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

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$_3$O–C$_6$H$_4$	p-NO$_2$–C$_6$H$_4$	p-(CH$_3$)$_2$N–C$_6$H$_4$
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

ring is not accompanied by charge separation. While >300° is needed for the cis,trans isomerization of 2-

(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).

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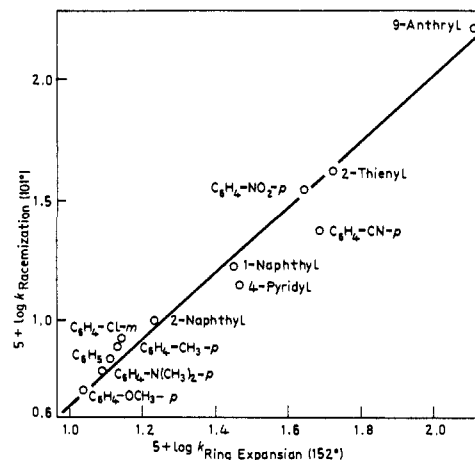
Figure 1. Correlation of log rate constants for racemization and ring expansion of N-arylidene-2,2-diphenylcyclopropylamines in benzonitrile.

deuterio-1-vinylcyclopropane,[4] a half-reaction time of 2.8 hr at 101° is sufficient for the racemization of 1, Ar = C$_6$H$_5$. 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.
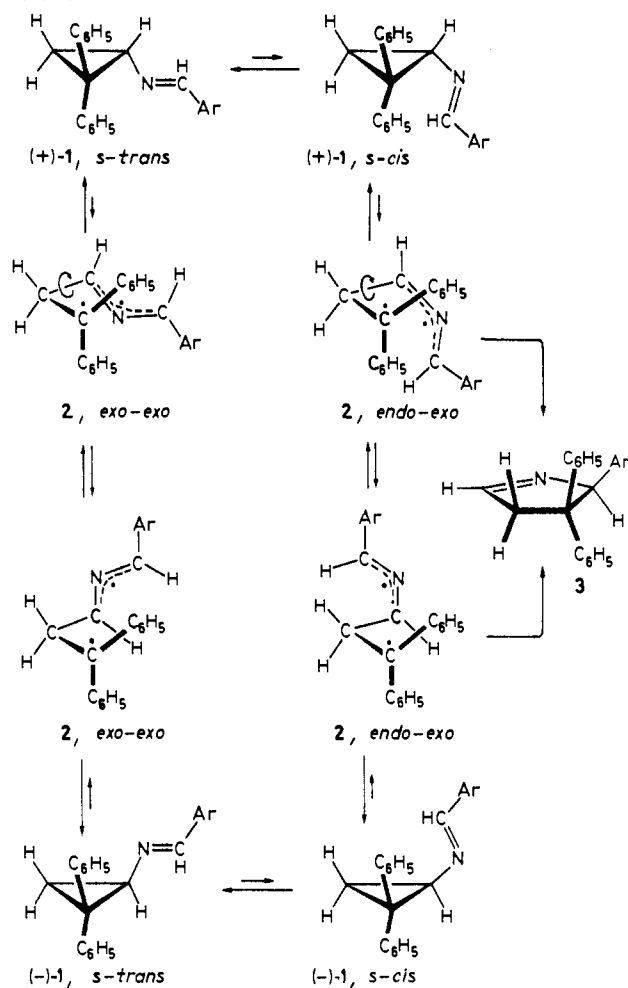
The measured rate constants do not refer to elementary reaction steps but are products of the ring-opening constant and partition factors that are composed of the rate constants of reclosure of the three-membered ring, rotation, and 1,5 combination. The closely related activity sequences of racemization 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$_6$H$_5$–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-

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

3000

Scheme I

(+)-1, s-trans   (+)-1, s-cis

2, exo-exo   2, endo-exo

3

2, exo-exo   2, endo-exo

(-)-1, s-trans   (-)-1, s-cis

Table II. Comparison of kinetic data for
N-p-Methoxybenzylidene-2,2-diphenylcyclopropylamine and
2,2-Diphenyl-1-trans-styrylcyclopropane in Decalin

I   II

	I	II
Racemization		
$10^7 k$, sec^{-1} (at 101°)	550	546
$\Delta H^{\ddagger}$, kcal mol^{-1}	26.8 ± 0.2	27.5 ± 0.8
$\Delta S^{\ddagger}$, eu	−7 ± 1	−5 ± 2
Ring expansion		
$10^7 k$, sec^{-1} (at 101°)	5.00	2.91
$\Delta H^{\ddagger}$, kcal mol^{-1}	33.2 ± 0.9[a]	30.9 ± 1.2
$\Delta S^{\ddagger}$, eu	1 ± 2[a]	−6 ± 2.6

[a] In benzonitrile.

ment of N by CH affects rate constants and Eyring parameters[6] of racemization and ring expansion. Of course, the nitrogen is located in the central position of the allyl radical where the electron density of the unpaired electron is zero.

The ring expansion rates of N-cyclopropylazo-methines reflect number and positions of the aryl substituents at the cyclopropane ring, as shown by follow-

(6) The activation parameters are apparent values; they concern multistep reactions.

ing half-reaction times. It is impressive that the three phenyls, in addition to the azomethine group, activate the ring opening to such an extent that the half-life at 50° is less than 1 hr.

$t_{\frac{1}{2}}$(min)	95	79	50
Temp.	190°	151°	50°
Solvent	Decalin	Decalin	Cyclohexane

The optical antipodes of 2,2-diphenylcyclopropane-carboxylic acid[7] are converted to 1 as described for the racemic acid.[5] Optical rotations are high, as $[\alpha]^{22}_{436}$ +1483° and −1514° for the enantiomers of 1, Ar = C_6H_4-N(CH$_3$)$_2$-p, testify.

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Formation of Remote Double Bonds by Ferrous Sulfate–Cupric Acetate Promoted Decomposition of Alkyl Hydroperoxides[1]

Sir:

The ferrous sulfate–cupric acetate promoted formation of olefinic alcohols from alkyl hydroperoxides (1) proceeds well in tertiary systems[2,3] while primary and secondary hydroperoxides have been reported, in closely related reactions, to yield only cleavage and oxidation products.[4]

$$\text{OOH} \xrightarrow[\text{HOAc}]{\text{Fe}^{2+}\text{-Cu}^{2+}} \text{OH} (\sim 50\%)^5 \qquad (1)$$
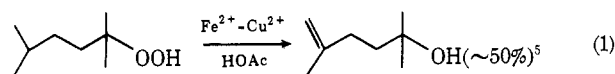
The synthetic attractiveness of forming remote least substituted olefinic alcohols, combined with the easy availability of primary and secondary hydroperoxides of variant structure[6–8] as well as the lack of theoretical justification for the restriction of this reaction (1) to tertiary hydroperoxides,[9] prompted us to carry out the current investigation. As may be seen in Table I, our expectations were justified thereby setting the stage

(1) We are grateful to the National Institute of General Medical Sciences (GM-16638) for support of this project.
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(5) See ref 3. The internal (4, 5) olefin is formed in one-tenth this yield.
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(9) J. K. Kochi, "Free Radicals," Vol. I, J. K. Kochi, Ed., Wiley-Interscience, New York, N. Y., 1973, Chapter 11, and references therein.