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THE STEREOCHEMISTRY OF THE METHYLENECYCLOPROPANE REARRANGEMENT: EVIDENCE AGAINST THE ORTHOGONAL-ALLYLIC INTERMEDIATE

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Abstract—The rearrangements of two optically pure derivatives of Feist's acid were studied: that of dimethyl *trans*-methylenecyclopropane-2,3-dicarboxylate (TRANS-diester) and *trans*-2,3-dicyanomethylenecyclopropane (TRANS-dinitrile). The optical purity and configuration of the products, methyl (*Z*)- and (*E*)-2-carbomethoxycyclopropylideneacetate (SYN- and ANTI-diesters) and (*Z*)- and (*E*)-2-cyanocyclopropylideneacetonitrile (SYN- and ANTI-dinitriles), establish that the rearrangements occur with predominant, but not exclusive, inversion of configuration at the migrating center. Investigation of the interconversions of SYN- and ANTI-diesters and dinitriles reveal that racemic product is not obtained, as would be expected from an orthogonal-allylic diradical intermediate, but that the enantiomer corresponding to antarafacial migration is slightly favored. All of the stereochemical results are explicable by application of the Doering–Sachdev diradical transition state hypothesis.

Thermal unimolecular rearrangements have long been attractive subjects for physical organic research because the classical tools of stereochemistry and kinetics can be used to great advantage to obtain insight into the details of covalent bond-breaking and bond-forming processes. The methylenecyclopropane rearrangement in particular has been studied quite extensively[1,2] in the decades since its elucidation by Ettlinger.[3] In addition to the inherent appeal of this fascinatingly simple reaction, the methylenecyclopropane rearrangement is also of interest because of its relationship to an even simpler reaction, the stereomutation of cyclopropane, and to the question of the involvement of 1,3-diradical intermediates in cyclopropane ring cleavage and closure. Both theoretical[4] and experimental[5] work have provided evidence that singlet 1,3-diradicals do not intervene in such processes as intermediates in the case of simple cyclopropanes. It is then of interest to answer the same question in the methylenecyclopropane case in view of the allylic resonance stabilization potentially available to a trimethylenemethane intermediate. The existence of a triplet diradical intermediate is not in doubt because of the important observation of trimethylenemethane electron spin resonance by Dowd and Sachdev.[6] Also, the elegant work by the Berson group[7] has shown that singlet trimethylenemethanes are intermediates when the planarity of an allyl moiety is enforced by an additional ring. Recent experimental work by Dowd and Chow,[8] however, has shown that the barrier to ring closure of the parent triplet trimethylenemethane is $\lesssim 7$ kcal/mol, leaving little room for a sizable barrier to the closure of singlet trimethylenemethane.

Theoretical calculations have also been equivocal on the existence of singlet trimethylenemethane intermediates, although most theoreticians have been concerned with the relative energies of triplet and singlet trimethylenemethanes of various geometries[9] and not with the details of the singlet surface including methylenecyclopropane. Of the two theoretical papers that have addressed the latter point, one[10a] calculated a rather large barrier (8 kcal/mol) to closure of a singlet trimethylenemethane, and the other[10b] a small or non-existent barrier (< 3.3 kcal/mol). The subject of this paper is some heretofore unpublished experimental evidence directly relevant to the question of involvement of singlet diradical intermediates in the carbon–carbon bond-breaking and bond-forming process that constitutes the methylenecyclopropane rearrangement.

RESULTS

Two aspects of the stereochemistry of the methylenecyclopropane rearrangement were investigated using two sets of methylenecyclopropanes, the dicarbomethoxy-substituted derivatives and the dicyano-substituted derivatives (see Scheme 1). The first aspect of the stereochemistry studied was the relative amounts of migration with retention and inversion of configuration at the migrating carbon. The second aspect concerned the relative amounts of suprafacial and antarafacial involvement of the allyl moiety across which the [1,3] sigmatropic shift occurs. The terminology used to describe the stereochemical possibilities is that used by Woodward and Hoffman[11] in their theoretical treatment of sigmatropic reactions. It should be noted, however, that the stereochemical possibilities are stated here without assumption as to mechanism—the stereochemical possibilities are distinguishable independent of the theory of concerted sigmatropic reactions.

Doering and Roth[1a] established that, in the rearrangement of dimethyl *trans*-methylenecyclopropane-2,3-dicarboxylate (TRANS-diester), predominant inversion occurred at the migrating carbon atom. The extent to which migration with retention at the migrating center occurred was not known, however, nor has it been unambiguously determined for any other methylenecyclopropane. Moreover, the

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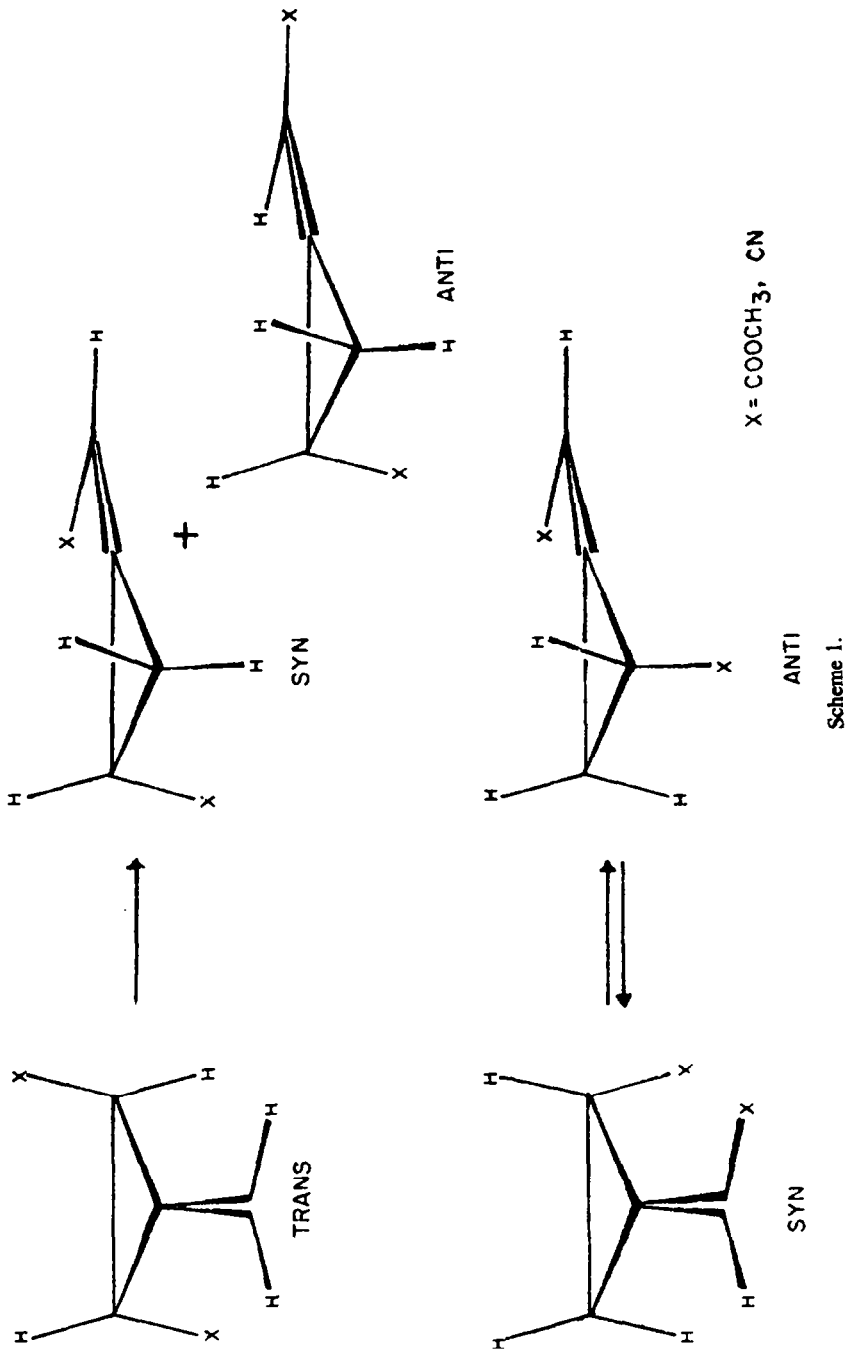
X
H
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ANTI
+
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TRANS
X = COOCH3, CN
H
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ANTI
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SYN

Scheme 1.

Table 1. Preservation of optical purity in the rearrangement of TRANS

Starting Isomer	Time[a] (hrs)	$[\alpha]_{546}$[b] (% Optical Purity) TRANS	SYN	ANTI	% Inversion[c]	% Retention
	0	+148° (100)	----	----		
	4	148 (100)	+136° (47)[d]	-69° (92)		
	8	148 (100)	128 (44)[d]	70 (93)		
	12	148 (100)	128 (44)	69 (92)		
TRANS-diester	16	149 (100)	129 (45)	70 (93)	92	8
	20	149 (100)	126 (44)	70 (93)		
	25	149 (100)	115 (40)	69 (92)		
	50	148 (100)	114 (39)	68 (90)		
	0	+183° (100)	-----	-----		
	2	174 (95)[e]	+34° (5)[d]	-16° (10)		
TRANS-dinitrile	3	174 (95)	35 (6)	14 (9)	54	46
	4	176 (96)	26 (4)	12 (8)		
	6	172 (94)	35 (6)	15 (10)		
	6[f]	170 (93)	35 (6)	14 (9)		

[a]At 126-127° and 56-57° for TRANS-diester and -dinitrile, respectively; [b]Except as noted, results are the average of two or more measurements in CCl_4 (diesters) or $CHCl_3$ (dinitriles); [c]Based on the known relative configurations of the isomers and the kinetic ratios of SYN and ANTI; [d]Single measurements. [e]Was increased to 99% by a vacuum transfer. [f]In oxygen-saturated benzene under an atmosphere of oxygen.

stereochemistry at the allyl moiety has not been examined except for the present work.

The stereochemical results are summarized in Tables 1 and 2. The salient features are the extent to which migration with retention at the migrating carbon competes with migration with inversion and the small but real preference for antarafacial migration across the allyl moiety. Both results have important implications for consideration of reaction mechanism, including the question of intermediacy of a singlet diradical. These implications are discussed in the next section.

The derivation of the stereochemical results presented in Tables 1 and 2 required structure determinations (see Experimental Section), correlations of relative configurations and optical purities, deuterium labelling studies, and measurements of reaction kinetics.

The maximum optical rotations of the chiral diesters and dinitriles were established by chemical

Table 2. Preservation of optical purity in the interconversion of SYN and ANTI

Starting Isomer	Time[a] (hrs)	$[\alpha]_{546}$ (% Optical Purity)[b] SYN	ANTI	% Antarafacial[c]	% Suprafacial
SYN-diester	0	+180° (62)[d]	----		
	144	163 (56)[d]	+11° (15)[d]	>62	<38
ANTI-dinitrile	0	-----	-16° (10)		
	24	-1.4° (0.2)	11 (7)	>51	<49

[a]At 126-127° and 79-80° for SYN-diester and ANTI-dinitrile, respectively; [b]Except as noted, results are the average of two or more measurements in CCl_4 (diesters) or $CHCl_3$ (dinitriles); [c]Based on the known relative configurations of the isomers. Values are minima and maxima because of possible competing processes (see text); [d]Single measurements.

correlation. The hydrogenation of optically active SYN- and ANTI-diesters[1a,12] was repeated. The optical rotations of the chiral products were consistent with the assumption that the resolutions of SYN- and ANTI-diacids were complete. The open chain product of hydrogenolysis, dimethyl α-methylglutarate,[13] was obtained independently by esterification of the resolved[14] diacid. The rotation of this material was also consistent with the above assumption. Finally, the maximum optical rotations were also consistent with the optical rotation of α-methylglutaric acid derived from natural sources.[15]

The inter-relationships were also applied to the optical purity of SYN- and ANTI-dinitriles by conversion of optically active samples of each to methyl *cis*-2-carbomethoxycyclopropylacetate. This correlation also established the absolute configuration of SYN- and ANTI-dinitriles, since it related them to SYN- and ANTI-diesters whose absolute configurations, and that of TRANS-diester, had been determined by Doering and Roth.[1a] The conversion was done in three steps: (a) catalytic hydrogenation; (b) hydrolysis with aqueous acid; (c) esterification with diazomethane. A control experiment with methyl *cis*-2-carbomethoxycyclopropylacetate showed that the conditions of the conversion did not racemize this material.

A final correlation was necessary to determine whether the conditions of the synthesis of TRANS-dinitrile from TRANS-diester caused any racemization. A three-step sequence similar to the one outlined above for SYN- and ANTI-dinitriles was used to convert TRANS-dinitrile to dimethyl 3-methylcyclopropane-1,2-dicarboxylate. This compound was also obtained from fully resolved and presumably optically pure TRANS-diester. Comparison of the material from the two sources showed that at most 2% racemization occurred in the synthesis of TRANS-dinitrile. Since the experimental error in measuring rotations was 1–2%, this material was assumed to be optically pure.

SYN-diester labelled with deuterium in the exocyclic ester group was prepared from the half-ester and heated at 126–127°. Thus, d_3-SYN-diester in which the ratio of upfield to downfield methoxy protons in the NMR spectrum was 95.2:4.8 gave d_3-ANTI-diester with a corresponding ratio of 29.8:70.2. This sample of ANTI-diester was then isomerized with light[16] back to SYN-diester in which the downfield methoxy resonance was larger than the upfield resonance.

Rate measurements were made for a number of the rearrangements. In the diester cases, samples were heated in benzene solution in sealed tubes at 126–127° and analyzed by vpc. First-order plots for the rates of disappearance of TRANS- and CIS-diesters were based on the assumption that the rearrangements behaved as irreversible reactions at the low (3–20%) conversions studied. The rate constants for disappearance were obtained by least squares.[17] The specific rate constants for the formation of the various products (Table 3) were obtained by partitioning the rate constants for disappearance according to the product ratios. In the case of TRANS-diester, the ratio of the two products—ANTI- and SYN-diesters—fell off rather rapidly with time, so an extrapolation to zero time was used to obtain an estimate of 4.3 for this ratio.

The rates of rearrangement of SYN- and ANTI-diesters were also studied. In these cases, however, irreversibility could not be assumed even at early points because these isomers were thermodynamically favored relative to CIS- and TRANS-diesters. Moreover, as α,β-unsaturated esters, these isomers were more reactive toward production of non-volatile products, as evidenced by the drop in recovery with time. Thus, accurate rate constants could not be obtained. It was possible, nevertheless, to conclude that SYN- and ANTI-diesters interconverted and rearranged to TRANS- and CIS-diesters with an overall rate constant of about 10^{-7} sec^{-1} at 126° and that the interconversion was the fastest process.

The rates of two other reactions of SYN-diester were also studied. The first of these was the rate of racemization of optically active SYN-diester at 126–127°. The data showed an increase in rate with time, but a least squares slope gave a rate constant of $2.36 \pm 0.09 \times 10^{-7}$ sec^{-1}. The second process was the rate of deuterium scrambling in labelled SYN-diester. Using NMR analysis, a first-order plot with $k = 2.8 \pm 0.1 \times 10^{-7}$ sec^{-1} was obtained. The poor agreement between the per cent deuteration from mass spectral analysis (82%) and from NMR integration (95%, based on the relative area of the methoxy peaks in unheated labelled SYN-diester) indicated that the rate constant should be considered approximate.

Rates of rearrangement were also measured for TRANS- and CIS-dinitriles in benzene solution. These rearrangements were apparently nearly irreversible, and thus the fact that the analysis by l.c.

Table 3. Specific rate constants for rearrangements of TRANS and CIS

Starting Isomer	Temperature (°C)	Overall (10^6 sec^{-1})[a]	TRANS (10^6 sec^{-1})[b]	SYN (10^6 sec^{-1})[b]	ANTI (10^6 sec^{-1})[b]
TRANS-diester	126.2-127.0	2.46±0.02	---	0.46	2.00
CIS-diester	126.2	32.3±0.4	1.7	14.3	16.4
TRANS-dinitrile	56.6-56.7	12.5±0.2	---	4.0	8.5
CIS-dinitrile	56.6-56.7	8.15±0.16	---	3.88	4.27

[a] Rate constant for disappearance with standard deviation from least squares treatment.

[b] Specific rate constants from product ratios (extrapolated to zero time in the case of TRANS-diester).

required rather high conversion probably did not introduce serious error. A single run in acetonitrile solution indicated that the rearrangement was not accelerated by this solvent. Specific rate constants were obtained by partitioning the overall rate constants according to the product ratios (Table 3). Interconversion of TRANS- and CIS-dinitriles was not observed under these conditions.

An experiment was also performed to obtain an approximate equilibrium ratio for TRANS- and CIS-diesters. These isomers were equilibrated with sodium methoxide in methanol at room temperature. After removal of the base, the mixture obtained from each pure isomer was analyzed by vpc and found to contain $99.19 \pm 0.04\%$ TRANS-diester and $0.81 \pm 0.03\%$ CIS-diester.

DISCUSSION

As noted earlier, one can pose two questions about the stereochemistry of the methylenecyclopropane rearrangement. The first concerns the extent of inversion and retention at the migrating center. The second question concerns the stereochemistry at the allyl moiety, two possibilities being discernible—suprafacial migration and antarafacial migration.

The stereochemistry at the migrating center is determined by the degree of optical purity of the SYN and ANTI products obtained on rearrangement of optically pure TRANS-diester or dinitrile. One enantiomer of each of the two products corresponds to migration with inversion, while the other corresponds to migration with retention. Before the experimental results (Tables 1 and 2) can be used confidently to answer the stereochemical question, it is necessary to consider three processes, in addition to the direct rearrangement of TRANS to SYN and ANTI, which could affect the observed degree of optical purity. These are: (a) rearrangement by way of the achiral CIS isomer; (b) secondary rearrangement of ANTI to racemic SYN and *vice versa*; and (c) racemization of SYN and ANTI subsequent to their formation from TRANS.

The first possibility, indirect rearrangement of TRANS to SYN and ANTI by way of CIS, can be evaluated quantitatively in the case of the diesters. The specific rate constant, $k_{t,c}$, is estimated using the known rate constant for conversion of CIS-diester to TRANS-diester ($k_{c,t} = 1.7 \times 10^{-6}$ sec^{-1} at 126°) and the equilibrium ratio of these two isomers (99.2:0.8 at 25°) whence $k_{t,c} = 1.4 \times 10^{-8}$ sec^{-1}. Since $k_{c,s}$ and $k_{c,a}$ are experimentally determined, amounts of racemic SYN- and ANTI-diesters formed by this process can be calculated[18] as a fraction of the initial concentration of TRANS-diester at various reaction times. Comparison of the experimental fractions of racemic SYN- and ANTI-diesters to the calculated fractions revealed that production of racemic products by way of CIS-diester is negligible. Even when an equilibrium ratio of TRANS:CIS of 90:10 is assumed, the production of racemic material by way of CIS-diester is calculated to be much slower than the actual production of such material.

A kinetic argument can also be used to rule out the second possible racemizing process, in which racemic SYN-diester is produced from ANTI-diester. The rate constant for the second step of this process, rearrangement of ANTI-diester to SYN-diester ($k_{a,s} \sim 10^{-7}$ sec^{-1} at 126°), is small enough that less than 1% of the ANTI-diester formed at short reaction times could have rearranged to SYN-diester. Since SYN-diester is over half racemic even at short reaction times and is formed only a factor of 4.3 slower than ANTI-diester, it is clear that little of the SYN-diester can be a result, at short reaction times, from the rearrangement of ANTI-diester.

The third racemizing process to be considered is subsequent racemization of the products. This possibility is inconsistent with the virtual constancy of optical rotations of SYN- and ANTI-diesters over the range 3–20% conversion of TRANS-diester. Although SYN-diester shows a slight decrease in optical rotation at higher conversions, the rate constant for its racemization ($k_{s,rac} = 2 \times 10^{-7}$ sec^{-1} at 127°) is much too small to account for the fact that the optical purity of SYN-diester is only 45% at early points in the rearrangement of TRANS-diester.

With these three racemizing processes eliminated, the degree of optical purity of SYN- and ANTI-diesters (see Table 1) can be taken confidently as the basis for concluding that the rearrangement of TRANS-diester occurs predominantly, but not exclusively, with inversion at the migrating center. SYN-diester is formed with 73% inversion and 27% retention while ANTI-diester is formed with 96% inversion and 4% retention.

The same three racemizing processes must be considered in the rearrangement of TRANS-dinitrile. A quantitative evaluation of the role of CIS-dinitrile cannot be made because no CIS-dinitrile is observed in the rearrangement of TRANS-dinitrile nor is any TRANS-dinitrile observed in the rearrangement of CIS-dinitrile. CIS-dinitrile, however, rearranges more slowly than TRANS-dinitrile by a factor of 1.5. Thus, CIS-dinitrile cannot be formed from TRANS-dinitrile at a rate great enough to affect the optical purity of SYN- and ANTI-dinitriles without accumulating and being detected. The other two racemizing processes—interconversion and racemization of SYN- and ANTI-dinitriles—can be rejected since these processes are much slower and require higher temperature to be observed.

Thus, from the degrees of optical purity of SYN- and ANTI-dinitriles, it can also be concluded that the rearrangement of TRANS-dinitrile occurs predominantly with inversion (see Table 1). The preference for inversion, however, is markedly lower than in the diester system. SYN-dinitrile is formed with 53% inversion and 47% retention, and ANTI-dinitrile is formed with 55% inversion and 45% retention.

The question of the stereochemistry at the allyl moiety can now be examined. The SYN–ANTI interconversion provides evidence on this point since both ends of the allyl moiety in this transformation are substituted (see Scheme 1). Thus, the sign of rotation and the degree of optical purity of ANTI-diester formed in the rearrangement of (+)-SYN-diester may reveal the relative amounts of suprafacial and antarafacial migration, provided two other processes do not interfere.

The first of these processes would involve isomerization of the double bond by a 180° rotation. Dewar[19] calculated the barrier for rotation of the methylenecyclopropane double bond to be 48.1 kcal/mol, which is considerably greater than

Chesick's[20] measured activation energy for the [1,3]-sigmatropic rearrangement (40.4 kcal/mol). Two lines of experimental evidence can also be cited against the 180° rotation. First, the rearrangement of SYN-diester labelled with deuterium in the methyl group of the double bond ester shows that this ester becomes a cyclopropane ester in ANTI-diester. Simple 180° rotation would have this ester group remain attached to the double bond in ANTI-diester. Second, rearrangement of SYN-diester gave ANTI-diester of opposite configuration. To establish the authenticity of this result, the product ANTI-diester was isomerized with iodine and light[16] to a mixture of SYN- and ANTI-diesters, from which SYN-diester with sign of rotation opposite to that of the original SYN-diester was obtained.

A second potentially interfering process is a two-step reaction proceeding by way of TRANS- or CIS-diester. This process is also inconsistent with the results of the deuterium-labelling experiment, as the two ester groups become equivalent in TRANS- and CIS-diesters. Moreover, based on the known inversion of configuration in such rearrangements and on the principle of microscopic reversibility, the excess enantiomer of ANTI-diester formed from SYN-diester by way of TRANS-diester would have the same configuration as the starting material and not the opposite configuration as is observed.

The unequivocal conclusion, then, is that there is a direct pathway for the SYN–ANTI interconversion involving sigmatropic migration of the methylene group from one end of the allyl moiety to the other (see Scheme 1). Moreover, it is clear that the sigmatropic migration is predominantly antarafacial. Antarafacial migration (i.e. migration of the methylene group from the face of the migration origin which ends up *below* the molecular plane in the product to the face of the migration terminus which starts out *above* the molecular plane in the starting material) corresponds to production of the enantiomer of ANTI-diester of opposite configuration to that of (+)-SYN-diester.

The extent of the preference for antarafacial migration depends on how much of the minor enantiomer produced is attributed to one or both of the other processes. If none of it is attributed to these processes (i.e. if 180°-rotation about the double bond and two-step rearrangement by way of TRANS-diester are negligible), then a minimum value of 1.63 (62% antarafacial and 38% suprafacial) for the ratio of antarafacial to suprafacial migration is obtained. The ratio 1.63 is also a minimum value with respect to the competitive racemization of starting material.

Isomerization by rotation about the double bond and rearrangement by way of TRANS- or CIS-dinitrile could also be competing paths in the SYN–ANTI interconversion in the case of the dinitriles. As in the diester case, however, both of these processes would produce the wrong enantiomer in excess. Moreover, when ANTI-dinitrile was heated at 80°, no TRANS- or CIS-dinitrile could be observed, indicating that rearrangement by way of these isomers is probably negligible. It is also important to note that the SYN-dinitrile obtained from heating ANTI-dinitrile was pure by analytical l.c., whereas 12% ANTI-dinitrile would have had to have been present to account for the observed optical rotation.

Thus, the sign of rotation and optical purity of SYN-dinitrile from ANTI-dinitrile (see Table 2) imply a minimum value of 1.04 (51% antarafacial and 49% suprafacial) for the ratio of antarafacial and suprafacial migration. The difference in minimum values for the ratios in the diester and dinitrile systems suggests a reduction in stereochemical preference in the dinitrile system, which is consistent with a similar reduction in the preference for inversion at the migrating center.

Discussion of the implications of these results on possible mechanisms will be divided into three parts: (a) continuous bonding concerted mechanisms, (b) mechanisms involving diradical intermediates, and (c) the diradical transition state mechanism.

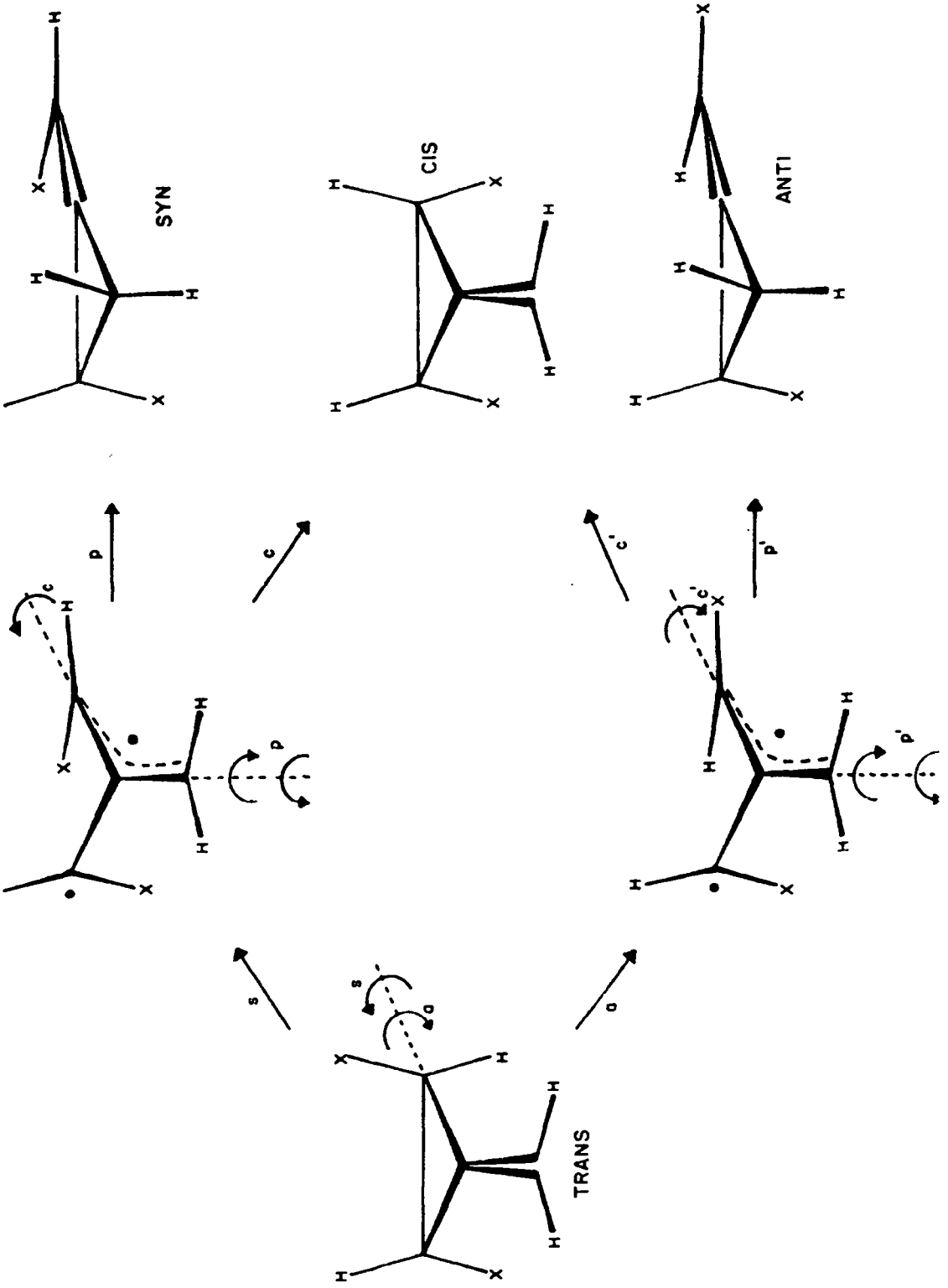
Concerted mechanisms. Previous work[1c] eliminated the Woodward–Hoffmann allowed concerted mechanism[21] as the sole mechanism of the methylenecyclopropane rearrangement. In order to explain the stereochemical results of this paper in terms of concert, i.e. simultaneous bond-breaking and bond-forming with continuous orbital overlap, one must assume that much if not most of the rearrangement occurs via Berson-Salem[22] pathways. There is no obvious feature, however, that would counteract the usual preference of concerted reactions for the Woodward–Hoffmann stereochemistry. In fact, Berson and Salem[22] indicate that the methylenecyclopropane structure does not allow the continuous orbital overlap necessary for a concerted rearrangement.

Diradical intermediates. Theory[23] and experiment[6] agree that the ground state of trimethylenemethane intermediates is the planar and necessarily achiral triplet. The early work of Ullman,[12] however, eliminated rearrangement *via* the planar intermediate as the sole mechanism. Moreover, both the parent trimethylenemethane[6] and the cyclic derivative of Berson *et al.*[7] form dimers. In the present work, the presence of oxygen, a well-known triplet scavenger, had no effect on either the percent recovery or the stereochemistry of the rearrangement of TRANS-dinitrile; and no dimers were observed. Thus, the planar triplet probably does not participate in the rearrangement.

The orthogonal-allylic diradical was suggested by Doering and Roth[1a] as a likely candidate for an intermediate in the methylenecyclopropane rearrangement. Formation of such an intermediate from TRANS (see Scheme 2) requires a 90° rotation at one of the ring carbons (e.g. **s** in Scheme 2) simultaneous with bond stretching. This rotation forms a planar allyl group with the *exo*-methylene and leaves the other ring carbon orthogonal. Rotation in the opposite sense (**a** in Scheme 2) forms a diastereomeric intermediate.

These intermediates can easily explain the *trans–cis* isomerization observed in Gajewski's system[1b] (X = CH_3). Rotation of the end of the allyl group bearing the substituent and ring closure with the orthogonal group can either regenerate starting material or form CIS(**c** or **c'**).

Rotation of the unsubstituted end of the allyl group (**p**) and ring closure with the orthogonal group leads to product SYN. Similarly, rotation and ring closure (**p'**) leads to product ANTI. The net result in each case is inversion at the orthogonal group (the migrating carbon), which is consistent with the pre-



Scheme 2.

dominant inversion observed in both the diester and dinitrile systems.

Because both systems also show appreciable retention at the migrating carbon, further elaboration of the mechanism is necessary. One must assume that a 180° rotation at the orthogonal group is competitive with the rotation leading to product.

Consideration of the results pertaining to the stereochemistry at the allyl group reveals a serious difficulty with the orthogonal-allylic mechanism. The relevant intermediate in the SYN–ANTI interconversion would be formed by rotation **a** (see Scheme 3) and would be achiral. The two rotations, **b** and **b′**, corresponding to antarafacial and suprafacial migration, respectively, would therefore be enantiomeric, would occur at identical rates and thus lead to racemic ANTI.

To the extent that some optical activity is preserved in the SYN–ANTI interconversion, participation by some mechanism other than that involving the orthogonal-allylic intermediate, as conventionally formulated, is demanded. In the case of the diester, at least 24% of the rearrangement of SYN to ANTI proceeds by some other mechanism, whereas, in the case of the dinitrile, only 2% of the rearrangement must involve a different mechanism. Ad hoc assumptions, e.g. a conformational memory effect at the allyl group, can accommodate these results. It is difficult, however, to propose an intermediate of sufficient lifetime to allow rotation around a single bond but too short-lived to establish planarity at an allyl group. Other modifications to the orthogonal-allylic mechanism may be proposed, but it may be opportune instead to consider a different conceptual model.

Diradical transition states. An alternative mechanism involves rearrangement without passing through an intermediate. The rearrangement is visualized in terms of diradical transition states, as hypothesized by Doering and Sachdev to explain the enantiomerization and diastereomerization of cyclopropanes.[24] Application of this hypothesis to the methylenecyclopropane rearrangement provides an attractive, unifying rationalization for all of the stereochemical results.

Upon collisional activation, the C_2–C_3 bond in methylenecyclopropane will undergo considerable stretching. At the point of maximum separation of sufficiently high amplitudes of vibration, bonding between the two carbon atoms may fall to zero or near zero. The bond is not broken by this process, however, because if nothing further happens, the next phase of the vibration brings the two carbon atoms back into bonding distance whereupon the vibrational energy can be dissipated into other vibrational modes and to other molecules by collisional deactivation.

At the higher amplitudes of the bond-stretching, what is required to break the bond is a twist of one or both of the carbon centers. In the methylenecyclopropane case, the possible consequences of such twists will be considered each in turn.

The first of these is geometrical isomerization. If one of the two centers undergoes a twist at the zero-bonding extension of the stretching vibration, vibrational collapse and completion of the 180° rotation will then lead to the geometrical isomer of the starting material.

This process can be viewed as fusion of the stretching vibrational modes of the two isomers. It is equivalent to the diastereomerizations observed in the cyclopropane case.[24] In the work described in this paper, geometrical isomerization is observed only in the case of CIS-diester. Gajewski,[16] however, found *trans–cis* isomerization to be about half as fast as sigmatropic rearrangement in *trans*-2,3-dimethylmethylenecyclopropane.

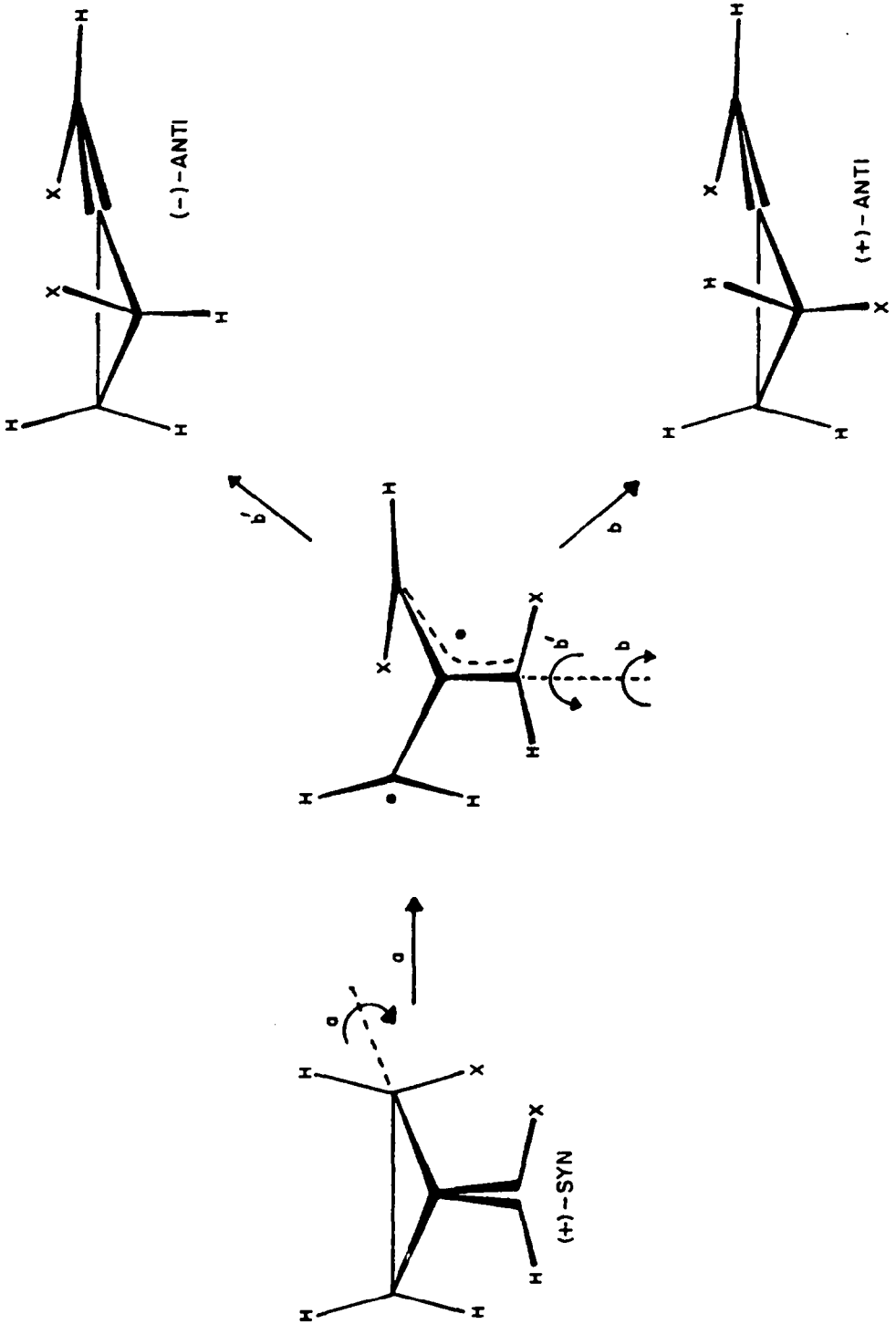
Enantiomerization, the other important process in cyclopropanes, is not observed in the rearrangement of either TRANS-diester or TRANS-dinitrile. It is possible that enantiomerization occurs in Gajewski's system, however. Enantiomerization would result from 180° rotations of both ends of the stretched bond and would correspond to fusion of the stretching modes of the two enantiomers.

To effect sigmatropic rearrangement within the framework of the hypothesis of the diradical as transition state, the stretching mode of the C_2–C_3 bond must be transformed into the stretching mode of a new C–C bond in the rearranged molecule. On the basis of the dimensions of the molecule, this transformation is quite reasonable. In unsubstituted methylenecyclopropane, the length of the C_2–C_3 bond is 1.54 Å,[25] and the distance separating each carbon atom of that bond from the *exo*-carbon atom is 2.7 Å (estimated using the molecular dimensions).[25] If the bond is stretched to 2.4 Å, the distance of each carbon atom of the bond from the *exo*-carbon atom also becomes about 2.4 Å.[26] Thus, a twist of the *exo*-carbon atom and further decrease of the distance separating it from one of the ring carbon atoms can lead to bonding, and only a 90° rotation of the other carbon atom of the original bond is necessary to form rearranged material. The geometry of methylenecyclopropane is such that, at the extensional extreme of the stretching vibration, collapse to form rearranged material seems nearly as likely as collapse to regenerate starting material.

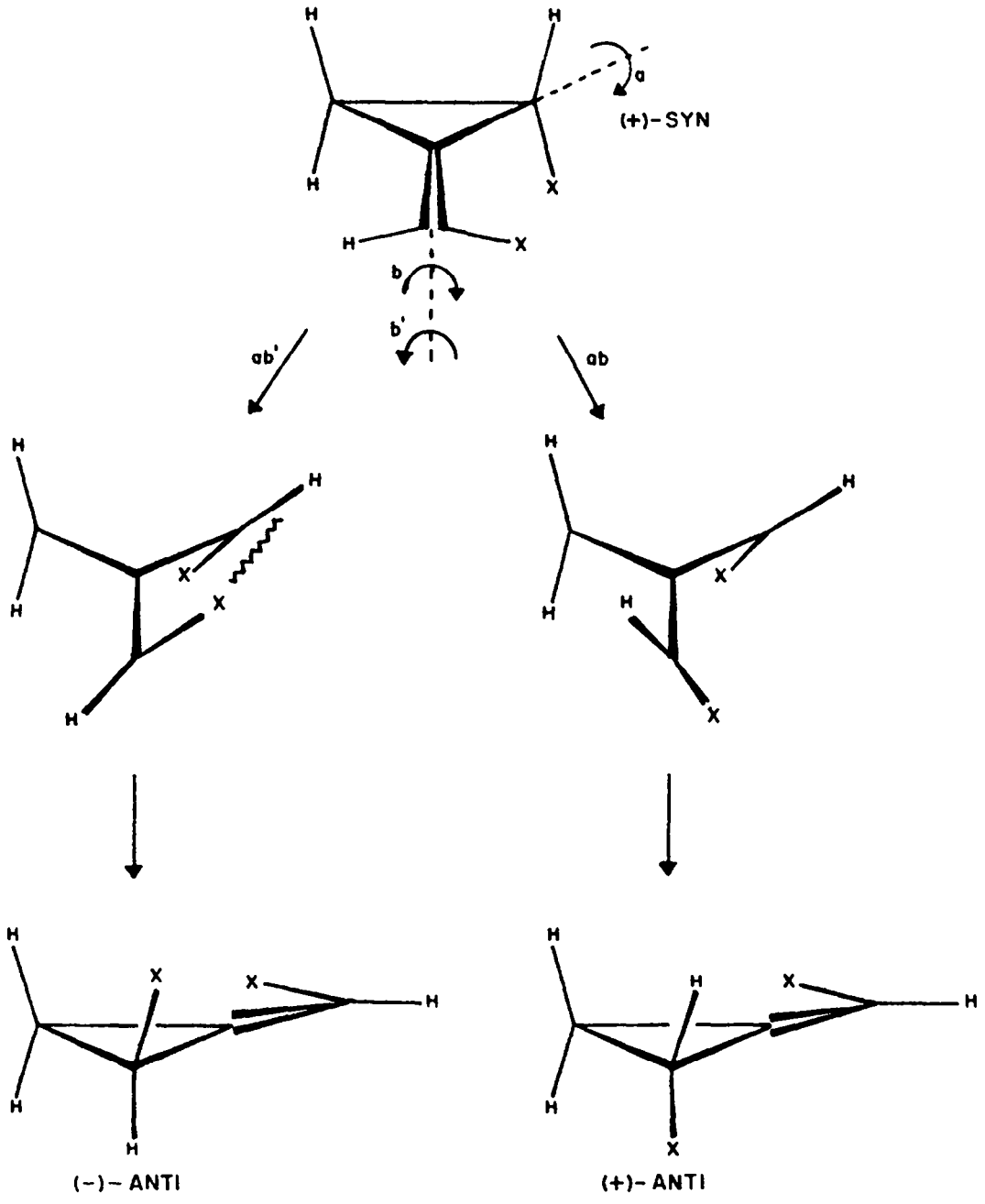
It is interesting to note that, formally, the migration with inversion can be viewed as a *trans–cis* isomerization interrupted by "capture" of the nontwisting end of the stretching bond by the *exo*-carbon atom. Similarly, the migration with retention can be seen as an interrupted enantiomerization.

The remarkable increase in the proportion of rearrangement occurring with retention caused by transforming TRANS-diester to TRANS-dinitrile can be explained by the diradical transition state hypothesis. Included in the hypothesis[24b] is the concept that substituent groups differ in their ability to undergo the rotations necessary to form product. If size is assumed to be the important factor in determining this "rotational propensity",[24b] then the small cyano group would have a greater rotational propensity than the large ester group. Thus, the increased rotational propensity of the cyano group over that of the ester group is manifested as an increase in the proportion of product resulting from "capture" of a stretched bond with both ends rotated (migration with retention) and a decrease in that resulting from "capture" of a stretched bond with only one end rotated (migration with inversion).

The stereochemistry at the allyl group can also be analyzed in terms of the hypothesis of the diradical as transition state. Starting with SYN (see Scheme 4),



Scheme 3.



Scheme 4.

rotation **a** must proceed in the direction shown in order to form **ANTI**, but either rotation **b** or **b'** can occur. The former causes antarafacial migration, leading to **ANTI** of configuration opposite to that of starting material; and the latter causes suprafacial migration, leading to **ANTI** of the same configuration as starting material.

Examination of the transition states of the antarafacial and suprafacial processes with molecular models shows that they are diastereomeric. At the transition state of the antarafacial migration (**ab** in Scheme 4), the hydrogen atom on the substituted ring carbon atom and the substituent on the *exo*-carbon atom are above and below the plane of the carbon atoms. At the transition state of the suprafacial migration (**ab'**), however, both are above the plane; and the distance separating them is not great. It is reasonable to expect that the greater steric interaction in **ab'** would be sufficient to make the antarafacial transition state slightly favored, consistent with the observed preference for antarafacial migration. The reduced preference for antarafacial migration in the dinitrile case is then seen to be the result of the expected reduction in this steric interaction in **ab'** when the much smaller nitrile group is substituted for the ester group.

In addition to rationalizing the stereochemistry of the rearrangement, the diradical transition state hypothesis provides an alternative, and perhaps more satisfactory, explanation for the kinetic preferences

that are observed in molecules with two non-identically substituted ring carbon atoms. The original explanation[1a] stemmed from the observation that in each case the kinetically preferred products were those that resulted from migration of the carbon bearing radical-stabilizing groups. It was assumed that the effect of the radical-stabilizing group was greater on the migrating carbon than on the other ring carbon.

Alternatively, it may be noted that in every case cited[1a] the radical-stabilizing substituents are also much larger than the other substituents. In terms of the diradical transition state hypothesis, the carbon bearing the larger substituent would have a lower rotational propensity. This difference in rotational propensity would favor the rearranged methylenecyclopropanes resulting from migration without rotation of the carbon atom bearing the larger substituents.

Examination of the results of Doering and Birladeanu[1c] yields evidence to support this explanation. In their system one ring carbon bears a cyano group while the other has the moderately large methyl substituent. Since the cyano substituent is a powerful radical-stabilizing group and the methyl is a poor one, the original explanation would predict that the products resulting from migration of the cyano-bearing carbon would be highly favored kinetically over that resulting from migration of the methyl-bearing carbon. Since the methyl group is larger than the cyano group, the new explanation would predict the opposite result. The actual results are in accord with the new explanation based on the diradical transition state hypothesis, taking the product ratios at the lowest conversion reported[1c] and correcting for the composition of the starting material.

The diradical transition state hypothesis offers an attractive rationalization for the methylenecyclopropane rearrangement. The attractiveness of the hypothesis lies in its ability to account for all of the stereochemical results in a unified manner. Continuous bonding is assumed to be absent; and therefore the *cis–trans* isomerization, in which continuous bonding is impossible, poses no problem. Without continuous bonding, the preference for the Woodward–Hoffmann allowed stereochemistry would disappear; and the stereochemistry might be expected to be sensitive to effects usually of secondary importance, such as steric interactions. Thus, the experimental observations of competitive, substituent-dependent *cis–trans* isomerization, sigmatropic migration with retention and inversion, and sigmatropic antarafacial and suprafacial migration are economically rationalized by the diradical transition state hypothesis.

The success of this hypothesis suggests that, as in the parent cyclopropane case, diradicals are not involved in bond-breaking and bond-forming processes as intermediates in the methylenecyclopropane rearrangement. If the methylenecyclopropane/trimethylenemethane singlet energy surface does contain secondary energy minima corresponding to non-Kekulé[27] structures, they are shallow enough to be indistinguishable from transition states. It is probable that such structures intervene as intermediates on the singlet surface only under special circumstances, such as pertain in Berson's systems[7] in which the methylenecyclopropanes are highly strained and planarity of an allyl moiety is enforced by an additional ring.[28] These added factors may deepen the minima sufficiently that, at low temperatures, non-Kekulé structures are detectable whereas in the less constrained parent energy surface, such structures do not intervene as intermediates.

EXPERIMENTAL

General. M.ps from a Hershberg apparatus were uncorrected except as noted. Boiling points were uncorrected. Infrared spectra (IR) were recorded on a Perkin–Elmer 137 spectrometer. Nuclear magnetic resonance spectra (NMR) were recorded on Varian T-60 and A-60 instruments. Optical rotations (or) were measured on a Perkin–Elmer 141 polarimeter in a 1-dm quartz cell thermostated at *ca* 25°. Concentrations for specific rotations were g/100 ml of soln. In most cases, duplicate measurements differed by less than 2%. In the few cases when the polarimeter reading was small enough (< 50 mdeg), the or was recorded with expected error from this source, e.g. $10 \pm 2°$. For liquid chromatography (lc), the Waters Associates ALC-201 instrument with M-6000 pump was used. Reagent $CHCl_3$ containing EtOH and cyclohexane were re-distilled prior to use in preparative lc. Varian Aerograph A700 and A90P3 instruments were used for preparative vapor phase chromatography (vpc). Analytical vpc was done using the Perkin–Elmer 990 with flame ionization detector. The vpc columns are listed in Table 4. Samples to be heated for thermal rearrangement were dissolved at 10 wt% in benzene, except as noted, and sealed under vacuum in Pyrex tubes of either of two sizes: 6 mm o.d. × 15 cm or 11 mm o.d. × 20 cm. Prior to use, the tubes were soaked in concd NH_4OH at least overnight, rinsed 15 times with dist water, dried in an oven and then again with a flame. For each experiment, one tube was kept aside as a control while the others were suspended in a well-insulated vapor bath. A liquid, chosen for its b.p., was refluxed in the bath, while the uninsulated top 10 cm of the bath was cooled on all sides with a rapid stream of air.

Dimethyl (+)-trans-methylenecyclopropane-2, 3-dicarboxylate. The literature preparation[29] of Feist's acid (TRANS-diacid) was used, and the resolution[1a] using the quinine salt was repeated. On hydrolysis with H_2SO_4 and ether extraction, the salt gave (+)-TRANS-diacid: 3.50 g (93% yield based on weight of salt); m.p. 203–204.5° (corr); $[\alpha]_D + 151.7°$, $[\alpha]_{546} + 179.9°$ (c 0.80, EtOH) [lit.[30] m.p. 203–205°; $[\alpha]_{546} + 176°$ (c 0.7, EtOH)]. The or was raised slightly by three recrystallizations from EtOAc: $[\alpha]_D + 155.3°$, $[\alpha]_{546} + 184.0$ (c 0.50, EtOH). Diazomethane was used to esterify 20.5 g (0.14 mol) of (+)-TRANS-diacid to obtain (+)-TRANS-diester: 23.4 g (96% yield); b.p. 69–70° (0.5 mm); $[\alpha]_D + 125.5°$, $[\alpha]_{546} + 148.4°$ (c 0.97, CCl_4) [lit.[1a] b.p. 66–67° (0.22 mm); $[\alpha]_{546} + 145°$ (c 0.7, CCl_4)].

Methylenecyclopropane-2,3-dicarboxylic anhydride.[31,1a] The literature procedure[31] was followed, starting from TRANS-diacid (10.0 g, 0.07 mol). Caution was required to prevent the ignition of the tarry residue after distillation. Colorless CIS-anhydride was obtained: 5.1 g (56% yield); b.p. 75–85° (0.08 mm) [lit.[31] b.p. 95–98° (3.5 mm)].

cis-Methylenecyclopropane-2,3-dicarboxylic acid. To 50 ml of ice-cold 6N HCl was added 2 g (0.016 mol) of CIS-anhydride. The mixture was stirred at room temp overnight. Ether work-up gave a crystalline residue: 0.55 g (31% yield). This material was recrystallized four times from ether and twice from $CHCl_3$ to yield 60 mg of pure CIS-diacid: m.p. 119.5–119.9° (corr) (lit.[31] m.p. 120.5–121.5°).

Dimethyl cis-methylenecyclopropane-2,3-dicarboxylate. An ice-cold ethereal solution of the purified sample of CIS-diacid (60 mg) was esterified with *ca* 1 mg of $AlCl_3$ and diazomethane. Ether work-up gave a quantitative yield of

Table 4. Vapor phase chromatography columns

Column	Liquid Phase	Support	Dimensions
A	15% Nitrile Silicone XE-60, 0.5% DEGS	50/60 Anakrom ABS	2.5m x 0.125 in
B	20% DEGS	50/60 Anakrom AB	1.5 x 0.25
C	18% DEGS	50/60 Anakrom AB	1.7 x 0.375
D	20% Dow-Corning 710	60/80 kieselguhr	3 x 0.25
E	18.5% DEGS	50/60 Anakrom AB	0.65 x 0.25
G	15% OV-101, 0.2% DEGS	50/60 Anakrom ABS	4 x 0.125
H	15% Nitrile Silicone XE-60, 0.2% DEGS	50/60 Anakrom ABS	2.5 x 0.25
I	Same as H		2 x 0.25
J	10% DEGS	50/60 Anakrom ABS	3 x 0.25
K	Same as E		1.7 x 0.25
OV-101	Perkin-Elmer capillary column		300 ft x 0.01 in
OV-225	Perkin-Elmer capillary column		50 ft x 0.02 in

the colorless liquid CIS-diester which was not purified further (> 99% pure by vpc).

Methyl (Z)- and (E)-carbomethoxycyclopropylideneacetates. The procedure for preparative rearrangement of TRANS-diester given by Doering and Roth[14] was followed. The starting material and products A and B were separated by prep vpc (column C, 125°, 120 ml/min He). According to retention times on a column similar to that of Doering and Roth (column D, 135°, 86 ml/min He), and comparison of NMR and IR, A and B are the isomers assigned by them the structures SYN- and ANTI-diesters, respectively. These structural assignments were confirmed by measurement of the dissociation constants of the corresponding diacids.[2c]

(Z)-2-Carboxycyclopropylideneacetic acid. SYN-diester (2.0 g, 11.8 mmol) was added dropwise to 100 ml of ice-cold 5% aq KOH (89 meq) with stirring. After the addition, the ice bath was removed. The mixture quickly turned pale yellow-green. After nearly an hour, the ester had all dissolved. The mixture was again chilled in ice before 5.1 g concd H_2SO_4 (104 meq, diluted with 25 ml H_2O and chilled) was added. Ether work-up gave SYN-diacid: 1.3 g (78% yield); m.p. 161–164° (d); NMR (d_6-acetone) δ 2.0 (m, 2H), 2.6 (m, 1H), 6.25 (m, 1H), 8.1 (s, 2H); ν_{max}(KBr) 3300–2500, 1760, 1680, 1420, 1320, 1290, 1240, 1215, 1070, 1010, 930, 863, 836 cm^{-1}. A sample was recrystallized twice from EtOAc: m.p. 164.2–164.5° (corr).

(E)-2-Carboxycyclopropylideneacetic acid. The same procedure applied to ANTI-diester (2.2 g, 12.9 mmol) yielded ANTI-diacid: 1.7 g (92% yield); m.p. 139–142° (d); NMR (d_6-acetone) δ 2.1 (m, 2H), 2.5 (m, 1H), 6.25 (m, 1H), 10.5 (s, 2H); ν_{max}(KBr) 3300–2500, 1760, 1680, 1410, 1330, 1297, 1280, 1252, 1220, 1095, 1035, 1020, 990, 972, 915, 866 cm^{-1}. A sample was recrystallized twice from EtOAc–pet ether: m.p. 142.5–144.5° (d) (corr).

(+)- and (−)-(Z)-2-carboxycyclopropylideneacetic acid. SYN-diacid (1.91 g, 13.5 mmol) in 70 ml of abs EtOH was treated with a soln of 4.36 g quinine (J. T. Baker, 13.5 mmol) in 20 ml of EtOH. The soln was concentrated under vacuum in a 35° water bath to about 75 ml during which time crystallization began, yielding the next day crop A_1 (2.16 g). Concentration to *ca* 40 ml gave crop A_2 (1.56 g).

To crop A_1 (2.15 meq) in 10 ml ice-cold water was added 0.49 g concd H_2SO_4 (10 meq) in 15 ml of water. Ether work-up resulted in colorless crystals, crop (+)-B: 630 mg (96% yield based on A_1); m.p. 155–157° (d); $[\alpha]_D$ + 137.1° (c 0.27, acetone). This was recrystallized from EtOAc to give crop (+)-C: 460 mg; $[\alpha]_D$ + 154.5° (c 0.21, acetone). Cooling the concd soln of (+)-C very slowly gave a heterogeneous crop of crystals, consisting of a small amount of white powdery material mixed in with larger transparent crystals. These were sorted by hand to give the former, crop (+)-D_1: *ca* 25 mg; $[\alpha]_D$ + 83.3° (c 0.20, acetone); and the latter, crop D_2: 250 mg; $[\alpha]_D$ + 168.2° (c 0.23, acetone). Crop D_2 was crystallized four more times to give crops (+)-E-(+)-H: (+)-E (134 mg) $[\alpha]_D$ + 187.4° (c 0.21, acetone); (+)-H (44 mg) mp 160–162° (d) $[\alpha]_D$ + 186.3° $[\alpha]_{546}$ + 225.2° (c 0.27, acetone).

Hydrolysis of crop A_2 and repeated crystallizations as described for crop A_1 gave crop (−)-H: 10 mg $[\alpha]_D$ − 187.3° $[\alpha]_{546}$ − 226.2° (c 0.21, acetone). A repeat of the resolution gave, after seven recrystallizations, material of the same or: $[\alpha]_D$ + 187.1°, $[\alpha]_{546}$ + 225.5° (c 0.18, acetone).

Methyl (−)-(Z)-2-carbomethoxycyclopropylideneacetate. To (−)-SYN-diacid [390 mg, 2.75 mmol, $[\alpha]_D$ − 144.3°, $[\alpha]_{546}$ − 174.1° (c 0.28, acetone)] in 40 ml of ether at 0°, was added with stirring $AlCl_3$ (1 mg) and ethereal diazomethane (50% excess). One min after the addition, 15 ml of 3N HCl soln was added. Then the ether phase was washed with 20 ml of 3N Na_2CO_3, dried and evaporated. The ester residue was purified by prep vpc (column E, 125°, 60 ml/min He). Yield was 310 mg (66%) of (−)-SYN-diester: $[\alpha]_D$ − 177.8°, $[\alpha]_{546}$ − 214.0° (c 0.79, CCl_4). The or was unchanged on re-passing through column E. Optically active samples of SYN-diester were indistinguishable in vpc and IR from racemic SYN-diester.

Optically pure (+)-SYN-diacid [21 mg, 0.15 mmol, $[\alpha]_D$ + 186.3°, $[\alpha]_{546}$ + 225.3° (c 0.27, acetone)] was also esterified, omitting $AlCl_3$. Yield was 7 mg (21%) of (+)-SYN-diester: $[\alpha]_D$ + 240.9, 238.2°, $[\alpha]_{546}$ + 290.1, 287.8° (c 0.61, 0.73, CCl_4).

Methyl (−)-(E)-2-carbomethoxycyclopropylidene acetate. ANTI-diacid (810 mg, 5.70 mmol) in 1 ml of warm abs EtOH was added to 944 mg (5.71 mmol) of ephedrine (from ephedrine sulfate, Fisher) in 0.5 ml EtOH. The soln was diluted to twice its volume with EtOAc, giving, after chilling overnight, crop A: 758 mg; m.p. 130.4–132.5° (d). Recrystallization of crop A from wet EtOH gave crop B with some apparent decomposition: 390 mg; m.p. 135.5–137.5° (d). Repeating gave crops C: 163 mg, m.p. 139.5–141.5°; and D: 50 mg; m.p. 142.5–144.5° (d). The resolution was stopped because of losses.

Crop D in 0.5 ml water, with 0.3 ml of 2N HCl, ether work-up, and esterification with diazomethane using $AlCl_3$ gave the diester which was purified by prep vpc (column E, 125°, 60 ml/min He). Yield was 5 mg (18% based on weight of D) of (−)ANTI-diester: $[\alpha]_D$ − 63.7°, $[\alpha]_{546}$ − 75.3° (c 0.24, CCl_4).

(Z)-2-Carbomethoxycyclopropylideneacetic acid (SYN-half ester). SYN-diacid (1.02 g, 7.20 mmol) was dissolved in 200 ml of ether. The stirred, ice-cold soln was treated slowly with 45 ml of standardized[32] ethereal diazomethane

(0.173M, 7.8 mmol). Fifteen min later, the ether soln was extracted with 60 ml ice-cold satd aq $NaHCO_3$. The aq layer was then acidified with 40 ml of 2N HCl. Ether work-up resulted in 0.98 g of a liquid residue which, when dissolved in 1 ml of $CHCl_3$ and chilled for a few min, gave 50 mg of white crystals mostly SYN-diacid (by NMR). The mother liquor was evaporated, leaving a viscous residue which solidified in the freezer. A small amount of this material was withdrawn for seeds before the bulk was re-dissolved in hot $CHCl_3$. The soln was then seeded and chilled to give the following: crop 1, 30 mg, m.p. 125–135°; crop 2, 100 mg, m.p. 84–87°; crop 3, 88 mg, m.p. 84–86°. Crops 2 and 3 were combined and recrystallized twice from CCl_4: 120 mg; m.p. 89.3–90.0° (corr); NMR ($CDCl_3$) δ 1.9 (m, 2H), 2.6 (m, 1H), 3.75 (s, 3H), 6.30 (m, 1H). A similar sample from another run [217 mg; m.p. 85.7–87.5° (corr)] was added to crops 2 and 3.

Trideuteriomethyl (Z)-2-carbomethoxycyclopropylidene acetate (d₃-SYN-diester). An ethereal soln of d_2-diazomethane was made from NaOD and d_5-N-nitroso-N-methylurea.[33] To the half-ester (220 mg, 1.41 mmol) in ether, was added 2 ml of D_2O through a septum. After an hour of stirring, $MgSO_4$ was added. This process was repeated three times. The $MgSO_4$ was filtered off inside a glove bag of dry N_2. The half-ester was then esterified with 21 ml of 0.08 M CD_2N_2 (1.68 mmol). The diester was purified by prep vpc (column B): 122 mg (49% yield); NMR was identical to that of SYN-diester except that a singlet replaced the doublet at δ 3.7. According to mass spectroscopy, this material was 82% deuterated of the following composition: 63.1%d_3, 24.7%d_2, 7.2%d_1 and 5.1%d_0.

Kinetics of rearrangement of TRANS-*diester.* A soln of vpc-collected, vacuum-transferred TRANS-diester was divided among eight small tubes. Since control experiments with naphthalene as internal standard showed that recovery was >99% up to 80% conversion with or without degassing prior to sealing, the tubes were merely evacuated to 0.01 Torr or less and sealed. The tubes were heated at 126.2–127.0° (refluxing pure n-octane) for 4–45 hr. The tubes were centrifuged for 5 min, and then the end containing the soln was chilled in liquid N_2 for five min before the tube was cracked open. The contents of each tube were analyzed by vpc (column A, 97°, 40 ml/min He). Each tube was analyzed by three injections with integration by cut and weigh of five photocopies of each injection.

Thermal rearrangement of (+)-TRANS-*diester.* (+)-TRANS-diester (3.1 g, 0.018 mol) in 25 ml benzene was heated at 126.4 ± 0.5° in 13 large tubes for 4–50 hr. The contents of each run were concentrated under vacuum at room temp before prep vpc (column C, 126°, 80 ml/min He). Recovery was 77–84% (actual by weight) for the various runs. Products SYN- and ANTI-diesters were re-passed to obtain pure samples for duplicate or. The purity of each sample was checked by vpc (column OV-101, 120°, 34 psi He). TRANS- and ANTI-diesters were >99% pure in every case, while SYN-diester invariably contained 1–3% CIS-diester (identified by co-injection of authentic CIS-diester). In one case SYN-diester also contained 3% TRANS-diester.

Kinetics of rearrangement of CIS-*diester.* The purified sample of CIS-diester (*vide supra*) was heated in small tubes at 126.2° for 15–100 min. Analysis was by cut and weigh using two vpc columns (column A, 100°, 40 ml/min He; column G, 99°, 40 ml/min He). Two columns were necessary because of a small unknown impurity.

Equilibration of TRANS- *and* CIS-*diesters.* Samples of TRANS- and CIS-diesters (35 and 21 mg, respectively) each in 1 ml of MeOH were treated with 5 mg of NaOMe. The solns were well stirred, then allowed to stand for five min before most of the MeOH was evaporated. The reactions were then quenched with 3 ml of satd aq $NaHCO_3$ soln and subjected to ether work-up and analysis by vpc (column OV-225, 115°, 4 psi, three injections) with electronic integration (Autolab 6300 digital integrator).

Rearrangement of ANTI-*diester.* A soln of ANTI-diester and a few crystals of naphthalene was heated in small tubes at 125.6–126.5° for 4–22 hr. Analysis was on column A (100°, 40 ml/min He) by cut and weigh. A first order plot of the kinetic data showed considerable curvature, and recovery was 96–88%.

Rearrangement of (+)-SYN-*diester.* A soln of (+)-SYN-diester [$[\alpha]_D$ + 148.3°, $[\alpha]_{546}$ + 179.4° (c 0.84, CCl_4)] and a few crystals of naphthalene was heated in small tubes at 126.0–126.8°. The contents of the tubes were first analyzed by vpc (column A, 100°, 40 ml/min He) by cut and weigh, then separated by prep vpc (column I, 110°, 60 ml/min He). The samples of SYN-diester were re-passed for or. Recovery was 100–87%. Samples of ANTI-diester from all five points were combined and re-passed for or: $[\alpha]_D + 4.7 \pm 0.4°$, $[\alpha]_{546} + 5.8 \pm 0.4°$ (c 0.45, CCl_4). All or samples were >99% pure by vpc (column OV-101).

Another sample of (+)-SYN-diester (200 μl, $[\alpha]_D$ + 149.8°, $[\alpha]_{546}$ + 179.8° (c 1.13, CCl_4)) was heated in one large tube in the octane vapor bath for 144 hr. ANTI-diester was then isolated by prep vpc (column I, two passes): $[\alpha]_D$ + 9.4°, $[\alpha]_{546}$ + 11.3° (c 1.70, CCl_4). The sample was pure by vpc (column OV-101). This sample of (+)-ANTI-diester was then isomerized in benzene containing a few crystals of I_2 by irradiating for 3 hr with two GE sunlamps.[16] SYN-diester was collected by prep vpc (column H): $[\alpha]_D$ − 23.7°, $[\alpha]_{546}$ − 33.1° (c 0.34, CCl_4).

*Kinetics of isotopic scrambling of d₃-*SYN-*diester.* A soln of d_3-SYN-diester (120 μl) was heated in small tubes at 126.2–127.0°. The contents of each tube were separated by prep vpc (column H, 110°, 60 ml/min He). In preliminary experiments with SYN-diester, it was found that the best separation of the methoxy-NMR resonances was obtained with 12 μl of diester, 30 μl of CCl_4, and 50 μl of a solution of Eu(fod)$_3$ (Willow Brook Lab., 200 mg in 1 ml of CCl_4). These proportions were used to analyze the samples of d_3-SYN-diester with respect to distribution of protium in the methoxy-groups. Each of the four samples were scanned on expanded scale in the methoxy-region. Photocopies of the spectra were cut and weighed. The ANTI-diester from the four runs was combined and analyzed by the same method. This d_3-ANTI-diester was isomerized with I_2 and light as previously described. The vpc-collected sample of d_3-SYN-diester was too small for accurate peak areas; however, the nmr obtained did show that the excess protium was opposite to that of starting d_3-SYN-diester.

Hydrogenation of (+)-TRANS-*diester.* The procedure of Ullman[12] and Doering and Roth[1a] was used. (+)-TRANS-diester [$[\alpha]_D$ + 126.6°, $[\alpha]_{546}$ + 149.8° (c 1.11, CCl_4)] was hydrogenated, and the two products were separated by prep vpc (column K, 130°, 75 ml/min He). The major component, dimethyl 3-methylcyclopropane-1,2-dicarboxylate, was re-passed: $[\alpha]_D$ + 104.8°, $[\alpha]_{546}$ + 125.5° (c 1.02, CCl_4) [lit.[1a] $[\alpha]_{546}$ + 124.5° (c 0.9 ± 0.2, CCl_4)]. Purity was 99.7% by vpc.

Hydrogenation of (−)-ANTI-*diester.* (−)-ANTI-diester was isolated by prep vpc (column I, 120°, 60 ml/min He, two passes, >99% pure, column OV-101). The sample ($[\alpha]_D$ − 47.0, 49.2°, $[\alpha]_{546}$ − 56.3, 58.5° (c 0.71, 0.66, CCl_4)) was then hydrogenated as in Doering and Roth[1a] with a modified work-up. The catalyst was removed by filtration, and the chilled filtrate was then treated with 50 ml of satd aq $NaHCO_3$. The concentrate from ether work-up was separated into its three components by prep vpc (column H, 120°, 60 ml/min, A (15%) 21 min, B (50%) 30 min, C (35%) 37 min). A and B each were re-passed (column J, 120°, 65 ml/min He). A was identified as dimethyl α-methylglutarate by IR vs an authentic sample.[34] The IR of B was identical to that of methyl *cis*-2-carbomethoxycyclopropylacetate prepared by Roth[34] from bicyclo[3.1.0]hex-2-ene.[35] These samples were >99% pure by vpc. C was assumed to be dimethyl adipate.[1a,12] A: $[\alpha]_D$ + 25 ± 2° $[\alpha]_{546}$ + 26 ± 2° (c 0.08, CCl_4). B: $[\alpha]_D$ + 70.7, 70.2°, $[\alpha]_{546}$ + 83.8, 83.2° (c 0.36, 0.24, CCl_4).

Hydrogenation of (+)-SYN-*diester.* Hydrogenation, as

above, of (+)-SYN-diester (pure by vpc, $[\alpha]_D$ + 169.1, 167.8°, $[\alpha]_{546}$ + 204.3, 202.8° (c 0.72, 0.72 CCl_4)) gave or for A: $[\alpha]_D$ + 21.7, 20.1°, $[\alpha]_{546}$ + 25.9, 26.0° (c 0.38, 0.36, CCl_4); and for B: $[\alpha]_D$ + 65.1, 65.9°, $[\alpha]_{546}$ + 78.0, 78.3° (c 0.57, 0.40, CCl_4). A and B were > 99% pure by vpc, and their IR were identical to those obtained above.

(+)-α-*Methylglutaric acid.* The resolution of Berner and Leonardsen[14] was followed closely: m.p. 82.2–83.2° (corr); $[\alpha]_D$ + 21.2°, $[\alpha]_{546}$ + 25.1° (c 1.03, abs EtOH) [lit.[14] m.p. 81°; $[\alpha]_D$ + 21.7° (c 5.27, abs EtOH); lit.[15a] m.p. 78.5–83°; $[\alpha]_D$ − 17° (in EtOH) and m.p. 82–84° $[\alpha]_D$ − 21° (in EtOH); lit.[15b] m.p. 78.5–81°; $[\alpha]_D$ + 18° (in EtOH) and m.p. 78.5–81°; $[\alpha]_D$ − 20° (in EtOH)].

Dimethyl (+)-α-*methylglutarate.* Optically pure (+)-α-methylglutaric acid was esterified with diazomethane and purified by prep vpc (column H, 135°, 65 ml/min He, two passes): $[\alpha]_D$ + 31.8°, $[\alpha]_{546}$ + 37.9° (c 0.36, CCl_4) [lit.[14] $[\alpha]_D$ + 24.5° (neat)].

(+) - trans - *Methylenecyclopropane* - 2,3 - *dicarboxamide.* (+)-TRANS-diester [5.0 g, 29.4 mmol, $[\alpha]_D$ + 125.5°, $[\alpha]_{546}$ + 148.4° (c 0.97, CCl_4)] was added to 25 ml of concd NH_4OH, whereupon the white diamide began precipitating out. After 2 hr, the mixture was chilled in ice for 30 min, and the product was filtered off. After thorough drying, the solid TRANS-diamide weighed 3.1 g. Evaporation of the filtrate gave 0.92 g (total yield 95%). A sample was recrystallized three times from MeOH–water and re-dried: m.p. 251–251.5° (d) (corr); ν_{max}(KBr) 3370, 3190, 1625, 1390, 1221, 1125, 1099, 949, 902, 770 cm^{-1}; $[\alpha]_D$ + 200.6° $[\alpha]_{546}$ + 241.3° (c 0.23, 1:1 aq EtOH). (Anal: Found: C, 51.5; H, 5.9; N, 20.1. Calc for $C_6H_8N_2O_2$: C, 51.4; H, 5.8; N, 20.0%.)

trans-2,3-*Dicyanomethylenecyclopropane.* An adaptation of the procedure of Sachdev[36] was used. The thoroughly dried TRANS-diamide (3.11 g, 22.1 mmol) dispersed in 90 ml dry benzene under N_2 was chilled to 5–10° before 3.40 ml $SOCl_2$ (3.56 g, 47.3 mmol) was added with a syringe through a septum cap. Dry DMF (3.90 ml, 3.68 g, 50.2 mmol) was then syringed in dropwise. The temperature was 5–10° during addition and for 2 hr following. The reaction mixture turned red, as nearly all the solid dissolved. The reaction was quenched with 20 ml of water, and the aq phase was extracted with CH_2Cl_2. The extract was combined with the benzene layer, dried ($MgSO_4$), and evaporated, leaving a red solid which was sublimed (45°, 0.1 mm) and recrystallized from CCl_4 to give TRANS-dinitrile (white needles): 1.09 g (49% yield), m.p. 61–64°. A sample was recrystallized four times from a small amount of CH_2Cl_2 by diluting to 2–3 times its volume with CCl_4: m.p. 64.1–64.8° (corr); ν_{max}(CH_2Cl_2) 3020, 2255, 1860, 1135, 1104, 1039, 960, 928, 865, 817 cm^{-1}; NMR ($CDCl_3$) δ 2.35 (t, 2H), 6.01 (t, 2H). (Anal: Found: C, 68.9; H, 4.0; N, 26.3. Calc for $C_6H_4N_2$: C, 69.2, H, 3.9; N, 26.9%.)

(+) - trans - 2,3 - *Dicyanomethylenecyclopropane.* The above procedure was used except for a modified work-up. After being dried, the extract and benzene solns were combined and passed through a column (1.8 cm o.d. × 50 cm) of Florisil (Fisher, 100–200 mesh, 12 g) with benzene as the eluent. The dinitrile was eluted with 250 ml of benzene, leaving the red component at the top. A total of 11.85 g of (+)-TRANS-diamide in 1-g portions was reacted and purified in this manner. The solns were combined and evaporated at room temp under vacuum. The slightly colored residue was recrystallized twice from CH_2Cl_2–CCl_4 without heating to yield crop 1: 2.82 g. Material from the mother liquors was chromatographed and recrystallized to raise the yield to 3.67 g (45%); m.p. 67–68° (corr); $[\alpha]_D$ + 152.0, 153.1°, $[\alpha]_{546}$ + 182.2, 184.1° (c 0.98, 1.83, $CHCl_3$). Later it was found that the yield was 62% if DMF and $SOCl_2$ were added in reverse order.

Preparative rearrangement of TRANS-*dinitrile.* TRANS-dinitrile (500 mg, 4.81 mmol) in 10 ml benzene was refluxed for 45 min in a 25-ml pear-shaped flask. The three-component mixture was separated by prep lc (Corasil II, 0.375 in × 4 ft, 2.8–3.4 ml/min of 30–32% $CHCl_3$ in cyclohexane, TRANS-dinitrile 23 min, products 34 and 59 min). The two products were isolated by evaporating the solvent under vacuum at room temp. The product of shorter retention time, assigned the structure (see below) (*E*)-2-cyanocyclopropylideneacetonitrile (ANTI-dinitrile), could be recrystallized from CH_2Cl_2–CCl_4: 78 mg; m.p. 50.5–51.5° (corr); ν_{max}(CH_2Cl_2) 3070, 3010, 2250, 2230, 1750, 1610, 1410, 1240, 1099, 1075, 1021, 934, 920, 825 cm^{-1}; NMR ($CDCl_3$) δ 2.20 (m, 3H), 6.16 (m, 1H); *m/e* 104.0374; Calc for $C_6H_4N_2$, 104.0374.

The product of longer retention time, assigned the structure (see below) (*Z*)-2-cyanocyclopropylideneacetonitrile (SYN-dinitrile), crystallized upon chilling but oiled out of every solvent system tried: 60 mg; m.p. 35.5–37.5° (corr); ν_{max}(CH_2Cl_2) 3070, 3010, 2250, 2230, 1750, 1610, 1401, 1320, 1210, 1081, 1020, 915, 810 cm^{-1}; NMR ($CDCl_3$) δ 2.20 (m, 3H), 6.05 (m, 1H); *m/e* 104.0375; Calc for $C_6H_4N_2$, 104.0374.

Lanthanide shifted NMR spectra of SYN- *and* ANTI-*dinitriles.* SYN- and ANTI-dinitriles (10–15 mg of each) were dissolved in $CDCl_3$ to which a small amount of TMS and $CHCl_3$ had been added. Eight NMR spectra were recorded for each soln—one prior to and seven after the addition of 6–8 mg portions of Eu(fod)$_3$ (Willow Brook Lab.). The distance from TMS for each distinguishable proton was measured in cm on each of the 16 spectra, using a distinctive feature of each multiplet. The $CHCl_3$–TMS distance was also measured on each spectrum. The relative rates of shift for the various protons (Table 5) were determined by a method devised by Doering and Dixon[37] and used to assign the structures of SYN- and ANTI-dinitriles.

cis-2,3-*Dicyanomethylenecyclopropane.* Attempted measurement of the optical rotation of (+)-TRANS-dinitrile in MeOH revealed a rapid racemization reaction, later shown to be a result of epimerization to CIS-dinitrile.[2c] This reaction was used to prepare CIS-dinitrile. Racemic TRANS-dinitrile (300 mg, 2.88 mmol) dissolved in *ca* 10 ml MeOH was left at room temp for 3 hr, then frozen overnight. The somewhat yellowed soln was then evaporated, and the residue was dissolved in $CHCl_3$. The two components were easily separated by prep lc (Corasil II, 0.375 in × 4 ft, 32% $CHCl_3$ in cyclohexane, 3.5 ml/min). The component of longer retention time was isolated by evaporating the solvent at room temp. The crystalline residue was recrystallized without heating from CH_2Cl_2–CCl_4: 162 mg; m.p. 64–65° (corr); NMR ($CDCl_3$) δ 2.71 (t, 2H), 6.08 (t, 2H); ν_{max}(CH_2Cl_2) 3040, 3010, 2235, 1420, 1255, 1099, 979, 918, 872, 839 cm^{-1}. (Anal: Found: C, 68.8; H, 4.1; N, 26.7. Calc for $C_6H_4N_2$: C, 69.2, H, 3.9; N, 26.9%.)

Rearrangement of (+)-TRANS-*dinitrile.* Solns of (+)-TRANS-dinitrile ($[\alpha]_D$ + 152.0, 153.1°, $[\alpha]_{546}$ + 182.2, 184.1° (c 0.98, 1.82, $CHCl_3$)) were sealed in large tubes with one freeze-thaw degassing. The tubes were then heated at 56.3–56.7° (refluxing MeOAc). The solns were then concentrated with a stream of N_2, and a small amount of $CHCl_3$ was added to keep the solids in soln. The mixtures were separated by prep lc (same conditions as above). The fractions containing SYN- and ANTI-dinitriles were evaporated at room temp under vacuum, and the white crystals were re-dissolved in a small amount of $CHCl_3$ and re-passed through the lc. SYN- and ANTI-dinitriles were nearly pure after one pass. All three fractions, TRANS-dinitrile and re-passed SYN- and ANTI-dinitriles, were then evaporated, and the residues were dried in a vacuum dessicator for 2 hr. Recovery by wt was 50–75%; low probably because of the false negative peak overlapping with TRANS-dinitrile (see below).

Initially, the dried samples were vacuum transferred prior to or measurements. This was very slow, especially for SYN- and ANTI-dinitriles, and increased the or of TRANS- and SYN-dinitriles by only 3–4%. ANTI-dinitrile, moreover,

Table 5. Lanthanide-shifted NMR Spectra of SYN- and ANTI-dinitriles.

Isomer (proton)	ppm from TMS (no $Eu(fod)_3$)	Relative slope of $Eu(fod)_3$ - induced shift
SYN $(H_2)^a$	2.2	(1.00)
$(H_{3a}, H_{3b})^b$	2.2	0.51
$(H_4)^c$	6.05	0.65
ANTI $(H_2)^a$	2.2	(1.00)
$(H_{3a}, H_{3b})^b$	2.2	0.66
$(H_4)^c$	6.16	0.90

[a]Cyclopropane proton alpha to cyano group. [b]Cyclopropane methylene protons, not resolved. [c]Olefinic proton.

seemed to suffer fractionation of optical purity. For these reasons, the remaining measurements were carried out on the dried residues from lc.

Kinetics of rearrangement of **TRANS**-*dinitrile.* A soln of **TRANS**-dinitrile and phthalonitrile (Eastman, recrystallized) was sealed in small tubes and heated at 56.6–56.7° for 6–12 hr.

The samples were analyzed by lc (Corasil II, 0.125 in × 2 ft, 2% EtOH in cyclohexane, 0.8 ml/min). A negative peak occurring just before that of **TRANS**-dinitrile made analysis difficult. That this peak was a false peak (perhaps due to de-mixing of the two solvents) was shown by several experiments. First, the peak was not present when benzene alone was injected. Second, when this peak was "collected", evaporation yielded only a very small residue, probably overlapping **TRANS**-dinitrile. Third, if optically active **TRANS**-dinitrile was injected and collected, the or of the recovered material was the same whether or not the negative peak was collected with **TRANS**-dinitrile. The negative peak was not present when single solvents were used, but no single solvent was found which separated the dinitriles. Satisfactory analysis could be performed if sample sizes were small enough that the negative peak did not overlap with the **TRANS**-dinitrile peak. Because of this limitation, the rate measurements are approximate. The peak integrations were done by cut and weigh. Weighed mixtures of **ANTI**-dinitrile and phthalonitrile and of **SYN**-dinitrile and phthalonitrile were also analyzed to calculate relative response factors. The composition of the 9 hr run was 65.0 ± 0.9 **TRANS**-dinitrile, 22.8 ± 0.2 **ANTI**-dinitrile and 11.2 ± 1.1 **SYN**-dinitrile. Recovery was quantitative.

Kinetics of rearrangement of **CIS**-*dinitrile.* The above procedure was used except that sebaconitrile was the internal standard. Heating was at 56.6–56.7° for 5–10 hr. In the analysis (Corasil II, 0.125 in × 4 ft, 20% $CHCl_3$ in cyclohexane, 1.0 ml/min). **CIS**- and **SYN**-dinitriles were not quite baseline separated, so a line perpendicular to the baseline was drawn between the two peaks. Recovery was 94–97%.

Rearrangement of **TRANS**-*dinitrile in the presence of* O_2. Half of a soln of **TRANS**-dinitrile and phthalonitrile in *ca* 150 μl of benzene was sealed without evacuation in a heavy-walled Pyrex tube. After being shaken for 5 min, the tube was heated for 9 hr at 56.8–56.9°. Analysis as above showed the composition of the colorless soln to be 62.1 ± 2.7% **TRANS**-dinitrile, 24.4 ± 1.9% **ANTI**-dinitrile, and 10.9 ± 0.3% **SYN**-dinitrile. The recovery was quantitative.

Some recovered (+)-**TRANS**-dinitrile ($[\alpha]_D$ + 148.9°, $[\alpha]_{546}$ + 178.2° (c 0.98, $CHCl_3$)) was dissolved in 1.7 ml of benzene that had been saturated with O_2. The soln was placed in a large (volume 50 ml) heavy-walled Pyrex tube into which a stream of O_2 was then directed for 3 min. The soln in the stoppered tube was chilled in dry-ice–acetone for 10 min before a hot flame (CAUTION!) was applied to seal the tapered end.

The sealed tube was heated for 6 hr at 56.2–56.5° before the contents were separated by preparative lc. The or of the components were the same as those obtained in the absence of oxygen.

Rearrangement of **TRANS**-*dinitrile in acetonitrile.* A soln of **TRANS**-dinitrile and phthalonitrile in acetonitrile was sealed in small tubes and heated at 56.5 ± 0.2° for 9 hr. The yellowed soln was evaporated with a stream of N_2. The residue was dissolved in benzene and analyzed by lc as above: 75.3% **TRANS**-dinitrile; 14.8% **ANTI**-dinitrile; 9.9% **SYN**-dinitrile and 94% recovery.

Determination of optical purity of (+)-**TRANS**-*dinitrile.* (+)-**TRANS**-dinitrile [63 mg; 0.61 mmol; $[\alpha]_D$ + 152.0, 153.1°, $[\alpha]_{546}$ + 182.2, 184.1° (c 0.98, 1.82, $CHCl_3$)] was dissolved in 1 ml of EtOAc and added to a H_2-satd dispersion of 35 mg of 10% Pd on charcoal in 2 ml EtOAc. The mixture was stirred under an atmosphere of H_2 until the uptake of H_2 had stopped (1 hr). After filtration, the solvent was evaporated, leaving a colorless liquid. This residue was dissolved in 3–4 ml of 12N H_2SO_4 and refluxed for two hrs (turned yellow). The concentrated soln from ether work-up was treated with ethereal diazomethane. The major components were separated by prep vpc (column J, 129°, 80 ml/min He, A (30%) 19 min, B (70%) 25 min). The two fractions each were repassed on column J and on column I (132°, 75 ml/min He). Component A, $[\alpha]_D$ − 7.69°, $[\alpha]_{546}$ − 9.50° (c 0.72, CCl_4), was 99.2% pure by vpc and had IR identical to that of authentic dimethyl ethylsuccinate.[1a,34] Component B, $[\alpha]_D$ + 103.3, 102.2°, $[\alpha]_{546}$ + 123.5, 122.6° (c 0.55, 0.54, CCl_4), was 99.4% pure by vpc and had IR identical to that of authentic dimethyl 3-methylcyclopropane-1,2, dicarboxylate.[1a,34]

Determination of optical purity of (−)-**ANTI**-*dinitrile.* A 27-mg sample of (−)-**ANTI**-dinitrile ($[\alpha]_{546}$ − 14.3, 15.5° (c 0.41, 0.46, $CHCl_3$)) was hydrogenated in 2 ml EtOAc, using 18 mg Pd on $BaSO_4$. Uptake was complete in 30 min. Hydrolysis and esterification were as described above for **TRANS**-dinitrile. The product mixture was then separated by prep vpc (column I, 145°, 70 ml/min He, A (2%) 14 min, B (24%) 19 min, C (74%) 23 min). Peak C had the same retention time as dimethyl adipate. Peak B was re-passed on column I (130°, 60 ml/min He): $[\alpha]_D$ + 8.6 ± 0.4°, 9.3 ± 0.6° $[\alpha]_{546}$ + 10.6 ± 0.4°, 10.9 ± 0.7° (c 0.49, 0.30, CCl_4). This material was 99.5% pure by vpc and had IR identical to that of authentic methyl *cis*-2-carbomethoxycyclopropylacetate.[1a,34]

Determination of optical purity of (+)-**SYN**-*dinitrile.* (+)-**SYN**-dinitrile [42 mg, $[\alpha]_{546}$ + 37.6,

33.3° (c 0.33, 0.62, CCl_4)] as obtained from (+)-TRANS-dinitrile was treated by the above procedure. A more complex mixture was obtained, with several unknown minor products, but the component corresponding in retention time to methyl *cis*-2-carbomethoxycyclopropylacetate was the largest. This material was re-passed, as above, to give pure material: $[\alpha]_D + 5.5 \pm 0.4°$, $4.6 \pm 1.0°$, $[\alpha]_{546} + 6.1 \pm 0.2°$, $6.2 \pm 1°$ (c 0.49, 0.19, CCl_4). Purity by vpc was 99.7%, and the IR again was identical to that of authentic material.

Hydrolysis of methyl cis-2-carbomethoxycyclopropylacetate in 12N H_2SO_4. As a control for the above correlations of optical purity, a pure sample [$[\alpha]_{546} + 52.7°$ (c 0.45, CCl_4)] of methyl *cis*-2-carbomethoxycyclopropylacetate was subjected to hydrolysis, esterification and recovery as above: $[\alpha]_{546} + 51.5 \pm 4.4°$ (c 0.04, CCl_4).

Rearrangement of ANTI-*dinitrile*. Solns of recrystallized ANTI-dinitrile and phthalonitrile were sealed in small tubes under vacuum after being degassed twice. One tube was heated at $79.9 \pm 0.1°$ (refluxing benzene) for 48 hr. Analysis by lc (Corasil II, 0.125 in × 2 ft, 2% EtOH in cyclohexane, 1.0 ml/min) showed the tube to contain *ca* 24% SYN-dinitrile and 76% ANTI-dinitrile. No CIS- or TRANS-dinitrile could be detected. Recovery was 100%.

(−)-ANTI-dinitrile (80 mg, $[\alpha]_{546} - 10.7°$ (c 1.02, $CHCl_3$)) was heated as above for 60 hr. The contents were separated by prep lc (Corasil II, 0.375 in × 4 ft, 32% $CHCl_3$ in cyclohexane, 3.4 ml/min). The collected SYN-dinitrile was re-passed, then dried under vacuum: $[\alpha]_{546} - 1.1 \pm 0.2$, $1.0 \pm 0.2°$ (c 1.50, 1.43, $CHCl_3$). Recovered ANTI-dinitrile was dried under vacuum: $[\alpha]_{546} - 6.2$, 6.1° (c 1.08, 1.32, $CHCl_3$). These samples were pure by lc (Corasil II, 0.125 in × 2 ft, 2% EtOH in cyclohexane, 1.0 ml/min).

A larger sample of (−)-ANTI-dinitrile (230 mg, $[\alpha]_{546} - 16.1$, 16.3° (c 1.33, 1.06, $CHCl_3$), recrystallized from CH_2Cl_2–CCl_4) was heated for 24 hr at 79.3–79.8°. Prep lc (two passes) gave 26 mg SYN-dinitrile: $[\alpha]_{546} - 1.4 \pm 0.1°$, $1.4 \pm 0.1°$ (c 2.08, 2.02, $CHCl_3$); and *ca* 150 mg recovered ANTI-dinitrile: $[\alpha]_{546} - 11.2$, 10.6° (c 2.36, 1.87, $CHCl_3$). Both isomers were pure by lc.

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