail our findings and to discuss the mechanisms of the formation and of the decomposition of the *cis*- and *trans*-1-pyrazolines.



(1)

Results and Discussion

Preparation and Structural Considerations. The reaction of *p*-methoxyphenyldiazomethane with *p*-methoxystyrene was investigated in order to determine the generality and the scope of the cycloaddition of aryldiazoalkanes to styrenes[3] (reaction 1). The low-temperature oxidation of *p*-anisaldehyde hydrazone[5]

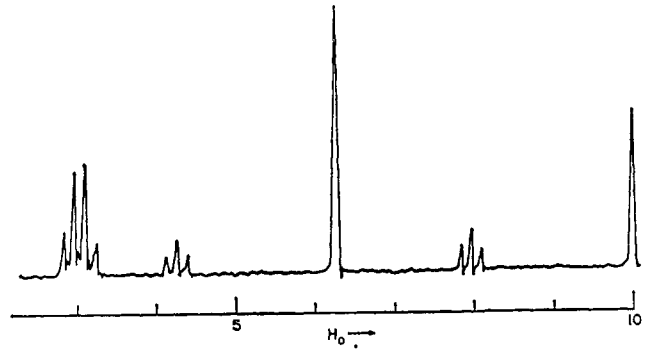
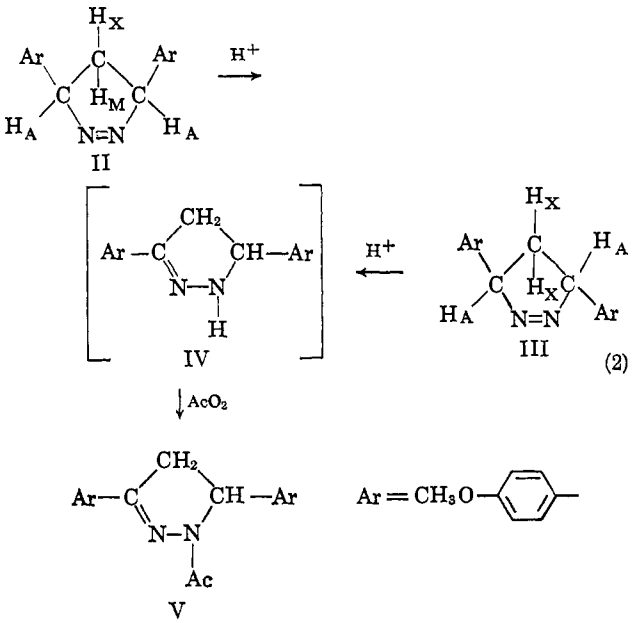


Figure 1. N.m.r. spectrum of *trans*-3,5-bis(*p*-methoxyphenyl)-1-pyrazoline (III).

proved to be the method of choice for the preparation of *p*-anisyldiazomethane as the Bamford–Stevens reaction of the tosylhydrazone of anisaldehyde[6] resulted in extensive decomposition. The addition of *p*-methoxystyrene to the cold solution of the diazoalkane gave after 10 days at −10 to 0° a 35% yield of adduct. However, the n.m.r. spectrum of this adduct, even after several recrystallizations from methanol, still exhibited extraneous peaks beside the absorptions expected for *trans*-3,5-bis(*p*-anisyl)-1-pyrazoline (III) which was eventually separated from the other compound by taking advantage of their different solubilities in benzene.

(5) R. L. Hinman, *J. Org. Chem.*, **25**, 1775 (1960).
(6) D. G. Farnum, *ibid.*, **28**, 870 (1963); C. L. Closs and R. A. Moss, *J. Am. Chem. Soc.*, 86, 4042 (1964).

The n.m.r. spectrum (Figure 1) of *trans*-3,5-bis(*p*-anisyl)-1-pyrazoline (III), m.p. 129° dec., had a quartet at τ 2.98 (aromatic protons), a triplet at 4.25 (benzylic protons), a singlet at 6.26 (methoxy protons), and a triplet at 7.95 (methylenic protons). These values compare very well with those reported for *trans*-3,5-diphenyl- and *trans*-3,5-bis(*p*-chlorophenyl)-1-pyrazolines (Table I). Its infrared spectrum had a –N=N– absorption[3b] at 1555 cm.$^{-1}$ and its ultraviolet spectrum exhibited a maximum at 332 mμ (ϵ_{max} 533). The spectral data of III coupled with its acid-catalyzed isomerization to 3,5-bis(*p*-anisyl)-2-pyrazoline (IV) (reaction 2)[7] left no doubt as to the position and configuration of the *p*-methoxyphenyl substituents.



(2)

The other product isolated, m.p. 114° dec., had λ_{max} 329 mμ (ϵ_{max} 329) and a band at 1545 cm.$^{-1}$ (–N=N–).[3b] These spectral data indicated that this compound also was an azo compound. It had the same elemental analysis as III and was isomerized to 3,5-bis(*p*-anisyl)-2-pyrazoline (IV)[7] (reaction 2). Its identity as the *cis* isomer (II) of 3,5-bis(*p*-anisyl)-1-pyrazoline was fully confirmed by its n.m.r. spectrum (Figure 2).

As anticipated[3b,8] for a *cis* isomer, the spectrum was more complex but in excellent agreement with that expected for an AMX system which would be the case for a *cis* configuration of the substituents. Indeed, the two nonequivalent methylenic protons H_M and H_X (II) each appeared as a sextet at τ 7.66 and 8.63,

(7) The n.m.r. spectrum and the N-acetyl derivative of IV were identical with that of authentic samples.
(8) J-P. Anselme, Ph.D. Thesis, Polytechnic Institute of Brooklyn, 1964, p. 13.

respectively. The diamagnetic shift (upfield) of H_X from the τ 7.95 value of the methylenic protons of the *trans* isomer bespeaks of the shielding (and lack of it in the case of H_M shifted downfield) by the adjacent aromatic ring, *cis* to the proton involved.[3c,9] Due to the *cis* configuration of II, H_X is flanked by two aryl groups while H_M is not, in contrast to the methylenic protons (H_X) in III (*trans*) which are equally shielded by only one aromatic group. The strong diamagnetic shift of H_X (taking the methylene hydrogens of III as reference, H_X is shifted upfield by τ 0.68 and H_M downfield by only 0.29) reflects the highly restricted rotation of the two *p*-anisyl substituents in the *cis* isomer.

Further support for this increased "freezing" of the two aryl groups of the *cis* isomer (II), as indicated also by the examination of molecular models, is provided by the position of the benzylic protons (see Table I). The α-protons of the *trans* isomer (III) which appeared as a triplet at 4.25 τ are shifted 0.55 downfield from the position (4.80) of the corresponding protons of the *cis* isomer (II). In the *trans* isomer where the aryl substituents have a much greater freedom of rotation around the C–C bond, the benzylic protons experience a strong deshielding effect. This is to be contrasted with the situation in the *cis* isomer where the two aryl groups are restricted to the position in which the plane of the aromatic rings is perpendicular to the axis of the benzylic C–H bond (the deshielding effect of the aryl group is at a minimum in this conformation).[10]

A quasi-planar ring has been assumed as the most stable conformation for the *trans*-3,5-diaryl-1-pyrazolines. However, several features of the n.m.r. spectrum of the *cis* isomer suggest that $-CH_2-$ is probably slightly puckered (away from the substituents).

A bond angle of 109–110° for H_M–C–H_X as indicated[11] by the geminal coupling constant J_{MX} = 12.4 c.p.s. cannot be accommodated by a planar unsaturated five-membered ring. Furthermore, the vicinal *trans* coupling constant J_{AX} = 11.5 c.p.s. was higher than that of *cis* coupling J_{AM} = 8.0 c.p.s. If the ring was planar, J_{cis} would be expected to be higher than J_{trans} on the basis of the dependence of the magnitude of the coupling constants on the dihedral bond angles.[12] Such a puckering of the $-CH_2-$ in effect decreases the interference of the *ortho* hydrogens of the anisyl groups with H_X while inducing considerable stretching of the C–N bonds.

Mechanism. The formation of the *cis* isomer of 3,5-bis(*p*-methoxyphenyl)-1-pyrazoline is without precedent in this type of cycloaddition reaction. Indeed, the currently accepted mechanism[13] invokes concerted bond formation. The possible explanation that the

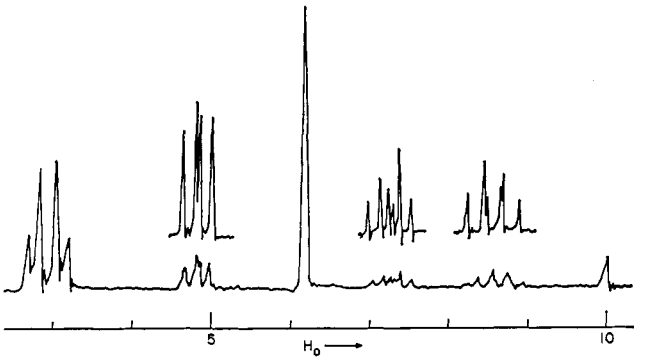
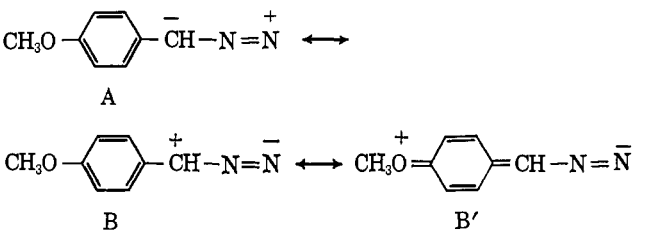


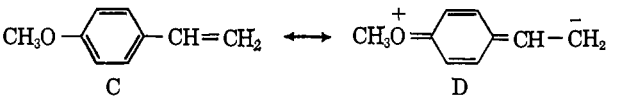
Figure 2. N.m.r. spectrum of *cis*-3,5-bis(*p*-methoxyphenyl)-1-pyrazoline (II).

trans isomer was the normal product which subsequently equilibrated is unlikely since it would involve an energetically unfavorable process. The observation that each isomer was formed in roughly equivalent amounts (*cis*/*trans* ratio = 58/42 ± 2) suggested that at some point along the reaction path the formation of either isomer was equally probable. Since from the previous reactions of aryldiazomethanes with the corresponding styrenes only the *trans* isomers could be isolated, the surprising formation of the *cis* isomer in this case must be ascribed to the influence of the *p*-methoxy substituents.

Diazoalkanes are best represented as resonance hybrids of several contributing structures. In the present case, it is not unreasonable to postulate that the *p*-methoxy group would confer considerable stabilization to a positive charge on the α-carbon,[14] thus favoring a large contribution of structure B to the resonance hybrid of *p*-methoxyphenyldiazomethane at least in the reacting state. This possibility is further enhanced



by the fact that by a similar mesomeric effect *p*-methoxystyrene possesses a particularly "nucleophilic" double bond by virtue of the participation of resonance



form D. From these considerations, the following mechanism can be visualized. Attack of the electron-rich double bond of the olefin on the positive center of *p*-methoxyphenyldiazomethane (B) would give species E which itself is resonance stabilized. The features of this species[15] are evident, and the formation of the *cis* and the *trans* isomers of the 1-pyrazoline in equal

(9) J. B. Hyne, *J. Am. Chem. Soc.*, **81**, 6058 (1959); D. Y. Curtin, H. Gruen, Y. G. Hendrickson, and H. E. Knipmeyer, *ibid.*, **83**, 4838 (1961); **84**, 863 (1962); G. L. Closs, R. A. Moss, and J. J. Coyle, *ibid.*, **84**, 4985 (1962); C. G. Overberger and J-P. Anselme, *Chem. Ind.* (London), 280 (1964); C. G. Overberger and A. Drucker, *J. Org. Chem.*, **29**, 360 (1964); S. J. Brois, *ibid.*, **27**, 3532 (1962); D. Y. Curtin and S. Dayagi, *Can. J. Chem.*, **42**, 867 (1964).

(10) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p. 126.

(11) H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, 31, 1278 (1959).

(12) M. Karplus, *ibid.*, **30**, 11 (1959).

(13) R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p. 831.

(14) A somewhat analogous argument has been advanced for the participation of azocarbonium ions during the solvolysis of hydrazidic halides: F. L. Scott and D. A. Cronin, *Tetrahedron Letters*, 715 (1963).

(15) The nature of this species, whether it be intermediate, transition state, ion pair, etc. is irrelevant to the discussion. Suffice it to observe that it has the requirements to undergo what is essentially an internal SN1 reaction to give *both* isomers.

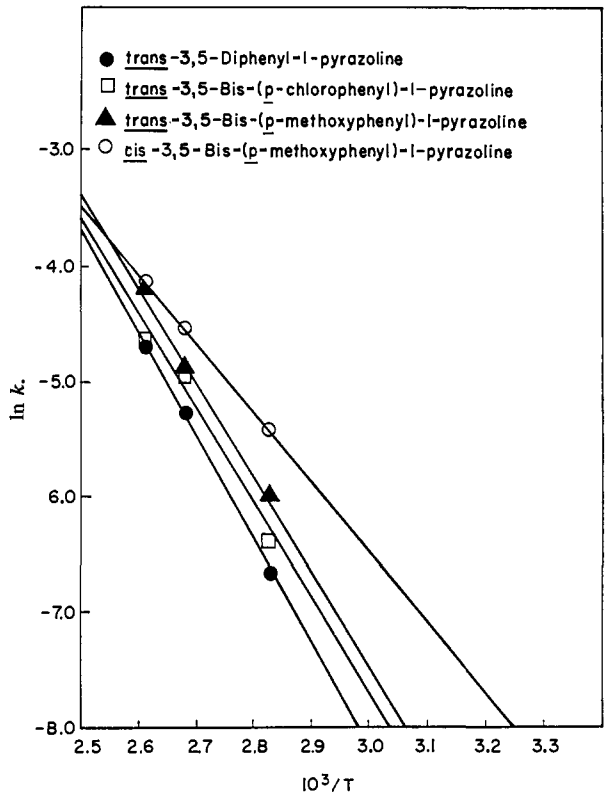
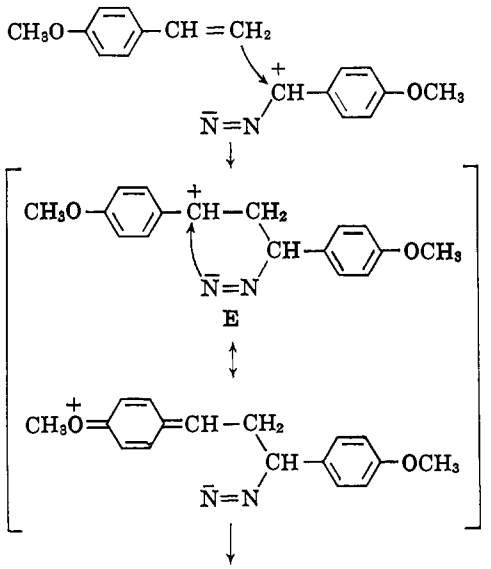


Figure 3. Energy of activation of the decomposition of 1-pyrazolines.

amounts thus becomes understandable. The fact that the *cis* isomer was isolated in slightly greater amount is probably due to its lesser solubility.



cis and *trans* isomers (II and III)

The recent report of the importance of electronic control (overriding steric effects) in the addition of aryl azides to enamines,[16] coupled with our results, indicates that several reaction paths are available and the specific reactants will determine which mechanism is operative. These findings point to the need for caution when the concerted mechanism is applied to 1,3-cycloaddition reactions. It would be indeed more surprising that a single mechanism could explain equally well all the various and diverse examples of such a versatile reaction.

Decomposition. The stereospecific thermal decomposition of *trans*-3,5-diphenyl- and 3,5-bis(*p*-chlorophenyl)-1-pyrazolines to the corresponding *trans*-1,2-diarylcyclopropanes has been rationalized in terms of fast coupling of the intermediate biradicals. The close proximity of the two radical moieties and the greater thermodynamic stability of the resulting *trans*-cyclopropanes support this theory. Thus, as expected, *trans*-3,5-bis(*p*-methoxyphenyl)-1-pyrazoline (III) underwent thermal decomposition at 100° to yield 93.3% of *trans*-1,2-bis(*p*-methoxyphenyl)cyclopropane (VII) along with a small amount (6.7%) of *cis*-1,2-bis(*p*-methoxyphenyl)cyclopropane (VI). The formation of the *cis*-cyclopropane VI could not be readily explained. The photolytic decomposition of III gave essentially the pure *trans*-cyclopropane VII. In no case could olefinic products be detected.

In contrast, the thermal decomposition at 100° of *cis*-3,5-bis(*p*-methoxyphenyl)-1-pyrazoline (II) resulted in the formation of a mixture of isomers in which, surprisingly, the *trans*-cyclopropane VII predominated (*trans*/*cis* 57/43). Not unexpectedly, the photolysis of II at 13° resulted in a reversal in the ratio of the *cis*–*trans*-cyclopropanes, the *cis* isomer being formed in 57% yield (see Table II). This increase in the rate of rotation around the C–C bonds with temperature is apparently able to compete successfully with the coupling of the biradical and thus explains the lack of stereospecificity from the thermal decomposition of II.

Table II. Decomposition of *cis*- and *trans*-3,5-Bis(*p*-anisyl)-1-pyrazolines[a]

Compd.	% of cyclopropanes (±1.5%) — Thermal — *cis*	*trans*	Photolytic[b] *cis*	*trans*
cis-1-Pyrazoline	43.0	57.0	57.2	42.8
trans-1-Pyrazoline	6.7	93.3	0.7	99.3

[a] The thermolyses were carried out at 100° in toluene and the photolyses at 13° in tetrahydrofuran and in benzene. Quantitative yields of cyclopropanes were obtained; no olefins were detected. The ratio of *cis* and *trans* isomers was determined by measuring the areas under the methoxy peaks of n.m.r. spectra of the decomposition products. [b] These values are corrected for the isomerization of the cyclopropanes under the reaction conditions; see ref. 4, Table I, and Experimental section.

Free radicals are relatively insensitive to substituent effects. Both electron-donating and electron-withdrawing groups will help stabilize benzyl-type free radicals.[17] Thus, electronic effects would contribute little if any to the rationalization of the present results. The kinetics of the decomposition confirmed a point of view (phenyl–phenyl interaction) that the *cis* isomer II should decompose at a faster rate than the *trans*-pyrazolines with a concomitantly smaller activation energy (Table II). The absence of any sizable electronic contributions of the substituents was further evidenced by the data of the *trans*-pyrazolines. Within the limits of experimental error, the value of the activa-

(16) M. Munk and Y. K. Kim, *J. Am. Chem. Soc.*, 86, 2213 (1964).

(17) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 380.

Table III. Kinetics of the Thermal Decomposition of 1-Pyrazoline[a]

Compd.	Rate constant (k), sec.$^{-1}$ [b]	Energy of activn. (Ea), kcal./mole
trans-3,5-Diphenyl-1-pyrazoline[c]	1.25	17.9
trans-3,5-Bis(*p*-chlorophenyl)-1-pyrazoline	1.65	15.6
trans-3,5-Bis(*p*-methoxyphenyl)-1-pyrazoline	2.55	16.3
cis-3,5-Bis(*p*-methoxyphenyl)-1-pyrazoline	4.25	11.8

[a] Rates measured by nitrogen evolution. [b] At 80°. [c] Corrected values from ref. 3c.

tion energy of the *trans*-pyrazolines was essentially the same.

The faster rate and the lower activation energy of the decomposition of II are in agreement with the greater strain of the C–N bonds and the increased steric hindrance of the two aryl substituents. Indeed, the n.m.r. analysis (*vide supra*) had indicated a strong puckering of the $-CH_2-$ away from the C—N=N—C plane of the ring. As a consequence, considerable stretching of the C–N bonds occurs and the two *p*-methoxyphenyl groups (*cis* to each other) move closer to each other. On the other hand, this effect would be opposed by the dipole–dipole repulsion of the π-electrons system of the aromatic rings, resulting in decreased stability of the ring. This, coupled with the fact that the *cis*-cyclopropane (VI) is the less stable isomer, suggests that the biradical generated from the *cis*-1-pyrazoline would possess sufficient energy to have free rotation around the C–C bond occur before coupling. The photochemical results, while in keeping with the trend of greater stereoselectivity, support this view. As in the thermal decompositions, no olefins were found.

Experimental[18]

p-Methoxyphenyldiazomethane. A mixture of 53.6 g. (0.20 mole) of anisalazine and 40.0 g. (1.25 moles) of anhydrous hydrazine was refluxed for 12 hr. The reaction mixture was poured into 500 ml. of ether (previously washed with aqueous sodium hydroxide[5]), the lower layer was discarded, and the remaining colorless ethereal solution was washed with two 250-ml. portions of cold water. This solution was then filtered into a flask containing 120 g. of anhydrous sodium sulfate. The mixture was cooled in an ice bath and 5 ml. of a saturated alcoholic potassium hydroxide solution was added. Then 170 g. (0.8 mole) of yellow mercuric oxide was added portionwise over a period of 1.5 hr. with stirring; almost immediately after the beginning of the addition a dark red color developed. After the addition was over, the mixture was stirred for an additional 45 min. at 0° and then filtered through Celite into a flask cooled to 0°. The dark red solution was used immediately for the preparation of 3,5-bis(*p*-methoxyphenyl)-1-pyrazoline described below.

(18) The melting points are uncorrected. The analyses were performed by the Schwarzkopf Microanalytical Lab., Woodside, N. Y. The n.m.r. spectra were obtained on a Varian Associates HR 60 spectrometer. The infrared spectra were run as KBr pellets on a Perkin-Elmer "21" spectrophotometer and the ultraviolet curves were obtained on a Bausch and Lomb Spectronic 505. The photolyses were carried out under nitrogen in n.m.r. tubes using a Hanovia high-pressure mercury lamp.

cis- and trans-3,5-Bis(p-methoxyphenyl)-1-pyrazoline (II and III). To the ethereal solution of *p*-methoxyphenyldiazomethane obtained above was added 26.8 g. (0.2 mole) of *p*-methoxystyrene in 25 ml. of pentane. The mixture was kept at 0 to −10° with slow stirring for 10 days during which time a white solid precipitated. The mixture was cooled to −78° and filtered rapidly. The solid was washed with pentane to remove the red color and sucked dry to give 20.0 g. (35.4% based on the styrene) of a mixture of isomers, m.p. 110–114° dec. The mixture was shown to consist of 56% of the *cis* and 44% of the *trans* isomer (a second similar preparation gave 58% *cis* and 42% *trans*) by measuring the areas under the methoxy protons in the n.m.r. spectrum (see Table I).

Separation of cis and trans Isomers II and III. The mixture of II and III obtained above (1.0 g.) was slurried in 10 ml. of benzene for 1 min. and filtered. The residue (A) was slurried in 5 ml. of benzene for 1 min. and filtered. This residue (B) was recrystallized twice from methanol to give 0.095 g. of *cis*-3,5-bis(*p*-methoxyphenyl)-1-pyrazoline (II), m.p. 114° dec., λ_{max}^{EtOH} 329 mμ (ϵ_{max} 329). This residue obtained by evaporation of the filtrate from A yielded after three recrystallizations from methanol 0.040 g. of *trans*-3,5-bis(*p*-methoxyphenyl)-1-pyrazoline (III), m.p. 129° dec., λ_{max}^{EtOH} 332 mμ (ϵ_{max} 533).

Anal. Calcd. for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92. Found (*cis* isomer): C, 72.20; H, 6.14; N, 10.07; (*trans* isomer) C, 72.06; H, 6.16; N, 10.10.

N-Acetyl-3,5-bis(p-methoxyphenyl)-2-pyrazoline (V).

A. From 3,5-Bis-(p-methoxyphenyl)-2-pyrazoline (IV). To 2.0 g. (7.1 mmoles) of the 2-pyrazoline[19] was added 10 ml. of acetic anhydride. The solution was heated on a steam bath for 2 hr. and the excess acetic anhydride was removed *in vacuo* to leave a viscous oil. This oil was dissolved in ether and the ether solution was washed with dilute sodium bicarbonate solution and water, then dried over anhydrous sodium sulfate. Removal of the solvent again left a viscous oil which was recrystallized three times from hexane–chloroform (20:1) to give colorless crystals, m.p. 91–92.5°.

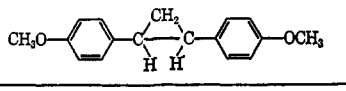
Anal. Calcd. for $C_{19}H_{20}N_2O_3$: C, 70.35; H, 6.22; N, 8.64. Found: C, 70.14; H, 6.38; N, 8.66.

B. From cis-3,5-Bis(p-methoxyphenyl)-1-pyrazoline (II). To 0.185 g. (0.66 mole) of the pyrazoline was added 2.0 ml. of acetic anhydride and a small crystal of *p*-toluenesulfonic acid. After 24 hr. at room temperature, the solution was heated on a steam bath for 0.5 hr. To the resuling brown solution was added 10 ml. of water and solid sodium bicarbonate until no more carbon dioxide was evolved. Extraction of the mixture with ether and purification as in part A gave 0.055 g. of the N-acetyl derivative of IV (V), m.p. 91–92.5°; mixture melting point with the product from A was 91–92.5°. Its infrared spectrum was identical with that of the material prepared in part A.

C. From trans-3,5-Bis(p-methoxyphenyl)-1-pyrazoline (III). Using the same conditions as in part B, 0.039 g. (0.14 mmole) of the 1-pyrazoline was converted to 0.030 g. of the N-acetyl derivative of IV (V), m.p. 91–92.5°, m.m.p. 91–92.5°. The infrared spectrum

(19) M. Hamada, *Botyu Kagaku*, 21, 22 (1956).

Table IV. N.m.r. Data of *cis*- and *trans*-1,2-Bis(*p*-methoxyphenyl)cyclopropanes[a]



Aromatic protons			Benzylic protons		
cis	*trans*	*cis–trans*	*cis*	*trans*	*cis–trans*
3.43	3.27	0.16	7.78	7.90	−0.22

β-Protons		Methoxy protons		
cis	*trans*	*cis*	*trans*	*cis–trans*
8.80	8.84	6.52	6.39	0.13

[a] Given in τ-values and taken in carbon tetrachloride at 60 Mc. with tetramethylsilane as an internal standard.

was identical with that of the material prepared in part A.

cis- and trans-1,2-Bis(p-methoxyphenyl)cyclopropane (VI and VII) from the Base-Catalyzed Decomposition of 3,5-Bis(p-methoxyphenyl)-2-pyrazoline (IV). The 2-pyrazoline[19] obtained from 130.5 g. (0.49 mole) of *p,p'*-dimethoxybenzalacetophenone and 50 ml. of anhydrous hydrazine was placed in a 1-l., three-necked flask equipped with two efficient condensers. The system was flushed thoroughly with dry nitrogen and 2.0 g. of powdered potassium hydroxide was added. The flask was then immersed in a Wood's metal bath preheated to 200°. The temperature was raised to 210° and the decomposition proceeded vigorously for 2 min. The cooled reaction product was dissolved in ether, washed with water, and dried over anhydrous sodium sulfate. Removal of the ether left 108.4 g. (88%) of a mixture of isomers which was dissolved in 550 ml. of warm methanol. Slow cooling gave 57.9 g. of the pure *trans*-1,2-bis(*p*-methoxyphenyl)cyclopropane (VII) as cream-colored crystals. Evaporation of the filtrate and distillation of the residue through a 12-in. column packed with stainless steel helices gave 10.2 g. of *cis*-1,2-bis(*p*-methoxyphenyl)cyclopropane (VI), b.p. 150–159° (0.3 mm.), and an additional 33.8 g. of the *trans* isomer, b.p. 163–167° (0.3 mm.).

The *cis* isomer solidified on standing and was crystallized from warm methanol to give the pure *cis* isomer, 10.2 g. (9.5%), m.p. 56.8–58°. The combined yield of the *trans* isomer was 91.7 g. (85.5% of the mixture), m.p. 70.5–71.5° (lit.[19] m.p. 70.5–71°). N.m.r. analysis[3c] showed each isomer to be greater than 98% stereopure (see Table IV).

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found (*cis* isomer): C, 80.27; H, 7.14.

Thermal Decompositions of cis- and trans-3,5-Bis(p-methoxyphenyl)-1-pyrazolines. The pure isomers of the *cis*- and the *trans*-3,5-bis(*p*-methoxyphenyl)-1-pyrazolines were decomposed by heating in 2 ml. of toluene at 100° for 1 hr. The solvent was then removed *in vacuo* and the residue was dried in a desiccator for 12–16 hr. In all cases, quantitative yields of cyclopropanes were obtained. The resulting oils or solids were dissolved *completely* in 0.5 ml. of Spectrograde carbon tetrachloride. These solutions were transferred to n.m.r. tubes and the ratios of products were determined by obtaining the spectra at very slow sweep speed and measuring the area under the methoxy peaks (see Table IV).

Photolytic Decompositions of cis- and trans-3,5-Bis(p-methoxyphenyl)-1-pyrazolines. The photolytic decompositions were carried out on approximately 50 mg. of each of the azo compounds dissolved in 0.5–1.0 ml. of purified tetrahydrofuran (distilled from methylmagnesium iodide). These solutions, in n.m.r. tubes, were irradiated (Hanovia high-pressure mercury lamp) for 3 hr. at 12–15° while nitrogen was slowly bubbled through the solutions by means of a capillary tube. Most of the solvent was then removed by allowing nitrogen to bubble rapidly through the solutions at room temperature. The last traces of solvent were removed by placing the tubes in a desiccator at 0.1 mm. for 12–16 hr. Quantitative yields of cyclopropanes were obtained in all cases. The analysis of the products was carried out as described for that of the thermal decomposition.

Decompositions. Control Experiments. Pure *cis*- and pure *trans*-1,2-bis(*p*-methoxyphenyl)cyclopropanes were subjected to the same conditions used in the thermal and photolytic decompositions of the azo compounds. Under the conditions of thermolysis no isomerization occurred. The cyclopropanes underwent isomerization[4] upon irradiation and the results are tabulated below.

	after irradiation	
pure cyclopropane	% *cis*	% *trans*
cis	90.7	9.3
trans	14.3	85.7

Kinetics. Spectrograde xylene was used as solvent for the decomposition, and the rate constants were calculated from the plots of nitrogen evolved against time.

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