Addition of 1-phenyl-2-methylbutadiene (**10**) to **3** in the presence of $SnCl_4$ also gave exclusively the nitro endo adduct **13**, while under thermal conditions the adducts **11** and **12** were formed in almost equal proportion. **13** mp 121–122°; nmr ($CDCl_3$); 4.62 (q, 4-H), 6 (d, 3-H), 6.55 (sextet, 5-H); $J_{3,4} = 5.5, J_{4,5} = 12, J_{5,6a} = 10.5, J_{5,6e} = 4.5$ Hz. **11** mp 146–147°; nmr ($CDCl_3$) 4.8 (m, 5-H), 6.5 (d, 3-H), 6.65 (t, 4-H); $J_{4,5} = 12$ Hz. **12** mp 159°; nmr ($CDCl_3$) 4.7 (m, 5-H), 6.15 (q, 4-H), 6.55 (d, 3-H); $J_{3,4} = 6, J_{4,5} = 12$ Hz.

The two common features of the above reactions are: (i) the formation of "ortho"–trans adducts in thermal reactions when 1,2-diphenylbutadiene is the diene; (ii) the exclusive formation of "ortho"-nitro–cis adducts in the presence of Lewis acids. These facts can be explained as follows. In the condensation of 1,2-diphenylbutadiene (**2**) with β-nitrostyrene, the presence of two phenyl rings on adjacent carbons would not allow both the rings to conjugate with the diene and would very likely force the 2-phenyl ring to take a position orthogonal to the plane of the diene. In the transition complex formed for cycloaddition reaction (Figure 1), by 1,3 interaction the 2-phenyl ring would offer steric hindrance to the terminal group of the nitrostyrene assuming an "ortho"–cis orientation, and the adducts formed would thus have an "ortho"–trans stereochemistry (**6** and **7**). In the case of 1-phenyl-2-methylbutadiene, when the steric effect at 2 position is less, both "ortho"–cis (**12**) and ortho–trans (**11**) adducts are formed.

In the presence of Lewis acids the complexing[12] of the nitro group would induce a strong dipole and favor its dipole–dipole or induced dipole[10a,14] and C–T bonding with the diene and its two phenyl rings and form a transition state having an "ortho"-nitro–cis stereochemistry leading to the formation of the adducts **5**, **8**, and **13**.

When **1** and cinnamic acid were treated in *o*-dichlorobenzene, **15** was exclusively obtained: mp 245°; methyl ester mp 150–151°; nmr ($CDCl_3$) 6.05 (d, 3-H), 6.22 (d, 6-H), 6.3 (q, 5-H), 7.0 (t, 4-H); $J_{3,4} = 10.5, J_{4,5} = 12, J_{5,6} = 6$ Hz. Condensation of 2 with cinnamic acid gave the adduct **14**: mp 235; methyl ester mp 134–135°; nmr ($CDCl_3$) 6.0 (d, 3-H), 6.8 (dd, 4-H), 6.95 (sextet, 5-H); $J_{3,4} = 10, J_{4,5} = 12, J_{5,6a} = 12, J_{5,6e} = 5, J_{6a,6e} = 15$ Hz. These assignments were confirmed by nmr of the adducts obtained from **1** and **2** with *trans*-α-*d*-cinnamic acid. The formation of "ortho"–trans adduct **14** in the case of **2** again points to the important role of the bulk of 2-substituent of the diene to stereoselectivity in the Diels–Alder reaction.

Thus in the Diels–Alder reaction a number of competing factors operate, and their relative dominance determines the stereo- and regioselectivity of the reaction. Under thermal conditions, other factors being equal, steric factors[15] seem to determine the nature of the products. However, when one of the substituents of the dienophile, a Lewis acid complexed nitro group in the present case, can associate strongly with the diene by dipole and C–T bonding,[5b] this can outweigh the steric constraints and form the thermodynamically less favored[16] products. By a proper choice of the various parameters related to these factors, one can preselect the stereochemistry of the adducts.

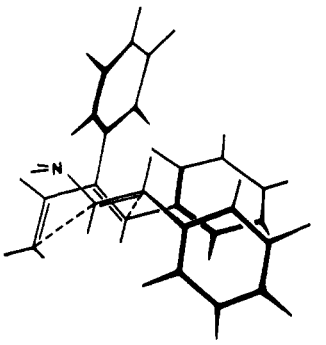

Figure 1.

(12) With ethyl acrylate it has been shown that the CO group complexes [9a,b] with $AlCl_3$ and the complex has been isolated[10] and studied by ir.[13]

(13) J. F. Norris and P. Arthus, *J. Amer. Chem. Soc.*, **62**, 874 (1940); M. F. Lappert, *J. Chem. Soc.*, 817 (1961).

(14) K. L. Williamson, Y. F. LiHsu, R. Lacko, and C. H. Youn, *J. Amer. Chem. Soc.*, **91**, 6129 (1969).

(15) M. J. Goldstein and A. H. Gevirtz, *Tetrahedron Lett.*, 4417 (1965).

(16) I. G. Dinuleseu, Gh. D. Mateeseu, and C. D. Nenitescu, *Rev. Roum. Chim.*, **13**, 505 (1968).

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Substituent Effects in the Ring Enlargement of *N*-Arylidene-2,2-diphenylcyclopropylamines

Sir:

Frey, *et al.*, measured the rearrangement rate of vinylcyclopropane to give cyclopentene at 340–390° and suggested a concerted pathway.[1] Later the same group preferred a trimethylene diradical, stabilized by allyl resonance, as an intermediate.[2] The problem has not been settled yet. Willcott and Cargle's finding, that cis,trans isomerization of *cis*-2-deuteriovinylcyclopropane is at least five times faster than conversion to cyclopentene,[3] is compatible with either mechanism. Neither of the two orbital symmetry allowed 1,3-sigmatropic processes[4] accounts for the steric course observed in the thermal isomerization of a trisubstituted vinylcyclopropane,[5] but a combination of concerted and diradical processes cannot be ruled out. We present kinetic evidence for the occurrence of a trimethylene intermediate in the ring expansion of a heteroanalog of the vinylcyclopropane system.

The rearrangement of the *N*-arylidene-2,2-diphenylcyclopropylamines (**1**) of Table I produces at 150° virtually quantitatively the 1-pyrrolines (**3**) which were

(1) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 3547 (1961); R. J. Ellis and H. M. Frey, *ibid.*, 4188 (1964); C. S. Elliott and H. M. Frey, *ibid.*, 345 (1965).

(2) H. M. Frey and D. C. Marshall, *J. Chem. Soc.*, 3981 (1962); R. J. Ellis and H. M. Frey, *ibid.*, 959 (1964); H. M. Frey, *Advan. Phys. Org. Chem.*, 4, 147, 155 (1966).

(3) M. R. Willcott and V. H. Cargle, *J. Amer. Chem. Soc.*, **89**, 723 (1967).

(4) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(5) P. H. Mazzocchi and H. J. Tamburin, *J. Amer. Chem. Soc.*, **92**, 7220 (1970).

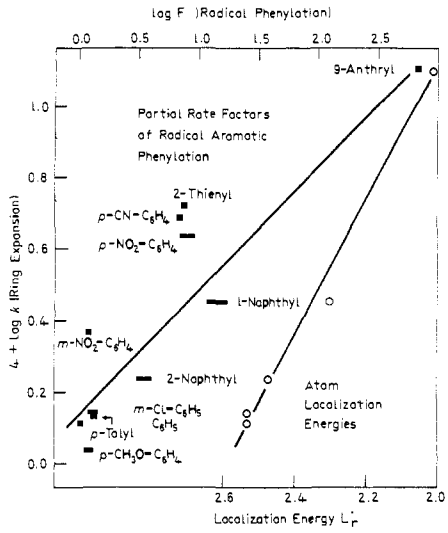


Figure 1. Correlation of log k (ring expansion) of **1** in benzonitrile with partial rate factors of radical phenylation (upper axis) and localization energies[11] (lower axis).

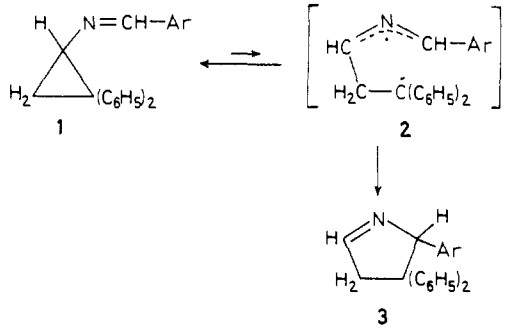


Table I. Rate Constants of Thermal Ring Expansion of Compounds **1** at 151.6°

Ar	10^5k_1 (sec^{-1})[a] Benzonitrile nmr	10^5k_1 (sec^{-1})[a] Decalin uv
C_6H_4-N(CH_3)$_2$-*p*	12.2	12.3
C_6H_4-OCH_3-*p*	10.9	11.4
C_6H_4-CH_3-*p*	13.6	14.0
C_6H_5	12.9	14.7
C_6H_4-Cl-*m*	13.9	16.9
C_6H_4-CN-*p*	23.4	
C_6H_5-NO_2-*p*	43.3	
1-Naphthyl	28.3	
2-Naphthyl	17.2	
4-Pyridyl	29.2	29.8
2-Thienyl	52.5	
9-Anthryl	128	

[a] Middle of two measurements.

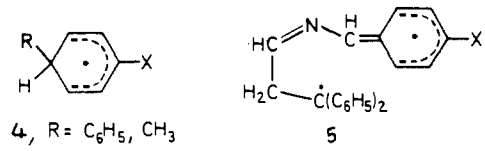
characterized by their spectra.[6,7] The rate of the first-order reaction can be measured by uv or nmr spectroscopy. The isomerization constant is neither affected by base (triethylamine) nor by acid (triethylammonium chloride) in dioxane. The log k_1 values of Table I for **1**, Ar = C_6H_4X, do not obey a linear relation with σ or σ^+. While the *p*-nitro and *p*-cyano compounds are three to four times faster than the benzylidene parent substance, electron-releasing substituents do not retard the isomerization. Replacing the side chain phenyl by 9-anthryl is accompanied by a tenfold rate increase. The ring expansion rate does not respond to solvent polarity (Table II).

Table II. Solvent Dependence of the Ring Expansion of **1**, Ar = *p*-CH_3O-C_6H_4 at 151.6°

Solvent	10^5k_1 (sec^{-1}) uv	10^5k_1 (sec^{-1}) nmr	E_T[a] (kcal mol^{-1})
Cyclohexane	11.1		31.2
Decalin	11.4		
Benzene		9.9	34.5
Dioxane	10.6		36.0
Chlorobenzene		9.9	37.5
Benzonitrile		10.9	42.0
Dimethylformamide	11.8		43.8
Dimethyl sulfoxide	13.0	14.7[b]	45.0
Acetonitrile	8.7	7.4[b]	46.0
Methanol	10.8		55.4

[a] Empirical parameter of solvent polarity: C. Reichardt, "Lösungsmitteleffekte in der organischen Chemie," Verlag Chemie, Weinheim, 1969. [b] Perdeuterated solvent.

A substituent effect of similarly modest size has been found for the radical phenylation of aromatic compounds.[8] The phenyl radical adds to the benzene derivative; the intermediate is the cyclohexadienyl radical **4** which is stabilized by the substituent X. The



unpaired electron of the aza-allyl radical, **2**, is delocalized into the aromatic ring as **5** shows. The expected analogy is confirmed by a rough correlation[9] between the ring expansion rate of **1** and partial rate factors, F, of aromatic phenylation[8] on a log scale (Figure 1). In both systems polynuclear aryls enhance the rate. Seven available numbers of "methyl affinities" of aromatic compounds[10] fit even better a straight line *vs.* log k_1 (ring expansion). The slopes of both lines are 0.35; *i.e.*, the participation of the aryl ring in the stabilization of the transition state is smaller for **5** than for **4**. That makes sense, because the influence of the aryl in **5** is attenuated by the allyl resonance.

Localization energies L_r[11] for the separation of one electron from the aromatic π cloud have been calculated by HMO. Figure 1 reveals a linear function of log k_1 with five L_r values. A linear correlation is also obtained with the parameter a_{or}[12] which measures the stabilization of the benzyl-type carbon by the aromatic π system; the slope suggests a 15% participation of Ar in the transition state. Thus, all the experimental

(6) For the corresponding ring expansion of *N*-*p*-nitrobenzylidene-1,2-diphenylcyclopropylamine, a structure proof of the 1-pyrroline by dehydrogenation and independent synthesis of the pyrrole has been described: R. Huisgen, R. Sustmann, and K. Bunge, *Chem. Ber.*, **105**, 1324 (1972).

(7) Satisfactory elemental analyses have been obtained for all compounds 1 and 3.

(8) Reviews: (a) D. R. Augood and G. H. Williams, *Chem. Rev.*, 57, 123 (1957); (b) D. H. Hey, *Advan. Free-Radical Chem.*, 2, 47 (1967).

(9) The linearity is probably impaired by the influence of polar factors in the radical arylation. The methoxyphenyl or nitrophenyl radical give distinctly different activity sequences compared with $C_6H_5\cdot$.[8b]

(10) M. Levy and M. Szwarc, *J. Amer. Chem. Soc.*, 77, 1949 (1955); W. J. Heilman, A. Rembaum, and M. Szwarc, *J. Chem. Soc.*, 1127 (1957).

(11) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, pp 335, 336, 398.

(12) M. J. S. Dewar and R. S. Sampson, *J. Chem. Soc.*, 2789 (1956).

data are well in accordance with a diradical intermediate **2** for the ring expansion **1** → **3**.

Diphenyldiazomethane reacts with excess methyl acrylate at 40° to give methyl 2,2-diphenyl cyclopropanecarboxylate (77%). The free acid is converted *via* the azide and isocyanate to 2,2-diphenylcyclopropylamine in 73% yield. Reaction with aromatic aldehydes furnishes **1**.

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Racemization and Ring Expansion of *N*-Arylidene-2,2-diphenylcyclopropylamines *via* a Common Trimethylene Intermediate

Sir:

The nature of the trimethylene species, which is responsible for cis,trans isomerizations of substituted cyclopropanes, constitutes one of the present-day problems for experimentalists[1] and theorists.[2] On describing the intermediate as "diradical,"[3] one has to be aware that the short lifetime does not allow trapping reactions. Though the assumption of a common trimethylene intermediate in ring expansion and cis,trans isomerization of vinylcyclopropanes[4] is tempting, there was no conclusive evidence so far. Kinetic studies of system **1** offer the first strong indication.

The racemization constant of (−)-**1** does not depend on the polarity of the solvent even if the *N*-benzylidene group bears electron-donating or -attracting substituents (Table I). Thus, the opening of the three-membered ring is not accompanied by charge separation. While >300° is needed for the cis,trans isomerization of 2-deuterio-1-vinylcyclopropane,[4] a half-reaction time of 2.8 hr at 101° is sufficient for the racemization of **1**, Ar = C_6H_5. Structural variation of the benzylidene group influences the racemization constant in the same way as it does the ring expansion to yield 1-pyrrolines[5] (Figure 1). The slope of the straight line (1.4) reveals that the racemization is slightly more sensitive to the change of the substituent than the ring expansion; *e.g.*, the rate ratio of 9-anthryl:phenyl amounts ot 23 and 10 for the two processes, respectively. The correspondence in the substituent reactivity scale, which is not of the usual Hammett or Taft type, strongly suggests the trimethylene diradical **2** as a common intermediate of racemization and ring expansion.

Table I. Variation of the Solvent in the Racemization of (−)-*N*-Arylidene-2,2-diphenylcyclopropylamines (**1**) at 101°

	$10^5 k_{rac}$ (sec^{-1}) for **1**, Ar =		
	p-CH_3O-C_6H_4	*p*-NO_2-C_6H_4	*p*-$(CH_3)_2N$-C_6H_4
Cyclohexane	6.46	37.3	
Decalin	5.50		6.80
Benzene	7.64	46.7	
Dioxane	5.34	31.8	6.88
Chlorobenzene	6.94		
Benzonitrile	5.35	35.2	6.33
Dimethylformamide	4.58		
Dimethyl sulfoxide	3.56	35.4	
Acetonitrile	4.19	27.2	
Methanol	4.10	32.2	7.17

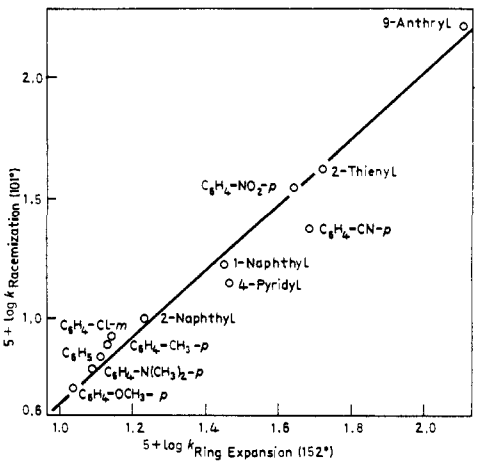

Figure 1. Correlation of log rate constants for racemization and ring expansion of *N*-arylidene-2,2-diphenylcyclopropylamines in benzonitrile.

The measured rate constants do not refer to elementary reaction steps but are products of the ring-opening constant and partition factors that are composed of the rate constants of reclosure of the three-membered ring, rotation, and 1,5 combination. The closely related activity sequences of racemization and ring enlargement appear to be mainly dictated by the ring opening constant which in first approximation reflects the stabilizing or destabilizing influence of the substituent on **2**. The steady-state treatment (published elsewhere) suggests that the other rate constants change in a systematic way on variation of the substituent.

Why is the experimental racemization constant of **1**, Ar = C_6H_5-OCH_3-*p*, at 101° 110 times faster than the ring expansion constant (extrapolated with the help of the activation parameters of Table II)? The aza-allyl radical **2** is produced from the s-trans conformation of **1** in the favored exo,exo-disubstituted configuration. This can only close to the three-membered ring (otherwise the pyrroline ring would contain a trans double bond) before and after rotation, thus bringing about racemization. The less-favored endo,exo configuration of **2** comes from the s-cis conformer of **1** and is capable of closing to the three-membered ring by 1,3- and to the pyrroline ring of **3** by 1,5-combination (Scheme I).

Is it allowed to transfer the mechanistic insight from the *N*-cyclopropylazomethine (**1**) to the vinylcyclopropane series? Table II betrays how little the replace-

(1) Only a few recent papers can be quoted here: (a) R. J. Crawford and A. Mishra, *J. Amer. Chem. Soc.*, **88**, 3963 (1966); (b) J. A. Berson and J. M. Balquist, *ibid.*, **90**, 7343 (1968); (c) R. G. Bergmann and W. L. Carter, *ibid.*, **91**, 7411 (1969); (d) J. P. Freeman, D. G. Pucci, and G. Binsch, *J. Org. Chem.*, **37**, 1894 (1972).

(2) (a) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968); (b) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968); (c) Y. Lean, L. Salem, J. S. Wright, J. A. Horsley, C. Moser, and R. M. Stevens, 23rd International Congress on Pure and Applied Chemistry, Boston Lectures, Vol. 1, Butterworths London, 197 (1971).

(3) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, 11, 92 (1972).

(4) (a) H. M. Frey, *Advan. Phys. Org. Chem.*, 4, 147, 155 (1966); (b) M. R. Willcott and V. H. Cargle, *J. Amer. Chem. Soc.*, **89**, 723 (1967).

(5) P. Caramella, R. Huisgen, and B. Schmolke, *J. Amer. Chem. Soc.*, **96**, 2997 (1974).