

STEREOCHEMISTRY OF THE METHYLENOCYCLOPROPANE REARRANGEMENT – II

EXCLUSION OF THE CONCERTED 45° PIVOT MECHANISMS*

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(Received in the USA 6 June 1972; Received in the UK for publication 26 September 1972)

Abstract—Mechanistic options for the thermal rearrangement of methylenecyclopropane are narrowed further by experiments with the four racemic diastereoisomeric 2-cyano-3-methyl-ethylidenecyclopropanes. The explicit assumption being made that these structural perturbations have neither weakened nor invalidated the mechanistic restrictions imposed by previously published work, it has been concluded that concerted birotational mechanisms involving transition states such as the 45° parallel twisted allylic (Woodward-Hoffmann, Möbius controlled) or the 45° perpendicularly twisted allylic (Berson-Salem subjacent orbital controlled) can be excluded from the presently acceptable set of structurally compatible, chirality-retaining, configuration-inverting mechanisms. A competitive rearrangement of the corresponding carboxylic esters to 1-methyl-2-ethyl-4-methoxyfuran makes these molecules unsuitable for study of the methylenecyclopropane rearrangement. Assignment of stereochemistry to the cyano compounds has been accomplished by application of base-catalyzed equilibration of the cyano center and photochemical iodine-catalyzed equilibration between geometrical isomers.

Historically, knowledge of the methylenecyclopropane rearrangement begins with the ravelling out of the uncommonly resistant structural elucidation of Feist's acid.¹ The pioneering mechanistic contribution, which we owe to Ullman,² reveals stereochemical retention of chirality during the rearrangement and allows all structurally compatible mechanisms to be divided into an accepted consonant set and a rejected, inconsonant set characterized by loss of chirality. The extent to which mechanisms belonging to the inconsonant set may operate as a minor pathway is being explored presently through an examination of the partial racemization which accompanies rearrangement.

Further subdivision of the consonant, chiral set

*Acknowledgement is made to the National Science Foundation for its support of this work.

†It has greatly facilitated our own visualization of the rotational elements of this and other similar rearrangements to use the Framework Molecular Models of Prentice-Hall, Inc., Englewood Cliffs, N. J. We first make a model of the intermediate (e.g., the orthogonal/allylic intermediate) with bonds of twice the normal length and the trigonal bipyramidal connectors to represent sp² atoms. *p*-Orbitals are added to these connectors as half-length bonds of one color for the (+) lobes and a second color for the (–) lobes. When two of the sp² atoms are now connected by a linear (octahedral) connector, a distorted but quite adequate sigma bond is formed which can be broken and remade between any other pair of sp² atoms.

‡Chirality of the various structures is described according to Kahn, Ingold and Prelog⁹ and geometrical isomerism according to the prescription of Blackwood *et al.*¹⁰

of mechanisms into an acceptable set involving inversion of configuration (the "pivot" mechanisms) and a rejected set involving retention of configuration has been accomplished by establishment of the relative configurational relationships between optically active starting material and product.³

Within this set of structurally compatible, chirality-retaining, configuration-inverting mechanisms, a further experimentally distinguishable division can be conceived.³ In one subset the two 90° internal rotations which are structurally essential to the consummation of the rearrangement may be coupled in two concerted ways controlled either by the symmetry of the highest occupied molecular orbital⁴ or by the symmetry of the subjacent orbital.⁵ In the other subset these rotations are not coupled and generate mechanisms involving two separated, independent steps and an intermediate.

The continuing effort to narrow the range of acceptable mechanisms by the imposition of additional independent conditions is justified by the increasing concern for internal rotation as a crucial component in the opening and closing of small rings^{6,7} and by the theoretical importance of the four-electron systems,^{4,8} among which are numbered the thermal rearrangements of cyclobutene, cyclobutane, vinylcyclopropane and vinylcyclobutane.

The concerted variations of the pivot mechanism involve simultaneous rotations of the two nonpivot atoms and reach their transition states when both rotations have proceeded, for example, to 45°. With (S,S)-2-cyano-3-methyl-(E)-ethylidenecyclopropane [(S,S)-(E)-*trans*; S 4c] serving as illustration, †‡ two concerted pathways can be described. In the

first, both Me-bearing atoms begin rotating at the same time as the cyclopropane ring is being opened and both rotate in the same sense (conrotatory), either S/S or R/R. When both have rotated 45° a transition state is reached which resembles an allylic radical twisted in a parallel manner. As a consequence of this twisting, bonding between the closer upper lobes of the ψ_2 orbital and the p -orbital of the pivotal atom exceeds the antibonding interaction with the more distant, lower lobes. Symmetry forbids overlap of the ψ_1 (S) orbital with the p -orbital (A). This 45° conrotatory pathway may be described as Woodward-Hoffmann, $2\pi_s + 2\sigma_a$, symmetry-allowed⁴ or as Dewar-Heilbronner-Zimmermann, Möbius aromatic (four electron with one phase dislocation).⁸

At the 45° stage the allylic radical has been twisted into a helix in which the planes of C atoms 1 and 3 are perpendicular to one another. Symmetry now forbids overlap of the ψ_2 orbital with the orthogonal p -orbital of the pivotal atom but it allows overlap with the ψ_1 orbital. This new factor has been discerned by Berson and Salem,⁵ and is designated "subjacent orbital control." Through its operation, it may be possible in favorable instances for concert to be maintained in otherwise Woodward-Hoffmann forbidden pathways. The stylized representation in Fig 2 of this 45° disrotatory transition state illustrates the possibility of overlap of one lobe of the p -orbital with the nearer, upper lobe of the helically twisted ψ_1 orbital and overlap of the other lobe of the p -orbital with the nearer lower

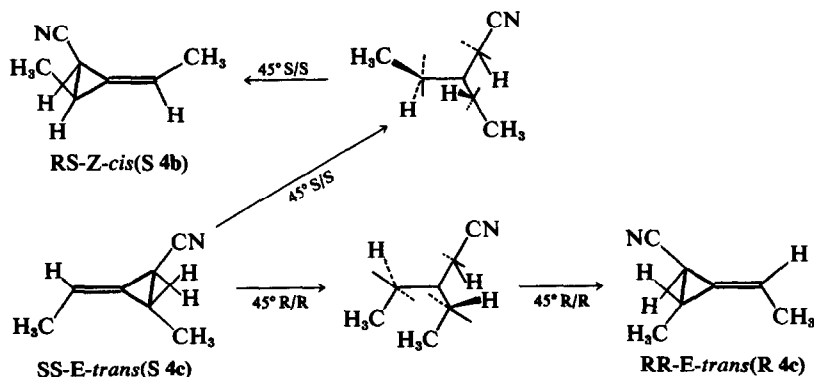


Fig 1. 45° Conrotatory birotational rearrangement of (S, S)-(E)-*trans* (S 4c).

The R/R coupled conrotation leads to the enantiomer of the starting material, (R, R)-(E)-*trans* (R 4c), whereas the S/S leads to a different diastereoisomer (R, S)-(Z)-*cis* (S 4b) in which the chirality of the nitrile-bearing atom, the *cis,trans* relationship of the ring substituents and the geometrical isomerism about the double bond are converted to their opposites (Fig 1). Since, by symmetry, (R, S)-(Z)-*cis* (S 4b), would be converted to its enantiomer, (S, R)-(Z)-*cis* (R 4b), by an S/S coupled birotation, at equilibrium a pair of racemic diastereoisomers, (E)-*trans* and (Z)-*cis*, would result. Thus, operation of coupled rotations in the same sense (45° conrotatory) would lead to a division of the four diastereoisomers into two mutually noninterconvertible pairs.

The second concerted pathway differs from the first in that the two simultaneous rotations are in the opposite sense (disrotatory), either R/S or S/R.

In this 45° disrotatory pathway, S 4c is transformed by S/R coupled rotations into R 4a and by the R/S rotations into S 4d. This mode is unable to generate 4b as a primary product.

The alternative nonconcerted mechanisms consist of two time-separated rotations of 90°. In one of these sequences, the first rotation may proceed in either an (S) or an (R) sense, to a pair of intermediates each containing a fully stabilized, planar allylic and an orthogonally oriented p -orbital on the pivotal atom [Fig 2 — "orthogonal/allylic" pS -(Z, E)_{CN}]. Symmetry forbids overlap of either the ψ_1 or ψ_2 allylic orbitals with the orthogonal p -orbital. (It may be noted that two 45° conrotations from this intermediate lead to the Woodward-Hoffmann transition states described above and two 45° disrotations lead to the Berson-Salem transition states). The second 90° rotation may then proceed from either of these two intermediates in either an (S) or an (R) sense *ad libitum*. In this two-step, "orthogonal/allylic" mechanism the entire set of four diastereoisomers may be generated. In the illustration of Fig 3, S 4c may be transformed into R 4a, S 4b and R 4d through the intermediate designated (pS)-(Z, E)_{CN} and into *rac* 4c and *rac* 4d through the meso (E, E)_{CN} intermediate.*

*The subscript "CN" designates the cyano-bearing atom as the pivot atom in the "orthogonal/allylic" mechanism and the pilot atom in determining planar chirality. The "orthogonal/allylic" intermediates are treated as an example of planar chirality⁹ in which "nearer" (Z) takes precedence over "further" (E).¹⁰

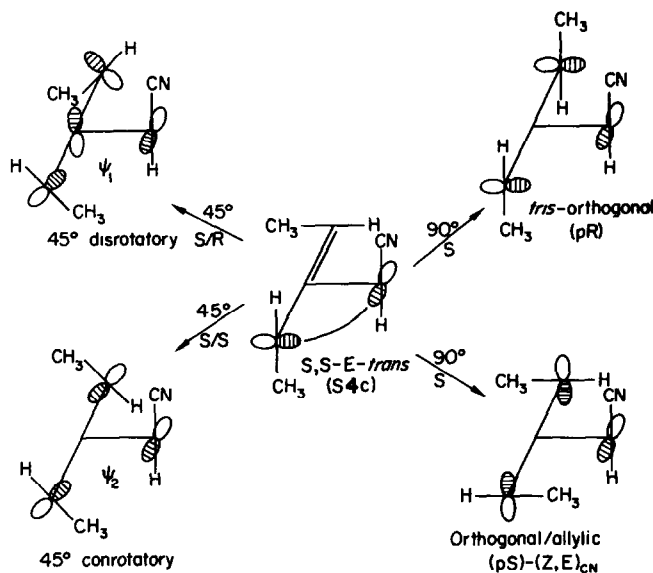


Fig 2. Four pivot mechanisms. Two concerted: 45° conrotatory, frontier orbital controlled and 45° disrotatory, subjacent orbital controlled; two nonconcerted with intermediate: Möbius "tris-orthogonal" and orthogonal with full allylic delocalization.

Whereas the 45° concerted pivot mechanisms permit the acquisition of stabilization at the sacrifice of an undetermined portion of the allylic delocalization energy, the "orthogonal/allylic" variation involves the rejection of four-electron stabilization in return for the achievement of full allylic stabilization.

In a second, nonconcerted birotational mechanism, the order of the two 90° rotations is reversed. This mechanism, first appearing in print as an illustration of the simple rules for identifying Möbius aromatic systems,^{8c} initially involves the 90° rotation of the olefinic methyl group in the (R) or (S) sense *ad libitum* simultaneous with the stretching of the cyclopropane 2-3 bond. The two resulting *tris-orthogonal** trimethylenemethanes, *meso-trans* and *pR*, are intermediates from which (R) and (S) rotations *ad libitum* generate *rac* 4a and *rac* 4c, and S 4a, S 4b and S 4d, respectively. Once again all three of the remaining four diastereoisomers may be generated in the rearrangement of any one. Stabilization in these intermediates is pure Möbius of unestimated magnitude.

The mechanistic division undertaken in this paper attempts to distinguish between a restrictive set of rotationally coupled pathways without intermediate in which at most two of the three diastereoisomers may be formed from any one and an unrestricted set of two-step pathways with intermediate defined in terms of freedom to form all

three diastereoisomers. The full statement of allowed outcomes for each of the four mechanisms, the 45° conrotatory and disrotatory pathways as illustrations of the restricted concerted set and the two-step "orthogonal/allylic" and "tris-orthogonal" as illustrations of the unrestricted set, is given in Table 1.

The initial experimental attack involved 2-carbo-(m)ethoxy-3-methyl-ethylidene-cyclopropanes, the analogues of the nitriles shown in the Fig 3. The four-diastereoisomers were obtained from the photochemical or copper-catalyzed reaction of 1,3-dimethylallene with (m)ethyl diazoacetate as nearly identical mixtures (ordered according to increasing retention time): Ia:19, Ib:4, Ic:100 and Id:35 parts. The two major isomers, Ic and Id, could be separated by preparative gas chromatography in 95% and 92% of purity, respectively, whereas isomers Ia and Ib were collected together and, in view of the subsequent behavior of all the isomers on thermal rearrangements, were not subjected to further attempts at separation in quantity. The NMR spectra of Ic, the mixture of Ia and Ib, and the mixture of all four isomers were similar.

When either Ic or Id (as the methyl esters) is heated at 160° some conversion to the other diastereoisomers occurs, but the major product is a new isomer (2). The formation of this material is irreversible, unaffected by the substitution of lead-potash glass for Pyrex and uninhibited by the introduction of triethylamine, diphenylamine or *p*-benzoquinone. On a larger scale, 2 is prepared easily by thermal rearrangement of the unseparated mixture of the diastereoisomers of 1.

*In view of the preceding discussion, the name "twist trimethylenemethane" applied to this assembly by Zimmermann^{8c} should better be replaced.

Table 1. The consequences of the operation of four birotational mechanisms on each of six stereoisomeric cyano-dimethyl-methylenecyclopropanes

Starting Isomer	Product Isomer	45° W.H. Conrotatory		45° B.S. Disrotatory		Orthogonal/Allylic				<i>meso</i> <i>trans</i>	
		P _{CN}	P _{CH₃}	P _{CN}	P _{CH₃}	Z, Z	Z, E pR	E, E pS	Z, E pS		pR
S 4a	4a	R		—		<i>rac</i>	—	—	—	—	<i>rac</i>
	4b			S		<i>rac</i>	R	S	S	S	
	4c			R			R			S	<i>rac</i>
	4d	S					S			S	
	<i>trans</i> -5 <i>cis</i> -5		R pS		R pS			R pR	R pS	R	R
S 4b	4a			S		<i>rac</i>	R	S	S	S	
	4b	R		—		<i>rac</i>	—	—	—	—	<i>rac</i>
	4c	S					S			S	
	4d			R			R			S	<i>rac</i>
	<i>trans</i> -5 <i>cis</i> -5		R pR		R pR			R pR	R pS	R	R
S 4c	4a			R			R			S	<i>rac</i>
	4b	S		—			S			S	
	4c	R				<i>rac</i>	—	—	—	—	<i>rac</i>
	4d			S		<i>rac</i>	R	S	S	S	
	<i>trans</i> -5 <i>cis</i> -5		R pR		R pR			R pR	R pS	R	R
S 4d	4a			R			R			S	
	4b	S		—			R			S	
	4c			S		<i>rac</i>	R	S	S	S	
	4d	R		—		<i>rac</i>	—	—	—	—	<i>rac</i>
	<i>trans</i> -5 <i>cis</i> -5		R pS		R pS			R pR	R pS	R	R
R- <i>trans</i> -5	4a		S		S	S	S			S	
	4b		S		S	S	S			S	
	4c		S		S			S	S	S	
	4d		S		S			S	S	S	
	<i>trans</i> -5 <i>cis</i> -5		—		—		pR	pS	pR	pS	
pS- <i>cis</i> -5	4a		R		R	S		R			<i>rac</i>
	4b		S		S	S		R			<i>rac</i>
	4c		S		S		S		R		<i>rac</i>
	4d		R		R		S		R		<i>rac</i>
	<i>trans</i> -5 <i>cis</i> -5		—		—		R	R	S	—	<i>rac</i>

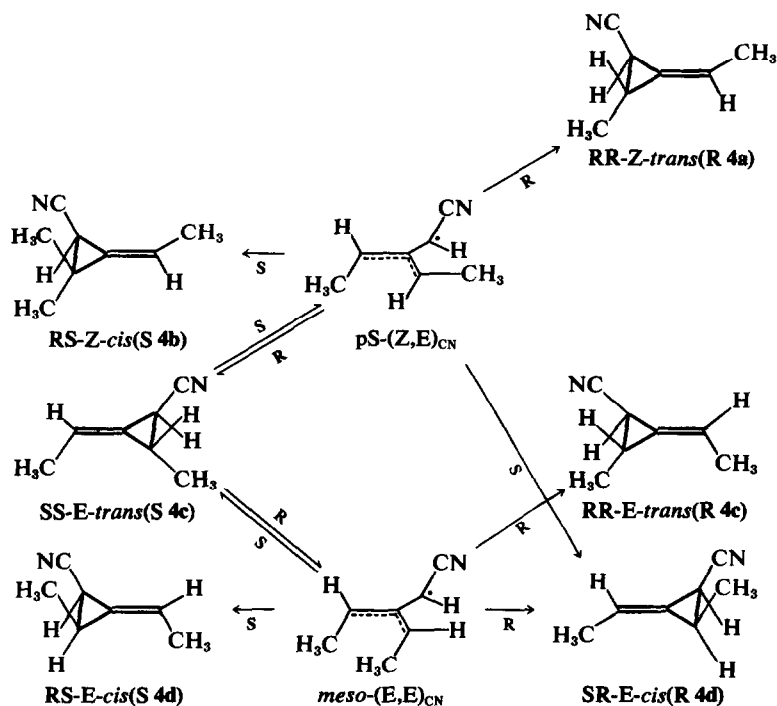


Fig 3. The operation of the "orthogonal/allylic" nonconcerted mechanism on (S, S)-(E)-trans (S 4c).

The NMR spectrum (δ scale) of **2** reveals singlets at 4.83 (1 H), 3.69 (3 H) and 2.09 (3 H), a quartet at 2.16 (2 H, $J = 6$ Hz) and a triplet at 1.09 (3 H, $J = 6$ Hz) ppm. That the latter resonances represent an Et group is confirmed by decoupling experiments. The proposed structure, **2**, is consistent with this NMR spectrum. The β -H atom of furan appears at 6.23 ppm but is expected to be shifted to 4.72 ppm according to the estimates of Gronowitz.¹¹ The protons of the α -OMe group in 1,3-dimethyl-4-methoxyfuran appear at 3.76.¹² The α -Me groups in 1,3-dimethyl-4-methoxyfuran¹² and 1-methylfuran¹³ are located at 2.12 and 2.17 ppm, respectively.

Confirmation of the structure is obtained by an independent synthesis based on the method of D'yakonov *et al.*, in which a 3-carbomethoxycyclopropane is rearranged to the isomeric furan by copper-catalysis.¹⁴ This reaction leads to a pair of furans which must share the structures 1-methyl-2-ethyl-(**2**) and 1-ethyl-2-methyl-5-methoxyfuran (**3**). One isomer has an NMR spectrum identical with that of **2**, the product of the thermal rearrangement of **1**. The other product, **3**, shows singlets at 4.80 (1 H), 3.69 (3 H) and 1.86 (3 H), a quartet at 2.46 (2 H, $J = 6$ Hz) and a triplet at 1.09 (3 H, $J = 6$ Hz) ppm. Little change in the chemical shift of the β -H or the OMe group is to be expected. The β -Me group in β -methylfuran is at 1.94 ppm, 0.23 ppm upfield from the α -Me group in sylvan at 2.17 ppm.¹³ Similarly the β -Me group in 1,3-dimethyl-4-methoxyfuran is located at 1.75 ppm, 0.37 ppm up-

field from the α -Me group at 2.12 ppm.¹² Consistently, the chemical shift of the β -methylene group in **2** at 2.16 ppm is upfield by 0.30 ppm from the 2-methylene group in **3**. The distinction between **2** and **3** seems assured.

The formation of the furan reinforces a persistent anxiety over the employment of the ester group in studies of thermal rearrangements. There are too many examples of the participation of the CO group of ketones and aldehydes to believe that the CO group of the ester shall remain immune. Mention may be made of the thermal equilibration of *cis*-1-formyl-2-vinylcyclopropane and 2,5-dihydro α -pin¹⁵ and the thermal conversion of 2,3-dichloro-5,6-dihydro-2H-pyran to 2-chloropenta-2,4-dienal.¹⁶ Suggestive but not mechanistically definitive are the formation of an acetoxyfuran in the thermal tetramerization of dimethyl acetylenedicarboxylate,¹⁷ the thermal addition of Feist's ester to dimethyl acetylenedicarboxylate,¹⁸ and the thermal rearrangement of 2,2-dicarbomethoxymethylenecyclopropane to 2-methoxy-3-carbomethoxy-4-methylfuran at 500°.¹⁹

A hypothetical mechanism, shown in Fig 4, involves abandonment by the ester group of its role as pivotal atom³ to the methyl group. Following a 90° rotation in the (R) sense, the carbonyl O atom may find itself properly positioned to form the protofuran without the need of any further rotational adjustment. Alternatively, the additional intermediacy of *cis*- or *trans*-1,2-dimethyl-carbo-

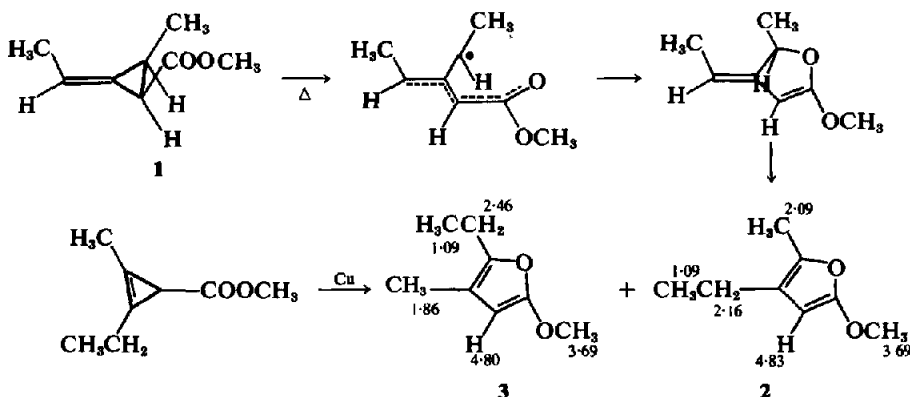


Fig 4. The thermal rearrangement of 2-carbomethoxy-3-methyl-ethylidenecyclopropanes (1) to 2-methyl-3-ethyl-5-methoxyfuran (2).

(methoxymethylenecyclopropane may be hypothesized. If the protofuran indeed be the intermediate, its subsequent transformation to the furan, being symmetry forbidden, would pose the same type of problem faced by Rhoads and Brandenburg in the rationalization of the thermal rearrangement of (*cis*-1-acetyl-2-vinyl)-2-methylcyclopropane.²⁰ Efforts designed to reveal surface effect by changing from Pyrex to a soft, lead-potash glass, copper-catalysis by using a sample of starting ester prepared photochemically, acid-catalysis by employing an amine as solvent, or involvement of free-radical chains by introducing inhibitors have been in vain. Whatever the mechanism, the competitive intervention of the ester permanently diverts the molecule from the methylenecyclopropane rearrangement and precludes any effective study of the pivot mechanism.

We have therefore turned to the cyano group, the linearity of which should prohibit cyclic interaction and be expected to remove the frustrations associated with the ester group at the inevitable cost of the three or four steps involved in transformation of the ester into the cyano group but not at the cost of the convenience of resolution associated with the carboxylic acid group. From recent work of Sachdev with optically active 2-cyano-isopropenylcyclopropane,^{21a} originally begun with the corresponding carboxylic esters,^{6b} and the earlier work of Walborsky and Hornyak^{21b} and Bergman,^{21c} the added benefits of a facile procedure for base-catalyzed epimerization and of significantly smaller, effective steric size are also to be associated with the cyano group.

In the present investigation, conversion of the mixture of the four diastereoisomeric esters (1) to the corresponding mixture of nitriles (4) is effected in an overall yield of 30% of theory by the 4-step sequence involving saponification to the acids, conversion to mixed anhydrides with ethyl chloroformate, amidation with ammonia and transformation to the nitriles with thionyl chloride and pyri-

dine. Four diastereoisomeric nitriles are produced, in order of their relative retention times, in nearly the same ratios as existed in the corresponding starting esters: 4a:20, 4b:6, 4c:100, 4d:56 from a mixture consisting of 1a:19, 1b:4, 1c:100, 1d:35. In order to support the conclusion that stereochemical integrity is largely preserved during the 4-step conversion of esters to nitriles and that the order of relative retention times has remained fortuitously unchanged, a sample consisting mainly of 1c [1a:2.7, 1b:2.7, 1c:94.0, 1d:0.6] was converted to 4c [4a:5.5, 4b:2.7, 4c:87.7, 4d:4.0].

Structural assignment to the four diastereoisomeric nitriles is based on three arguments. (1) When a sample of 4d (95.4% contaminated with 4-6% 4c) is treated according to the procedure of Sachdev with a solution of potassium *t*-butylate in anhydrous dimethylsulfoxide at room temperature for a few minutes,^{21a} an equilibrium mixture consisting of 4d (58.7%) and 4c (41.3%) is obtained. Thus, 4c and 4d are cyano-epimeric, as are 4a and 4b.

(2) When the same sample of 4d is irradiated in benzene solution with a little iodine, a mixture is obtained consisting of 4a:3.1, 4b:53.1, 4c:3.1 and 4d:40.7%. Thus, 4d and 4b represent a pair of geometrical isomers, as do 4c and 4a.

(3) Tentative assignment of a configuration to one of the four interrelated diastereoisomers is based on a steric argument. It is proposed that the reaction of methyl diazoacetate with 1,3-dimethylallene to form the four diastereoisomeric esters be sterically biased. The less hindered reaction paths would favor the isomers in which the exocyclic Me group and the ester group were *entgegen* (E) one another and the cyclopropane Me group and the ester group were *trans* to one another. Should these hypothetical steric factors be valid, they would combine to favor the product with the configuration, (E)-*trans*. This structure could then be assigned tentatively to the isomer, 1c, predominating among the esters and corresponding to the nitrile, 4c. The three other assignments would follow from

the arguments in (1) and (2). Consistently, the kinetically, sterically least favored ester (**1b**) should have the structure (*Z*)-*cis*.

Definitive assignment of configuration and complete confirmation of the validity of conclusions based on (1), (2) and (3) has been obtained by application of the pseudocontact model of Willcott and Davis²² to each of the four isomeric nitriles.²³ R values resulting from testing the experimental slopes of the lanthanide shifts of each of the four diastereoisomers, **4a**, **4b**, **4c** and **4d** against each of the four structures (a), (b), (c) and (d) are brought together in Fig 5. There can be little doubt about the correctness of the structures, nor the power of the Davis-Willcott method.

One of the ancillary advantages accruing from the change to the cyano group is a marked reduction in steric interaction. On the assumption that equilibrium has been reached in the base-catalyzed epimerization, the *trans/cis* ratio (**4c/4d**) of 41.3/58.7 corresponds to a free energy difference of +0.21 kcal/mole. By comparison, the same difference between two Me groups would have been ≥ -1.00 kcal/mole. Sterically, the cyano group in this type of geometrical relationship seems to be comparable to a hydrogen atom.

On thermal rearrangement in the gas-phase for 16 hr at 150°, the mixture of 2-cyano-3-methyl-ethylidenecyclopropanes, **4a-d**, as it is obtained from the preparation, is converted to an equilibrium mixture of these four diastereoisomers and two new isomeric compounds, *trans*-**5**, having a shorter retention time and *cis*-**5**, having a retention time between those of **4b** and **4c**. The amounts of the six isomers at equilibrium are given: **4a**: 13.2, **4b**: 17.4, **4c**: 21.1, **4d**: 23.1, *trans*-**5**: 22.9 and *cis*-**5**: 2.3%. Equilibrium has also been approached from pure samples of **4c**, **4d** and *trans*-**5**.

Support for the structure of *trans*-**5** is based on its NMR spectrum (δ scale): 5.66 (broad s, 1 H), 1.26 (d, $J = 5$ c/s, 6 H) and two additional protons

underneath the Me doublet (total area corresponds to 8 H). In *trans*-1,2-dimethylmethylene-cyclopropane, the Me protons appear at 1.13 ppm and the cyclopropane protons at 1.00 ppm.²⁴ In 1,1-dicyano-methylene-cyclopropane the *anti* vinyl proton appears at 5.80 ppm,²⁵ while in a variety of methylenecyclopropanes the vinyl protons range between 5.1 and 5.5 ppm.²⁶

The structures assigned to the two new isomers are consistent with the view that the Me group has usurped the role of pivot from the cyano group. In accord with previous experience, the *trans* relationship between Me groups should be favored. The actual free energy difference, -1.9 kcal/mole, is somewhat larger than the -1.0 kcal/mole to which one has become accustomed. This abdication of the role of pivot appears to be the cyano counterpart of the thermal rearrangement of the esters to the furan derivative.

Parenthetically, it is noteworthy that the negligible difference in free energy between *trans*-**5** and (E)-*trans* (**4c**) (0.07 kcal/mole) is indicative of the near identity of the conjugative interactions of the Me group and the cyano group with a double bond.

The appearance of *cis*- and *trans*-**5** raises the question whether any useful information bearing on a distinction between the 45° concerted mechanisms and the 90° nonconcerted mechanisms can be obtained. The 45° conrotatory mechanism, for example, applied to (R, R)-*trans*-**5** may involve two pairs of coupled rotations (at the right, Fig 6), and could lead to all four diastereoisomers. Thus 45° S/S rotations applied to the (Z) and (E) Me groups lead to (S, S)-(Z)-*trans* (**4a**) and (R, S)-(Z)-*cis* (**4b**), respectively, while 45° R/R rotations lead to (R, S)-(E)-*cis* (**4d**) and (S, S)-(E)-*trans* (**4c**), respectively. The nonconcerted "orthogonal/allylic" variation (first left, then right, Fig 6) may likewise lead to all four diastereoisomers. A summary of the consequences of the other two mechanisms is given in Table 1. It follows that no useful

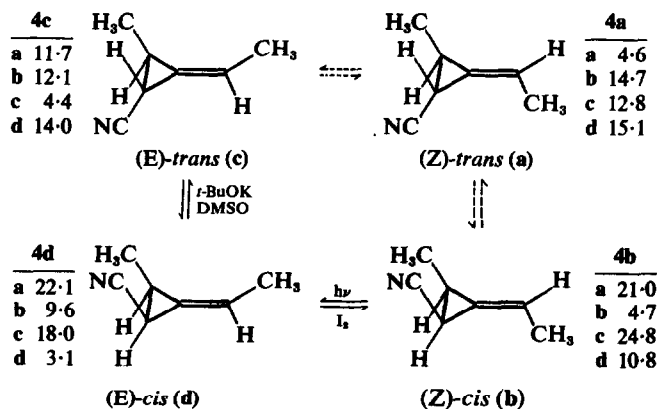


Fig 5. R values for the best fits of the slopes of the lanthanide shifts for each of the diastereoisomeric 2-cyano-3-methyl-ethylidenecyclopropanes against each of the four possible structures.

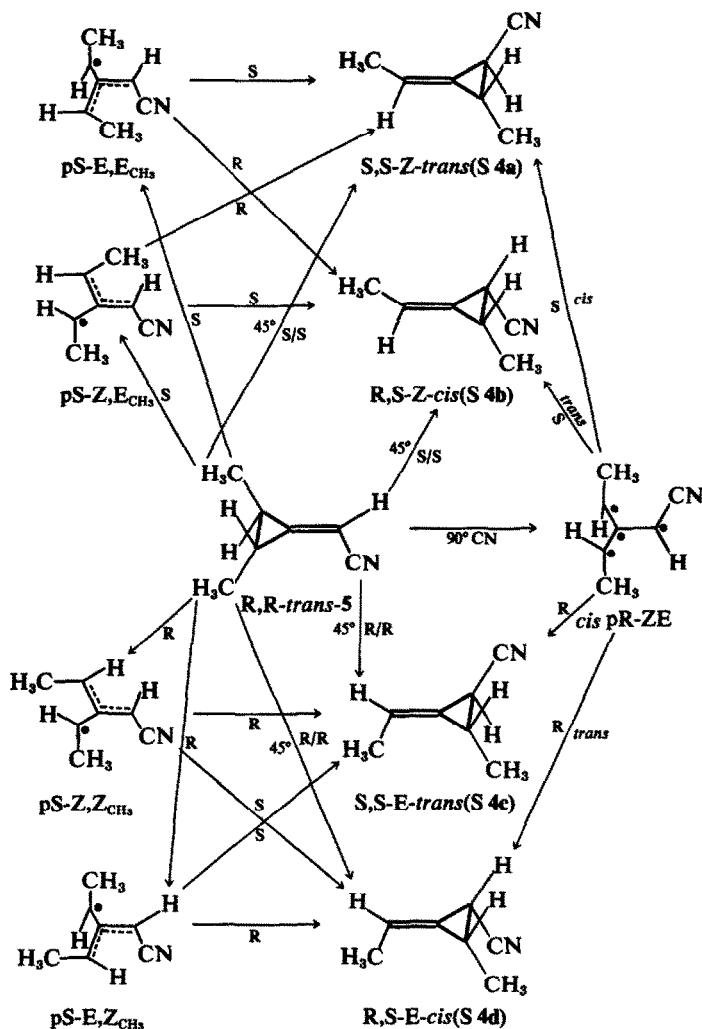


Fig 6. Possible transformations of (R,R)-trans-5 by the "orthogonal/allylic" (left), the 45° conrotational and the "tris-orthogonal" (far right) mechanism (see Table 1).

information bearing on the mechanistic question can be derived from an examination of the rearrangement of 4 if once formed *cis*- or *trans*-5 is given an opportunity to rearrange back to 4a-d; that is, no useful information can be derived from a rearrangement which is allowed to approach equilibrium.

In the face of the spoiling intervention of *cis* and *trans*-5, only the determination of the specific rate constants for the formation of each of the three diastereoisomers from a fourth can in principle lead to a distinction between two sets of mechanisms. Under the operation of the 45° rotationally coupled mechanisms, any one of the four racemic diastereoisomeric nitriles may rearrange to only one different isomer if the coupling is in the conrotatory sense (e.g., 4c may lead to 4b) or to two different isomers if the coupling is in the disrotatory sense

(e.g., 4c may then lead to 4a and 4d but not to 4b). Under the set of nonconcerted mechanisms with intermediate (e.g., the "orthogonal/allylic" or the "tris-orthogonal") all three diastereoisomeric nitriles may be produced in the rearrangement of any one of them. A complete summary of possible results is shown in Table 1.

The rearrangements of 4c and 4d have been examined near the beginning of the reaction and, from satisfactorily linear plots of extent of reaction versus time, first order rate constants at zero time have been determined. More significant is the fact that linear extrapolations back to zero time intersected the origin within experimental error in all instances. In other words, there was no indication of an initial rate of zero, rising only after other products had been formed to an appreciable extent.

From Fig 7, in which the specific rate constants

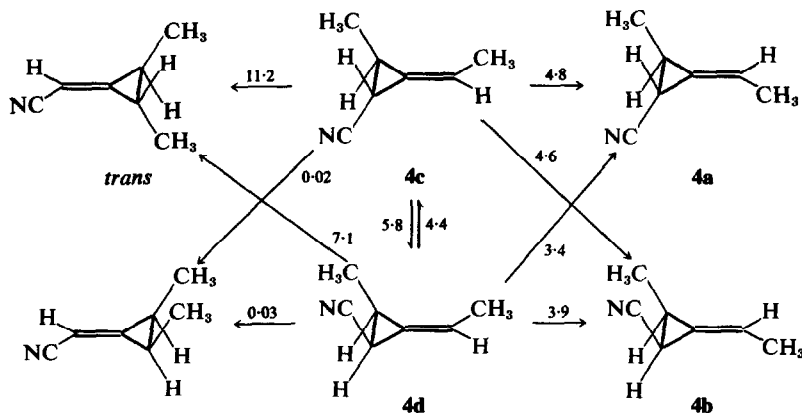


Fig 7. Initial specific first-order rate constants at 110.6° in units of 10^{-7} sec^{-1} for the rearrangements.

of the formation of the other five isomers from both **4c** and **4d** at 110.6° in units of 10^{-7} sec^{-1} are noted, it is apparent that **4a**, **4b** and **4d** are formed from **4c** at comparable rates (4.8, 4.6 and 5.8, respectively) and that **4a**, **4b** and **4c** are similarly formed from **4d** (3.4, 3.9 and 4.4, respectively). Although *trans*-5 is formed faster than any one of the diastereoisomers, the reliability of the initial rates is not affected. *cis*-5 is formed much too slowly to be disturbing.

The firm exclusion may be drawn that neither of the restrictive, 45° coupled birotational pathways is predominant. The 45° conrotatory, Woodward-Hoffmann concerted pathway requires that **4b** be the single product of the rearrangement of **4c** (Fig 1) and that **4a** be the single product of the rearrangement of **4d** (Table 1). The 45° disrotatory, Berson-Salem concerted pathway requires that **4a** and **4d** but not **4b** be the products of rearrangement of **4c** and that **4b** and **4c** but not **4a** be the products of rearrangement of **4d** (Table 1). While it is admitted that the fortuitous operation of both pathways in approximate ratio, Woodward-Hoffmann, 4.2 parts – Berson-Salem, 10.0 parts, offers a consistent hypothesis, we prefer to draw the conclusion that neither pathway operates in significant measure and to note that the burden of proof falls on him who shuns the razor of William of Ockham.

*On the strength of theoretical calculations of A. S. Kende and R. Greenhouse, it is highly unlikely that the *tris*-orthogonal state can play a role in the rearrangement. We take pleasure in acting on their generous permission to include their results here. Relative to the planar state ($0^\circ, 0^\circ, 0^\circ$) as reference, the *tris*-orthogonal state ($90^\circ, 90^\circ, 90^\circ$) is calculated by the extended Hückel and INDO-CI methods to be 2.14 and 2.2 e.v., respectively, higher in energy and therefore not remotely competitive.

†The geometrical isomerism among the planar trimethylenemethane intermediates is described by designating first the methyl group on the carbon atom nearer (*cis*) to the cyano group as either nearer (Z) or further (E) and second the (Z) or (E) nature of the methyl group on the carbon atom further (*trans*) to the cyano group.

The nonrestrictive set of pathways which admit of the formation of all three diastereoisomers constitutes a more economical hypothesis. At the current stage of the present investigation no experimental distinction between the “orthogonal/allylic” and “*tris*-orthogonal” alternatives (Fig 2) can be made.* It can be seen by inspection of Table 1 that racemic *cis*-5 may afford racemic *trans*-5 under the operation of the “orthogonal/allylic” pathway, but not under the operation of the “*tris*-orthogonal” pathway or the two 45° coupled rotational pathways. It is also apparent that examination of the rearrangement with optically active starting materials of known optical purity affords an even more incisive (and at the same time more arduous) means of distinguishing among the four pathways. Thus, optically active S **4c** must give racemic or S **4a** to the extent that the “*tris*-orthogonal” mechanism operates, but only R **4a** under the operation of the 45° B.-S. or “orthogonal/allylic” pathways; and to the extent racemic or R **4d** is produced the “orthogonal/allylic” but not the 45° B.-S. or “*tris*-orthogonal” is admitted.

An incidental benefit from the examination of optically active materials is the opportunity to confirm the assumption that the structural perturbations in the present system, which appear to have led to a weakening of the pivotal role of the ester and cyano bearing atom, have not introduced new mechanisms of the planar tetrarotational trimethylenemethane type (Table 2).† On the basis of theoretical calculations in which the angle between the planes occupied by the methylene and allyl groups are varied, Dewar and Wasson find the planar, closed shell singlet structure to be 24 kcal/mole higher in energy than the singlet “orthogonal/allylic” structure admitted by the present work.²⁷

It may be noted that the trimethylenemethane pathways require four rotations for their realization and can be subdivided into two restricted modes in which the two pairs of bond-breaking and bond-making rotations may be coupled conrotationally or

Table 2. The consequences of the operation of three tetrorotational mechanisms on each of six stereoisomeric cyano-dimethyl-methylenecyclopropanes

		Tetrorotational trimethylenemethane						
		Conrotatory		Disrotatory		Random		
		Z, Z	Z, E	E, Z	Z, Z	Z, Z	Z, E	E, Z
S 4a	4a	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>
	4b	<i>rac</i>			<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>
	4c		<i>rac</i>	<i>rac</i>			<i>rac</i>	<i>rac</i>
	4d						<i>rac</i>	<i>rac</i>
	<i>trans</i> -5 <i>cis</i> -5	<i>rac</i>		<i>rac</i>		<i>rac</i>	<i>rac</i>	<i>rac</i>
		Z, Z	E, Z	Z, E	Z, Z	Z, Z	Z, E	E, Z
S 4b	4a	<i>rac</i>			<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>
	4b	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>
	4c						<i>rac</i>	<i>rac</i>
	4d		<i>rac</i>	<i>rac</i>			<i>rac</i>	<i>rac</i>
	<i>trans</i> -5 <i>cis</i> -5	<i>rac</i>		<i>rac</i>		<i>rac</i>	<i>rac</i>	<i>rac</i>
		E, E	Z, E	E, Z	E, E	E, E	Z, E	E, Z
S 4c	4a		<i>rac</i>	<i>rac</i>			<i>rac</i>	<i>rac</i>
	4b						<i>rac</i>	<i>rac</i>
	4c	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>
	4d	<i>rac</i>		<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>
	<i>trans</i> -5 <i>cis</i> -5	<i>rac</i>		<i>rac</i>		<i>rac</i>	<i>rac</i>	<i>rac</i>
		E, E	E, Z	Z, E	E, E	E, E	Z, E	E, Z
S 4d	4a			<i>rac</i>			<i>rac</i>	<i>rac</i>
	4b		<i>rac</i>				<i>rac</i>	<i>rac</i>
	4c	<i>rac</i>			<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>
	4a	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>
	<i>trans</i> -5 <i>cis</i> -5	<i>rac</i>		<i>rac</i>		<i>rac</i>	<i>rac</i>	<i>rac</i>
		Z, Z	E, E	Z, E	E, Z	E, E	Z, Z	Z, E
R- <i>trans</i> 5	4a	<i>rac</i>			<i>rac</i>		<i>rac</i>	<i>rac</i>
	4b	<i>rac</i>			<i>rac</i>		<i>rac</i>	<i>rac</i>
	4c		<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>
	4d		<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>
	<i>trans</i> -5 <i>cis</i> -5	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>
		Z, E	E, Z	E, E	Z, Z	E, E	Z, Z	Z, E
pS- <i>cis</i> 5	4a	<i>rac</i>			<i>rac</i>		<i>rac</i>	<i>rac</i>
	4b		<i>rac</i>		<i>rac</i>		<i>rac</i>	<i>rac</i>
	4c	<i>rac</i>		<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>
	4d		<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>
	<i>trans</i> -5 <i>cis</i> -5	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>	<i>rac</i>

disrotationally or may be left uncoupled or random. Although the 2-cyano-3-methyl-ethylidenecyclopropanes do not contain sufficient information to distinguish between the conrotatory and disrotatory pathways, they do allow distinction to be made between this pair, neither member of which allows, for example, 4b to be formed from 4c, and the ran-

dom process which permits the formation of all five isomers (see Table 2). The exclusion can be drawn that neither of the coupled tetrorotational pathways may be predominant. Further comment awaits elucidation of the fate of optical activity.

In principle (see Table 1), examination of *trans*-5, which may not proceed to *cis*-5 directly by either of

the 45° coupled birotational pathways or by way of the "tris-orthogonal" intermediate, can provide distinguishing information, but, in practice, *cis*-5 is present to such a small extent at equilibrium and is formed from *trans*-5 (as well as 4c and 4d) so slowly that its initial rate of formation by extrapolation to zero time cannot be determined, without unseemly difficulty, with an accuracy sufficient to significance. Nonetheless, it is of some interest that *trans*-5 proceeds much faster to 4a and 4b than to the other isomers.

In the opening of a small ring, as in the present rearrangement of methylenecyclopropane, excitation of the stretching mode of the bond to be broken does not of itself lead to bondbreaking unless a rotational component is added.⁷ The activation energy can be imagined to consist of the sum of the activation energy for the hypothetical stretching of the bond and an additional activation energy associated with the torsional component.

The formation of 4a and 4b is determined by the direction of the initial rotation of the first Me group. If this group rotates away from the adjacent Me-bearing C atom [(S) with reference to (R, R)-*trans*-5], the "orthogonal/allylic" intermediates, (pS)-(Z, E)_{CH₃} and (pS)-(E, E)_{CH₃}, must terminate in 4a and 4b by contraction *cum* torsion, (S) or (R) *ad libitum* (Fig 6). From models it appears that this (Z)-generating, (S) rotation carries the bulkier Me group away faster from the adjacent, Me-bearing pivot radical than would an (R) rotation. Viewed alternatively the (S) rotation brings the Me group into proximity with the sterically surprisingly undemanding cyano group whereas the R rotation would bring the Me group into proximity with the *p*-orbital of the Me-bearing pivotal atom. The former process has the lower free energy of activation owing, in this interpretation, to a lower incremental energy of activation of an (S) rotational component.

This type of analysis, based on stretching *cum* torsion as the dynamic conceptual scheme, serves also to explain the strong favoring of *syn* products in the thermal rearrangement of optically active dimethyl dideuteriomethylenecyclobutane-*cis*-2,3-dicarboxylate.²⁸

EXPERIMENTAL

NMR spectra were obtained on a Varian Associates T-60 spectrometer with TMS as internal standard. IR spectra were recorded on a Perkin-Elmer Model 337 Grating Infrared spectrophotometer as neat liquids. GLC analyses were performed on a flame ionization Perkin-Elmer Model 990 instrument. Preparative GLC separations were done on an Aerograph Model A-90-P instrument.

Analytical columns. Capillary column A, 300 ft OV101. Capillary column B, 150 ft Zonyl A.

Preparative columns. Column C, 6 m ¼" 20% SE-30 on Anakrom ABS 50/60 mesh. Column D, 6 m ¼" 10% Carbowax 20M on Anakrom ABS 70/80 mesh.

2-Methyl-3-carbomethoxyethylidenecyclopropane (1)

Method A. A soln of 9 g, (0.09 mole) methyl diazoacetate in 20 ml 2,3-pentadiene (Chem. Samp. Co., > 99% pure) was added dropwise under N₂ to a stirred, refluxing soln of 0.1 g of *bis*-[N,N-phenethylsalicylaldiminato]-copper²⁹ in 10 ml of 2,3-pentadiene over a period of 4.5 hr. After 20 min additional stirring, excess allene (23 ml) was recovered by bulb to bulb distillation at 0° on a vacuum line. The residue was distilled *in vacuo*, b.p. 30–31°/0.8 mm. After purification by preparative GLC (column C, 135°, He 50 ml/min) 6.5 g of 1 (51%) (mixture of four stereoisomers) was obtained. Relative retention time: isomers 1a + 1b, 18 min; 1c, 20 min; 1d, 23 min. Composition of mixture (column A, 100°, He pressure 34 lb): 10.4% 1a (rel. retention, 18.5 min), 1.5% 1b (18.7 min), 67.3% 1c (20 min), 20.8% 1d (21.5 min). NMR spectrum of the mixture: (δ) 5.66 (m, 1H), 3.57 (s, 3H), 2.06–1.32 (m, 5H), 1.12 (m, 3H). IR 1750 cm⁻¹ (ester C=O); *m/e* observed 140-083510; calcd for C₈H₁₂O₂: 140-083724.

Method B. A soln of 3.5 g methyl diazoacetate in 20 ml 2,3-pentadiene was irradiated with a GE 275 watt sun lamp with water cooling. The reaction was monitored on column A and stopped after 13 hr when peaks with longer retention time started to appear. The mixture was washed with 1% ice-cold HCl aq, water and dried over MgSO₄. Excess pentadiene was removed by distillation at atm pressure, and the residue (1.9 g) was purified by preparative GLC (column C, same conditions as above), yield 1.7 g (35%). NMR and IR spectra were identical with those of 1 obtained by method A.

Separation of the mixture of stereoisomers on column C (135°, He 50 ml/min) afforded 3 fractions: a mixture of 1a + 1b (rel. amount unknown) (purity 92%); 1c (95%); 1d (92%). The NMR spectra of the individual isomers were essentially identical with that of the mixture.

Thermal rearrangement of 1
Analytical runs. Individual isomers or the mixture of the four isomers (1–2 μl portions) were heated in sealed ampoules at 160° in an electric oven under the conditions stated in Tables 3 and 4 and analyzed on column A (100°, He pressure 34 lb). Nonane was used as internal standard. The ampoules of lead-potash glass were made of Corning No. 0120 glass.

2-Methoxy-4-ethyl-5-methylfuran (2)

A degassed 1% solution of 1 (0.250 g) in dry benzene was sealed in a 480 ml Pyrex tube and heated at 160° for 48 hr. The solvent was removed at 40 mm pressure and the residue was separated by prep GLC (column C, 150°, He 50 ml/min), yielding 0.145 g (60%) of 2; rel. retention time 14 min; b.p. 31–32°/0.8 mm; λ_{max}^{MeOH} 230 mμ; IR 1640 (s), 1610 (vs), 1462, 1290 (vs), 1170 (vs); *m/e* 140-083772; calcd for C₈H₁₂O₂: 140-083724. Purity 95% (column A, 110°, He pressure 34 lb; ret. time 31.5 min).

2-Methoxy-4-ethyl-5-methylfuran (2)

A degassed 1% solution of 1 (0.250 g) in dry benzene was sealed in a 480 ml Pyrex tube and heated at 160° for 48 hr. The solvent was removed at 40 mm pressure and the residue was separated by prep GLC (column C, 150°, He 50 ml/min), yielding 0.145 g (60%) of 2; rel. retention time 14 min; b.p. 31–32°/0.8 mm; λ_{max}^{MeOH} 230 mμ; IR 1640 (s), 1610 (vs), 1462, 1290 (vs), 1170 (vs); *m/e* 140-083772; calcd for C₈H₁₂O₂: 140-083724. Purity 95% (column A, 110°, He pressure 34 lb; ret. time 31.5 min).

Furans 2 and 3 from 1-methyl-2-ethylcarbomethoxycyclopropene

Following the procedure of D'yakonov *et al.*¹⁴ a soln of 3.5 ml methyl diazoacetate in 15 ml 2-pentyne (Chem. Samp. Co., 99%) was added dropwise under N₂ to a stirred mixture of 5 ml 2-pentyne, 20 ml heptane and 170 mg anhyd CuSO₄ over a period of 3 hr. Oil bath temp 90°. After 30 min additional stirring the mixture was decanted and excess pentyne removed at ordinary pressure under N₂. At this point the crude mixture consists of 77.5% 1-methyl-2-ethylcarbomethoxycyclopropene, 1.7% furan 3, 1.2% furan 2, 1.7% maleate and fumarate and 18.6% higher boiling material (column A, 100°; relative

Table 3. Thermal rearrangement of 2-Methyl-3-carbomethoxyethylidenecyclopropane (temp 160°)

Run	Reaction time, hr	Ampoule	Solvent	Yield of rec. products in %	Composition in %	
					furan	s. mat.
36/2 ^a	48	Pyrex	benzene	86	93.0	7.0
36/1 ^a	48	lead-potash	benzene	86	66.3	33.7
41 ^b	48	lead-potash	gas phase	75	86	14
28 ^c	48	Pyrex	triethylamine		96	4
17 ^{c,d}	41	Pyrex	benzene		91	9
25 ^c	20	Pyrex	THF		76	24
48 ^{c,e}	48	lead-potash	gas phase	72	59	41

^aMixture of 4 isomers by method A; ^bmixture of 4 isomers by method B; ^cisomer 1c; ^d10% diphenylamine added; ^e30% *p*-benzoquinone added.

Table 4. Thermal rearrangement of individual fractions of 1^a (7% soln in benzene, Pyrex ampoules)

	Initial composition			Composition after heating for 8 hr			
	1a + 1b	1c	1d	1a + 1b	1c	1d	2
Isomers 1a + 1b ^b	92	3	—	48	7	—	45
Isomer 1c	5	85	10	6.5	58.7	—	34.8
Isomer 1d	2	8	90	9	17	—	74

^aData obtained with column C; ^bcontains 5% unknown impurity.

retention time: cyclopropene 22.8 min; furan 3 23.4 min; furan 2 24.6 min). NMR of 1-methyl-2-ethylcarbomethoxycyclopropene (δ) 3.44 (s, 3H), 2.41 (q, $J = 7$ c/s, 2 H), 2.01 (t, $J = 1$ c/s, 3 H), 1.86 (s, 1 H), 1.26 (t, $J = 7$ c/s, 3 H), IR 1910 cm^{-1} (C=C), 1748 cm^{-1} (C=O).

The decanted soln of the crude reaction mixture in heptane was refluxed under N_2 (b.p. 96°) while monitoring the rearrangement on column A. Refluxing was stopped after 2 hr, when the amount of higher boiling material started to increase. Heptane was removed under atmospheric pressure, and the residue distilled at 20 mm (b.p. 105–110°), yielding 1.784 g of mixture containing 1-methyl-2-ethylcarbomethoxycyclopropene, furan 3 and furan 2 in the ratio 16.5:50:33.5, respectively. Separation on a 5 m $\frac{1}{4}$ " Dow-Corning 710 on Chromosorb P 50/60 mesh column (135°, He 50 ml/min) yielded a first fraction (retention time 28 min) consisting of 20% 1-methyl-2-ethylcyclopropene and 80% furan 3 and a second fraction (ret. time 30 min) consisting of 96% furan 2, 2.5% furan 3 and 1.5% of the cyclopropene. NMR identical with that of the furan obtained by thermal rearrangement of 1.

After a second separation furan 3 was obtained 90% pure: *m/e* 140.083772; calcd for $\text{C}_8\text{H}_{12}\text{O}_2$: 140.083724.

2-Methyl-ethylidenecyclopropane-3-carboxylic acid

A mixture of 0.236 g (1.61 mmole) of 1 (mixture of isomers) and 1 ml 10% KOH aq (10% excess) was stirred for 3 hr at room temp. The alkaline soln was extracted with ether, acidified with 10% HCl and the acid extracted with ether. The ethereal soln was dried over MgSO_4 and the ether removed *in vacuo*, yielding 0.202 g (85%) of acid. It was used in the following step without further purification. NMR: (δ) 5.72 (m, 1 H), 2.06 (m, 1 H), 1.77 (m, 4 H), 1.12 (m, 3 H). The same procedure was used for saponification of individual isomers.

2-Methyl-ethylidenecyclopropane-3-carboxamide

A mixture of 0.192 g acid and 1.137 g triethylamine in 1.5 ml chloroform was added over a period of 40 min to a stirred soln of 0.143 g ethyl chloroformate in 2 ml chloroform maintained at -30° . Stirring was continued for 1.5 hr at -25° to 0° and NH_3 bubbled through the cold soln ($0-5^\circ$) for 20 min. After 30 min additional stirring at room temp, the mixture was filtered, the filtrate washed with 5% NaOH and water, dried over MgSO_4 , and chloroform removed *in vacuo*, yield 0.136 g (70%), m.p. 104–114°. NMR (δ): 5.97 (m, 3 H), 1.86 (m, 5 H), 1.23 (m, 3 H); IR (nujol): 3390 cm^{-1} , 3220 cm^{-1} (NH), 1650 cm^{-1} (C=O).

2-Methyl-3-cyano-ethylidenecyclopropane (4)

A stirred suspension of amide (1 g) in 2.5 ml dry pyridine and 25 ml dry benzene was treated under N_2 with 1.5 ml SOCl_2 at 0° (ice bath). Stirring at 0° was continued for 5 hr. The mixture was poured over 5 ml of ice-cold 1% HCl, the organic layer separated, washed with 5% NaHCO_3 aq and water, and dried over MgSO_4 . Benzene was removed *in vacuo* (100 mm) and the residue vacuum transferred, yielding 0.680 g (68%) of a mixture of isomeric nitriles; composition (column B, 79°, He pressure 20 lb): 11.7% 4a (ret. time 12 min), 3% 4b (12.8 min), 56% 4c (14.5 min), 31.3% 4d (15 min).

NMR (δ): 6.04 (m, 1 H), 1.83 (d with fine structure, 3 H), shoulder centered at 2.00 (1 H), broad resonance centered at 1.50 (1 H), 1.26 (d, 3 H). *m/e* 107.071257; calcd for $\text{C}_7\text{H}_9\text{N}$: 107.073496; IR 2234 cm^{-1} (C \equiv N sat).

The mixture of stereoisomers was separated on column D (120°, He 50 ml/min). The major isomers 4c and 4d were obtained in 98.3% purity with retention times of 36.5 min and 38.8 min, respectively. Their compositions are given in Table 5 in the "initial" rows. Isomer 4a (ret. time 30.6 min) was obtained in 80% purity; isomer 4b could not

Table 5. Results of isomerization of 4d and 4c at 110-6°

Time, hr	Composition, %					Ratio		Recovery, %
	<i>trans</i> -5	4a	4b	<i>cis</i> -5	4c	4d	isomers:decane	
Initial	0.4	0.1	0.3	—	0.9	98.3	68.3 31.7	
6	2.7	1.0	0.9	—	1.0	94.4	69.8 30.2	102.0
12	3.9	1.7	1.8	—	2.1	91.5	67.2 32.8	98.3
21	6.7	2.8	3.1	—	3.3	84.1	67.5 32.5	98.8
33	8.4	4.1	4.6	0.2	5.4	77.3	68.5 31.5	100.2
48	12.0	6.1	6.7	0.6	6.3	68.3	68.2 31.8	99.8
Initial	0.2	0.2	0.9	—	98.2	0.5	74.3 25.7	
6	3.7	1.0	1.0	—	93.0	1.3	73.0 27.0	98.2
12	6.2	2.3	1.9	—	86.9	2.7	73.8 26.2	99.3
21	9.6	4.1	3.5	0.2	78.3	4.3	74.9 25.1	100.8
33	12.3	5.9	5.4	0.3	69.5	6.6	72.1 27.9	97.0
48	14.5	7.8	8.1	0.4	59.6	9.6	74.2 25.8	99.8

be separated from isomer 4c. NMR of isomer 4c was identical with that of the mixture.

Nitrile 4c was also obtained from its corresponding ester 1c by the same procedure: a sample of ester 1c consisting of 1a (2.7), 1b (2.7), 1c (94.0) and 1d (0.6%) furnished a sample of nitrile 4c consisting of 4a (5.6), 4b (2.7), 4c (87.7) and 4d (4.0%).

trans-2,3-Dimethyl-cyanomethylenecyclopropane(*trans*-5)

Nitrile 4 (mixture of isomers) (0.250 g) purified by GLC on column D was sealed in a 360 ml Pyrex tube and heated in an electric oven at 150° for 16 hr. The mixture consisted of *trans*-5 (22.9), 4a (13.2), 4b (17.4), *cis*-5 (2.3), 4c (21.1) and 4d (23.1%).

Separation on column D (120°, He 50 ml/min) yielded 99.4% pure *trans*-5 (ret. time 23.5 min). NMR (δ): 5.66 (broad s, 1H), 1.26 (d, 6H, $J = 5$ c/s), two additional protons underneath the Me doublet (total area corresponds to 8H); IR 2225 cm^{-1} (C=N unsat); *m/e* observed 107.070857; calcd for $\text{C}_7\text{H}_9\text{N}$: 107.073496.

Epimerization of isomer 4d

A soln of 5 μl of 4d (95.4% 4d; 4.6% 4c) in 100 μl of DMSO was treated, with stirring and water cooling, with 3 mg of *t*-BuOK under N_2 . After 3 min of additional stirring, 0.5 ml of pentane was added and the soln quenched with H_2O . The separated organic layer was washed with water, dried over MgSO_4 , and analyzed on column B (70°, He 20 lb): 58.7% 4d; 41.3% 4c.

cis-*trans* Isomerization of 4d

A soln of 5 μl of 4d (95.4% 4d; 4.6% 4c) and 4 mg I_2 in 95 μl dry benzene was irradiated for 2 hr with a GE 275 watt sun lamp under N_2 and water cooling. The pale yellow mixture was washed with 5% NaHCO_3 , dried over K_2CO_3 , and analyzed on column D: 3.1% 4a; 53.1% 4b; 3.1% 4c; 40.7% 4d.

General procedure for kinetic runs

The nitriles (4c, 4d and *trans*-5) (2 μl) and the internal standard decane (1 μl), were degassed and sealed under vacuum (10^{-3} mm) in Pyrex ampoules (5 \times 80 mm) which had been washed with NH_4OH , water and acetone. The ampoules were suspended in a boiling toluene bath and heated in toluene vapor ($110.6^\circ \pm 0.2$). The temp was measured with an iron-constantan thermocouple connected to a Leeds and Northrup Model 8686 Millivolt

Potentiometer (ice-water reference junction). At the end of the run the ampoules were centrifuged, the bottom placed in liquid N_2 and the top heated with a heat gun for 5 min. To the opened ampoules, 50 μl of benzene was added and the mixture was analyzed by GLC (column B, 70°, He 20 lb). The reaction was followed over a period of 48 hr and points taken after 6, 12, 21, 33, and 48 hr. Three injections were made for each point and peak area was determined by cutting and weighing. To reduce errors five Xerox copies of each chromatogram were made, cut and weighed together. Mean values of the three determinations were taken.

Rate constants were calculated using the GLC data for the appearance of the various isomers. Corrections were made for the amounts of these isomers present in the starting material. The results are given in Table 5.

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