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STEREOCHEMISTRY OF THE METHYLENECYCLOPROPANE REARRANGEMENT

FEIST'S ESTER

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Abstract Establishment of the relative configuration of optically active dimethyl methylenecyclopropane-*trans*-2,3-dicarboxylate and its two products of thermal rearrangement, methyl *syn*- and *anti*-2-carbomethoxycyclopropylideneacetate, has allowed the exclusion of a planar transition state and the construction of a unique mechanism in which the substituents at a pivotal atom remain perpendicular to the plane of the system of four atoms that constitute the methylenecyclopropane of starting material and product.

FEIST'S ACID[1] in the form of its dimethyl ester (Feist's ester; *trans*-I) was recognized many years ago by Kon and Nanji[2] to isomerize when heated at about 200°. Not until acceptable structures were assigned to these substances by Ettlinger[3] in 1952 could the isomerization be recognized as the first example of a fundamentally degenerate rearrangement of methylenecyclopropane. Although the rearranged product, originally thought to be a single substance, is in fact[4] a mixture of two isomers, the evidence on which the structure is based is equally applicable to either isomer.[3,5] The structure of Feist's ester was the more firmly established[3,6–10] and was placed on an unequivocal basis by analysis of the X-ray crystallographic diffraction pattern.[11,12]

The existence of the simplest rearrangement is implicit in the observation that the addition of CD_2 to allene in the gas-phase leads to a mixture of dideuteriomethylenecyclopropane and 2,2-dideuterio-methylenecyclopropane.[13]

The activation and thermodynamic parameters have been elucidated by Chesick in a study of the reversible interconversion of 2-methylmethylenecyclopropane and ethylidenecyclopropane.[14] The relevant constants are an enthalpy of activation of 40·4 ± 0·6 kcal/mole, log A = 14·26, K = 1·18 (300°) and 1·33 (197°) from which an enthalpy difference of −0·5 ± 0·2 kcal/mole and an entropy difference of −0·55 e.u. were calculated. From heats of hydrogenation and estimates of heats of formation, an extra strain over cyclopropane of 11·5 kcal/mole is indicated for methylmethylenecyclopropane.[15] From the heat of combustion of methylenecyclopropane, an incremental strain of 13·9 kcal/mole can be estimated.[16] Since these estimates of the incremental strain are significantly larger than the value used by Chesick to assess the likelihood of concert in the rearrangement,[14] it is necessary to repeat his analysis with the newer values. If the entire incremental strain of 13 kcal/mole is available to lower

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the activation energy below that of the *cis-trans*-isomerization of cyclopropane (64 kcal/mole),[17] an activation energy of 51 kcal/mole is predicted for the rearrangement of methylenecyclopropane. The discrepancy of 11 kcal/mole is satisfactorily equated with the further assistance of resonance from the incipient allylic system. The geometrical situation is comparable to that encountered in the rearrangement of methylenecyclobutane, where no steric inhibition to the contribution of allylic resonance is indicated.[18] A sufficient rationalization of the energy of activation is then obtained with two factors: the incremental energy of strain in methylenecyclopropane and the contribution of the energy of one allylic delocalization. It is not necessary to invoke an additional element of concert to further lower the energy of the model transition state, since a satisfactory estimation is achieved without its help.

Other examples of rearrangements of the type of methylenecyclopropane include the equilibration at 250° of methyl methylenecyclopropaneacetate and methyl β-cyclopropylidenepropionate,[19] the isomerization of 2-isopropyloxy-3-methylmethylenecyclopropane at 100° to a mixture of *syn*- and *anti*-2-isopropyloxyethylidenecyclopropane,[20] the rearrangement of 2-carbethoxy-2,3-dimethyl ethylidenecyclopropane at 135° to 2-carbethoxy-2-methyl-isopropylidenecyclopropane,[21] and the interconversions among *cis* and *trans*-2,3-dimethylmethylenecyclopropane and *syn*- and *anti*-2-methylethylidenecyclopropanes.[22] Additional examples include the rearrangement at 360° of penta- and hexamethyl-vinylidenecyclopropane to dimethylenecyclopropanes,[23] the rearrangement of 2,2-diphenyl-1-(dideuteriomethylene)-cyclopropane into 2,2-diphenyl-3,3-dideuterio-methylenecyclopropane,[24] the rearrangement of 2,2-dichloro-methylenecyclopropane at 215° to 1-(dichloromethylene)cyclopropane,[25] and the racemizations of 2-phenyl- and 2-methyl-2-phenylmethylenecyclopropane.[26]

To Ullman, we owe a most remarkable discovery about the mechanism of the rearrangement of Feist's ester. Taking advantage of the fact that the acid was known to be chiral and resolvable,[1b,27] he rearranged optically active Feist's ester and found retention of activity in the mixture of products.[4] Although neither the quantitative extent of this retention nor the configuration of the predominating enantiomers relative to that of starting material was determined, this observation ruled out the exclusive intermediacy of achiral intermediates. Ullman's discovery was the more remarkable in having been made at a time when rearrangements of derivatives of cyclopropane were widely believed to involve freely rotating, often consequentially achiral, diradicals and at a time when a particularly strong theoretical attachment for the achiral planar trimethylenemethyl radical had already been accepted.* That the retention of optical activity in the rearrangement of Feist's ester is not dependent on interaction with one or both of the ester groups and more probably reflects a general characteristic of the rearrangement of methylenecyclopropanes, has been given strong support recently by Gajewski[22] in an extension of Ullman's approach to optically active *trans*-2,3-dimethyl-methylenecyclopropane, obtained by reduction of the carbalkoxy groups of Feist's ester to methyl groups. Thermal rearrangement of this dimethyl-methylenecyclopropane produced an inseparable mixture of *syn* and *anti*-2-methyl-1-(ethylidene)cyclopropane, which revealed significant amounts of optical activity.

* For references to theoretical work, see the experimental communications of P. Dowd[28] and R. J. Crawford and D. M. Cameron.[29]

The purpose of the present work is the definition of the configurational relationship between Feist's ester and the two products of its rearrangement. The goal has been achieved in two stages involving establishment of the relative configurations of the two products, first, to each other and, then, to Feist's ester.

The rearrangement of *trans*-2,3-dicarbomethoxy-methylenecyclopropane (Feist's ester: *trans*-I) in both racemic and optically active form is effected at 164° in benzene solution with the results given in Table 1. The two products, *syn* and *anti*-2-carbo-

TABLE 1. REARRANGEMENT OF FEIST'S ESTER (*trans*-I) AT 164° IN BENZENE

Time in hr	Yield in %	*trans*-I %	*trans*-I $[a]_{546}^{25}$	*syn*-II %	*syn*-II $[a]_{546}^{25}$	*anti*-II %	*anti*-II $[a]_{546}^{25}$	*anti/syn*
0·5		86	+ 145°	3		11	− 60°	3·39
1·0		72	+ 142°	7	+111°	21	− 60°	2·93
2·0		51	+ 141°	14	+ 90°	35	− 61°	2·53
4·0		28	+ 137°	26	+ 76°	46	− 54°	1·77
8·0	50	11		44		45		1·01
16·0	30	6		59		35		0·59
32·0	15	6		62		32		0·52

methoxy-1-(carbomethoxymethylene)-cyclopropane (*syn*-II and *anti*-II) are separated by GLPC and assigned their geometrical configurations on the basis of chemical shift in the NMR spectra. That isomer in which the single allylic H atom on the carbomethoxy-bearing C atom, 2, is shifted further downfield from the pair of allylic H atoms on C atom, 3, is assigned the *syn* structure (Fig 1). Neither *syn*-II nor *anti*-II having been resolved, the magnitudes of the rotations of optically pure materials remains unknown. Minimum values are, of course, +111° for *syn*-II and −60° for *anti*-II.

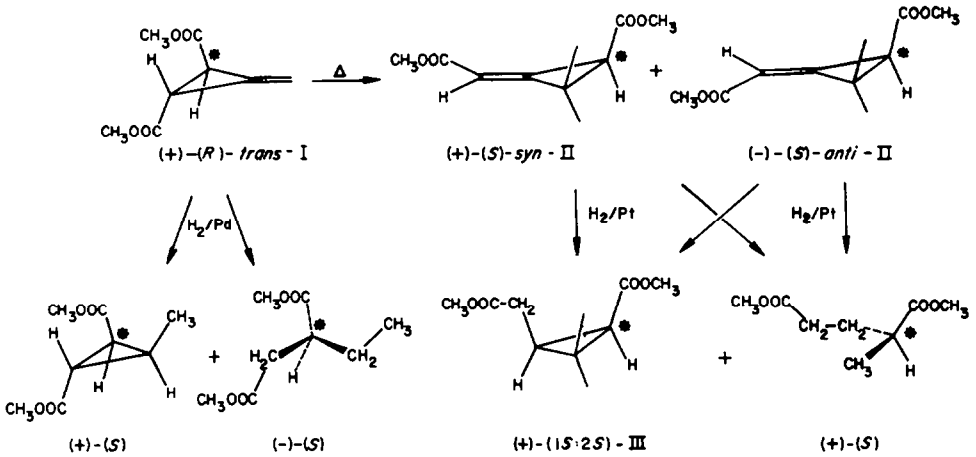
Both isomers are hydrogenated to the known methyl *cis*-2-carbomethoxycyclopropaneacetate (III).[30] A sample of optically active *syn*-II of $[\alpha]_{546}^{25}$ +67° affords III of $[\alpha]_{546}^{25}$ +44°, whereas, *anti*-II of $[\alpha]_{546}^{25}$ −49° affords III of $[\alpha]_{546}^{25}$ +74°. Corrected by the minimum values of rotation for optically pure materials, *syn*-II would have given III of $[\alpha]_{546}^{25}$ +72° and *anti*-II, III of $[\alpha]_{546}^{25}$ +90°. This minimum value for *syn*-II is doubtless too low since its rate of racemization is the fastest of the three substances. If the true value* is 135°, *syn*-II would have given III of $[\alpha]_{546}^{25}$ +89°.

The unequivocal conclusion is drawn that the major enantiomer in the samples of *syn*-II and *anti*-II have identical relative configurations.† For the time being, the quantitative degree of stereospecificity of the rearrangement of Feist's ester cannot be determined owing to ignorance of the specific rotations of optically pure *syn*-II and *anti*-II and to the absence of positive information about the possibility of racemization in their hydrogenation.

* Estimated from the rotations at the 1·0- and 2·0-hr points on the assumption that the racemization can, through this period, be treated as a first order process.

† It is worth noting that *syn*-II and *anti*-II can be considered to have structures approximating the type to which Brewster's rules might apply.[31] In such an analysis, *syn*-II and *anti*-II of the same configuration at C_2 are predicted to have opposite signs of rotation in full accord with the experimental fact.

Stereochemical interconnection between Feist's ester (*trans*-I) and the configurally identical products of its rearrangement, *syn*-II and *anti*-II, has been indicated by examination of certain felicitous by-products of their catalytic hydrogenation. Hydrogenation of Feist's ester was repeated without modification of Ullman's original procedure[5] on an optically pure sample, $[\alpha]_{546}^{25}$ +145°. A major (89%) product, dimethyl 3-methylcyclopropane-*trans*-1,2-dicarboxylate, $[\alpha]_{546}^{25}$ +124·5°, and a minor product (11%), dimethyl 2-ethylsuccinate $[\alpha]_{589}^{25}$ −8·6° were isolated by gas chromatography. A higher specific rotation, $[\alpha]_{589}$ −14·9°, is reported by Berner and Leonardsen[32] for optically pure dimethyl ethylsuccinate. Although it is clear that some loss of activity has accompanied the hydrogenolysis of the ring, we believe that the lowered rotation can safely be ascribed to racemization rather than to enantiomerization.



The assignment of an (*R*)-configuration to (+)-ethylsuccinic acid rests on the establishment of a relationship to strychnine by a combination of the works of Hill and Barcza,[33] and Nagarajan, *et al.*[34] Since the absolute configuration of strychnine has been established by X-ray fluorescence,[35] the absolute configuration of ethylsuccinic acid is known. Previous assignments relative to methylsuccinic acid are based on quasi-racemate formation[36] and by examination of the Cotton effect.[37] Since an (*R*)-configuration has been established for (+)-methylsuccinic acid by chemical relationship to ergoflavin, the absolute configuration of which has also been determined by X-ray crystallography, it follows from this line of evidence as well that (+)-ethylsuccinic acid has the (*R*)-configuration. The dimethyl ester of ethylsuccinic acid of $[\alpha]_{589}^{25}$ −14·9° is related to (−)-(*S*)-ethylsuccinic acid.[32]

To the extent that catalytic hydrogenolysis did not cause inversion of the α-ethyl center of asymmetry, dextrorotatory dimethyl methylenecyclopropane-*trans*-1,2-dicarboxylate has the (*R*)-configuration. The product of hydrogenation of dextrorotatory (+)-*trans*-I, dextrorotatory dimethyl *cis*-3-methylcyclopropane-1,2-dicarboxylate, has the (*S*)-configuration.*

Catalytic hydrogenolysis also provides the means of establishing the configurations of the rearrangement products. *Syn*- and *anti*-II afford, in addition to the previously

* Dextrorotatory *trans*-2,3-dicarbomethoxycyclopropane is configurationally closely related to these two molecules and has the same absolute configuration.[39]

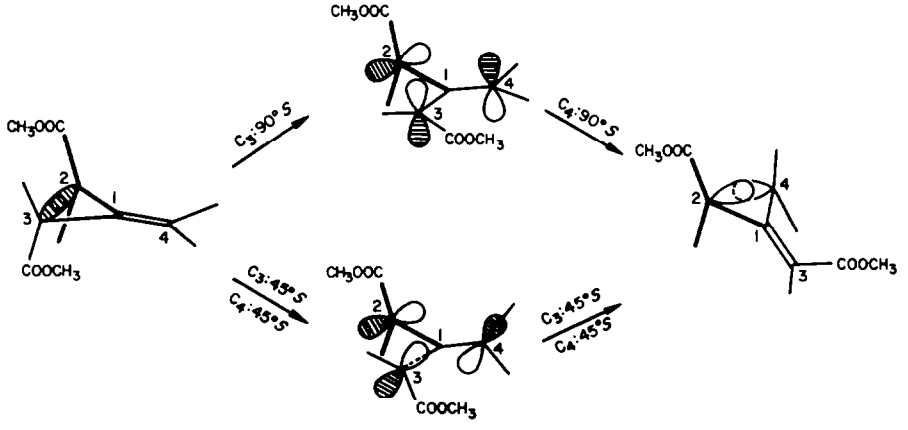
discussed product of hydrogenation, a product of hydrogenolysis, dimethyl 2-methylglutarate. A sample of *syn*-II of $[\alpha]_{546}^{25}$ +67° gives 2-methylglutarate of $[\alpha]_{589}^{25}$ +10°. Corrected on the previous assumption that optically pure *syn*-II might have a specific rotation of 135° (the reader can replace the following values by more accurate ones when the rotations of pure materials become known), the sample of dimethyl 2-methylglutarate would have had a specific rotation of 20·3°. Similarly, *anti*-II of $[\alpha]_{546}^{25}$ −49° gives dimethyl 2-methylglutarate of $[\alpha]_{589}^{25}$ +19° (corrected in similar approximate fashion, this value becomes $[\alpha]_{589}^{25}$ +23·6°). The specific rotation reported by Berner and Leonardsen[32] for optically pure dimethyl 2-methylglutarate is $[\alpha]_{589}^{25}$ +24·46°.

(−)-(*R*)-2-Methylglutaric acid is related configurationally to (+)-(*R*)-methylsuccinic acid by the method of quasi-racemates[40] and the observation of a positive Cotton effect.[37] A direct, chemically reliable interrelationship has been established through hecogenin.[41] 2-Methylglutaric acid and its configurationally related dimethyl ester have been shown to have the same sign of rotation.[32]

It follows that (−)-(*S*)-*anti*-II and (+)-(*S*)-*syn*-II have the absolute configurations shown above. To the extent that the rules of Brewster are applicable to this imperfect approximation of a spiropentane system,[31] the geometrical configurations must be assigned as they are shown if signs of rotation are to be consistent. It should be noted that the correctness of the *syn* and *anti* structural feature is not essential to the main conclusion of this work.

The stereochemistry of the rearrangement of Feist's ester is such that the asymmetric C atom common to the cyclopropane rings of both the starting ester and the rearranged product retains its position relative to the plane of the two systems of methylenecyclopropane. Alternatively, the rearrangement can be said to occur with inversion of configuration about the asymmetric sp^3 carbon atom common to the old and new rings. The two substituents of the asymmetric atom remain in a plane perpendicular to the plane of the four atoms of the methylenecyclopropane throughout the rearrangement. This atom is designated the pivot atom about which the reaction occurs.

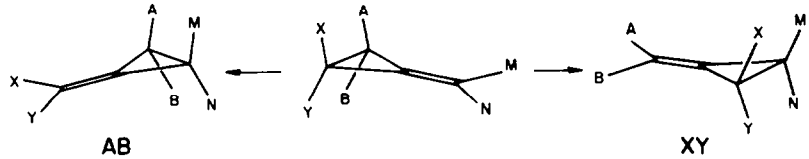
The orbital characteristics of this pivot mechanism may be illustrated in a concerted and a non-concerted version. As outlined in the earlier discussion, the energetics of the reaction can be accommodated by a non-concerted or, at best, weakly concerted



mechanism, but certainly do not demand strong concert. In the non-concerted version the half-way stage is a planar allylic radical, to the central carbon atom of which there is attached a free radical in its perpendicular and non-bonding arrangement. This intermediate is achieved by a 90° rotation about the C_3—C_1 axis and proceeds to product by a 90° rotation about the C_4—C_1 axis. If the original rotation is in the (*S*)-sense, *anti*-II is the product; if the original rotation is in the (*R*)-sense, *syn*-II is the product.

In the concerted version, which is a modification of the non-concerted version, the allylic radical never becomes fully planar and therefore is itself never fully developed. At the half-way stage both pairs of substituents at atoms 1 and 3 are tilted (e.g., at 45° to the plane of the central 4-atom system) and lie in a tilted common plane. Such a tilting of an allylic radical may be accomplished at little cost to the energy of the π_2 orbital which has a node at C_2, but would be expected to increase significantly the energy of the π_1 orbital. It is hypothesized that this increase would be more than compensated by bonding between the nearer, upper lobes of the slantindicular π_2 orbital and the lobes of the perpendicularly oriented 2p orbital of the pivot atom. To reach this transition state two rotations in identical senses are required; one about the C_3—C_1 axis, the other about the exocyclic C_4—C_1 axis. In the illustration two (*S*)-rotations of 45° bring the assembly to the half-way stage for the formation of *anti*-II.

Inherent in the new pivot mechanism, regardless of the presence or absence of concert, is the question whether the energy-lowering effect of a radical-stabilizing substituent will be claimed by the pivot atom or by the allylic moiety. Of the nine other examples of the methylenecyclopropane rearrangement cited earlier, six are relevant to this question. Examination of these examples, set out below, leads unambiguously to the hypothesis that the atom which bears the substituent(s) more highly stabilizing a free radical assumes the role of pivot in the rearrangement. It is intended to explore the range of validity of this hypothesis by synthesizing and rearranging a number of additional unsymmetrically substituted methylenecyclopropanes.



(1)	A = Me	B = H;	M = H;	N = H;	X = H;	Y = $OCHMe_2$:	ref. 20
(2)	A = Me	B = Me_3;	M = H;	N = H;	X = Me;	Y = COOMe:	ref. 21
(3)	A = H;	B = H;	M = H;	N = H;	X = H;	Y = C_6H_5	ref. 26
(4)	A = H;	B = H;	M = H;	N = H;	X = Me;	Y = C_6H_5	ref. 26
(5)	A = H;	B = H;	M = D;	N = D;	X = C_6H_5	Y = C_6H_5	ref. 24
(6)	A = Me	B = H;	M + N = $=CMe_2$;		X = Me	Y = Me:	ref. 23

If the hypothesis of dominance by the pivot be extended to Chesick's system, methylmethylenecyclopropane and ethylidenecyclopropane,[14] it must be concluded that the activation parameters determined in that work refer to the higher activation process in which the weakly, radical-stabilizing Me group is assisting the recessive allyl moiety rather than the pivot. For a complete definition of the effect of a Me group, the activation parameters relating to the degenerate rearrangements of

2,2-dideuterio-methylenecyclopropane and 2,2-dideuterio-3-methylmethylenecyclopropane need to be determined.

Despite some discrepancies between the fragmentary kinetic results reported by Ullman[4] and by us, both workers agree that racemization is a feature of the rearrangement of Feist's ester. Although a thorough kinetic study is overdue, we would like to report some preliminary kinetic results on the rearrangement of the *cis* ester (Table 2) and to call attention to the remarkably fast racemization of *syn*-II (Table 1).

TABLE 2. REARRANGEMENT OF *cis*-2,3-DICARBOMETHOXYMETHYLENECYCLOPROPANE (*cis*-I) at 164° IN BENZENE

Time in hr	*cis*-I in %	*trans*-I in %	*syn*-II in %	*anti*-II in %	*anti/syn*
0·25	38·8	4·2	26·0	31·0	1·19
0·50	12·4	6·3	39·0	42·3	1·08
1·00	1·6	6·6	45·2	46·6	1·03

Primary racemization is not occurring rapidly in *trans*-I nor does it appear that active *syn*-II rearranges rapidly to achiral *cis*-I, for were this true, racemic *anti*-II would be formed essentially as fast as *syn*-II. Perhaps the special structural feature in *syn*-II allows the otherwise unfavored trimethylenemethyl radical to be favored by a weak oxygen–oxygen interaction.*

The major mechanistic question of concert or lack of concert appears in principle to be capable of solution. Consider, for example, any of the four stereoisomers of the (*R*)-configuration of 2-carbomethoxy-3-methylethylidenecyclopropane. In the concerted, rotationally coupled mechanism, each of the two senses of rotation, C_3-*R*, C_4-*R* and C_3-*S*, C_4-*S*, leads to the formation of enantiomer and a product of opposite stereochemical, geometrical and absolute configuration: *trans* if starting with *cis*, *anti* if starting with *syn*. The end-result would be a racemic mixture of two of the four possible stereoisomers, *cis-anti* and *trans-syn* or *cis-syn* and *trans-anti*.

In the non-concerted rearrangement, the first 90° rotation at C_3 in any one of the (*R*)-isomers may be in the (*R*)- or (*S*)-sense and may be followed by the second 90° rotation at C_4 quite independently in either the (*R*)- or (*S*)-sense. Thus all four of the possible (*S*)-isomers may be formed. In addition, the first 90° rotation at C_3 may be reversed *ad libitum* in either the (*R*)- or (*S*)-sense. This process leads to *cis-trans* interconversion without change in either the (*R*)-configuration or the *syn* or *anti* geometrical configuration.

Under kinetic control rearrangement by the non-concerted mechanism can lead to three more products than can the concerted process. Under thermodynamic control the non-concerted mechanism produces all four stereoisomers in racemic form while the concerted mechanism leads to only two racemic forms. It is intended to attempt the experimental solution of the problem.

* By analogy with the recent report of Rhoads and Cockroft[42] that an aldehyde group can replace one vinyl group in the 1,2-divinylcyclopropane rearrangement, both ester oxygen atoms of *syn*-II, but not *anti*-II, might be able to produce 3,6-dimethoxy-4,5-*bis*-oxamethylenecycloheptadiene as an achiral intermediate. See also, the example of the Schiff bases of 1,2-diaminocyclopropanes.[43]

EXPERIMENTAL

Optically active dimethyl ester of trans-1-*methylenecyclopropane*-2,3-*dicarboxylic acid*

Feist's acid; trans-I. The dicarboxylic acid was prepared according to the procedure of Feist[1] as developed by Blomquist and Longone.[4a] Feist[1b] effected the first resolution by way of the acid quinine salt (1:1). Brucine was employed by Goss, *et al.*[27] Although there is one other report of optically active Feist's acid,[4] a detailed description of the resolution does not appear in the literature.

Addition of a soln of 32·4 g (0·1 mole) quinine in 115 ml commercial absolute EtOH to a soln of 14·2 g (0·1 mole) Feist's acid in 60 ml commercial absolute EtOH gave a ppt which was dissolved by refluxing for 15 min. Although crystallization sets in soon after cooling, 3 days is required for completion. In the usual manner a fractional crystallization is undertaken, although the full pyramid cannot be developed owing to the non-crystallinity of the quinine salt of the laevorotatory acid. The head fraction of the succeeding levels of crystallization had the following properties; first: 28·6 g (moist), mp 184–186°, $[\alpha]_{546}^{25}$ − 154°; second: 20·2 g, mp 191–193°, − 146°; third: 13·2 g, mp 194–195°, − 140·5°; fourth: 11·4 g, mp 196–197°, − 140·3°; fifth: 9·6 g, mp 196–197°, − 139·7°. Further recrystallizations did not change the rotation or mp. Feist[1b] reports mp 157°. From the pure salt, $[\alpha]_{546}^{25}$ − 140·0° (c = 0·4 g in 100 ml 1:1 aq EtOH), free acid is regenerated in 80% of theory: mp 203–205°; $[\alpha]_{546}^{25}$ + 176° (c = 0·7 g in EtOH). Feist[1] reports mp 200°; $[\alpha]_{589}$ + 266°.*

The dimethyl ester is obtained in the usual way by treatment of the acid with diazomethane: bp 66–67°/0·2 mm; mp 32·5°–33·5°; $[\alpha]_{546}^{25}$ + 145° (c = 0·7 g in CCl_4). Feist[1b] reports bp 122°/20 mm; mp 32°; but no specific rotation.

Thermal rearrangement of racemic dimethyl ester of Feist's acid (trans-I). The dimethyl ester of Feist's acid (100-μl portions) in 900 μl benzene was heated in sealed ampoules in a bath, maintained at 164° by boiling mesitylene. For isolation of products, the benzene was frozen and separated by centrifugal filtration. Ratios of the products were determined by weighing the traces of gas chromatographic analysis of these filtrates (obtained on a 3-m column, GE silicon oil 710, 20% on kieselguhr, 138°: Column A). Under these conditions, some interconversion of the esters (less than 5%) occurs on the column which makes quantitative evaluation of peak areas subject to error. Along with the thermal isomerization, a decomposition occurs, attested by the yellow colour of the recovered solns and a steady decline in recovered material. The data are reported in Table 1 and are uncorrected for decomposition or interconversion.

The IR spectrum of the ester follows: 3005(w); 2955(m); 1740(s); 1437(m); 1308(s); 1273(m); 1264(m); 1197(m); 1165(s); 1106(m); 1052(m); 924(m); 904(m).

Thermal rearrangement of the dimethyl ester of Feist's acid (trans-I) in a flash apparatus. Dimethyl ester of Feist's acid (1-g portions) was pyrolyzed by passing through a carefully neutralized, 25-cm tube of 0·8-cm i.d. filled with Pyrex helices. The products of pyrolysis were analyzed on column A at 138°: Feist's ester (*trans*-I): retention time of 42 min; *syn*-II, 65 min; *anti*-II, 77 min. At temps up to 315°, the starting material was recovered unchanged. At higher temperatures, the results shown in Table 3 were obtained. Above 400° recovered material was dark brown. Under no conditions was the *cis*-isomer of Feist's ester present in the reaction mixtures (retention time: 54 min under same condition as above).

The products of pyrolysis were separated by GLPC and isolated in sufficient quantity for the determination of their nmr spectra (*cis* and *trans* ester are included for comparison).

The IR spectrum of methyl *syn*-(carbomethoxycyclopropylidene)acetate (*syn*-II) follows: 3025(w);

TABLE 3. THERMOREACTION OF FEIST'S ESTER (*trans*-I) IN A HEATED TUBE

Temp	*trans*-I in %	*syn*-II in %	*anti*-II in %	% recovery
345°	86	3	11	89
365°	63	11	26	92
385° (1st pass)	56	17	27	91
385° (2nd pass)	31	32	37	92
385° (3rd pass)	16	40	44	86

* Feist[1b] also reports the resolution of an unsubstantiated, hypothetical tautomer of *trans*-acid of mp 189° by means of the quinine salt to give optically pure acid of mp 189° and $[\alpha]_{589}$ = + 179·8°.

3000(w); 2955(m); 1773(m); 1740(s); 1726(s); 1440(s); 1355(s); 1325(s); 1268(s); 1197(s); 1165(s); 855(w); 840(m).

The IR spectrum of methyl *anti*-(carbomethoxycyclopropylidene)acetate (*anti*-II) follows: 3025(m); 3000(w); 2955(m); 1770(m); 1740(s); 1725(s); 1436(s); 1360(s); 1318(s); 1269(s); 1196(s); 1165(s); 858(m); 840(w).

TABLE 4. NMR SPECTRA OF DIMETHYL ESTER OF FEIST'S ACID (*trans*-I), *cis*-I, METHYL *syn*- AND *anti*-CARBOMETHOXYCYCLOPROPYLIDENE ACETATE (*syn*-II AND *anti*-II)

Type of proton		Chem shift[a] τ	Chem shift[a] δ	Multiplicity	J in c/s
Trans-I					
Olefinic		4·36	5·64	triplet	2·4
Methyl		6·33	3·67	singlet	
Cyclopropyl		7·23	2·77	triplet	
Cis-I					
Olefinic		4·32	5·68	triplet	2·4
Methyl		6·36	3·64	singlet	
Cyclopropyl		7·36	2·64	triplet	
Syn-II[b]					
Olefinic	(A)	3·81	6·19	quartet	2·1 (AB)
					2·1 (AC)
					2·1 (AD)
Methyl		6·32	3·68	singlet	
		6·34	3·66	singlet	
Cyclopropyl	(B)	7·52	2·48	multiplet	6·5 (BC)
					9·4 (BD)
	(C)	8·11	1·89	multiplet	10·5 (CD)
	(D)	8·27	1·73	multiplet	
Anti-II[b]					
Olefinic	(A)	3·79	6·21	multiplet	1·6 (AB)
					2·6 (AC)
					2·6 (AD)
Methyl		6·30	3·70	singlet	
		6·37	3·63	singlet	
Cyclopropyl	(B)	7·68	2·32	multiplet	6·0 (BD)
					9·7 (BD)
	(C)	7·95	2·05	multiplet	11·0 (CD)
	(D)	8·13	1·87	multiplet	

[a] In ppm on the τ and δ scale; a standard error ± 0·05 ppm is assumed

[b] See Fig. 1 for elucidation of the assignments of coupling constant

Thermal rearrangement of optically active dimethyl ester of Feist's acid (trans-I). Samples (100 μl) of optically active ester, $[a]_{546}^{25}$ + 145°, were heated at 164° as described above. Specific rotations, $[a]_{546}^{25}$ were determined at concentrations between 0·5 and 1·6 g/100 μl CCl_4. The uncertainty introduced by this range should not exceed the uncertainty due to interconversion of the esters on the GLPC column. The results are shown in Table 1.

Thermoreaction of dimethyl 1-methylenecyclopropane-2,3-cis-dicarboxylate (cis-I). The corresponding anhydride was prepared according to Ettlinger and Kennedy[45] and converted to the dimethyl ester by refluxing in methanol (5 g in 50 ml) containing saturated methanolic HCl (2 ml) for 2 hr. Removal of solvent *in vacuo* leaves a residue which is dissolved in ether and treated with excess ethereal diazomethane to complete the esterification. Concentration and distillation afforded 4·3 g *cis*-I (63%); bp 62–64°/0·5 mm. The

NMR spectrum is reported in Table 4. The IR spectrum follows: 3005(w); 2955(m); 1740(s); 1438(s); 1345(s); 1198(s); 1165(s); 1110(m); 905(m); 865(m).

Thermal rearrangement was effected in benzene soln at 164° in the manner of Feist's ester. The results are reported in Table 2.

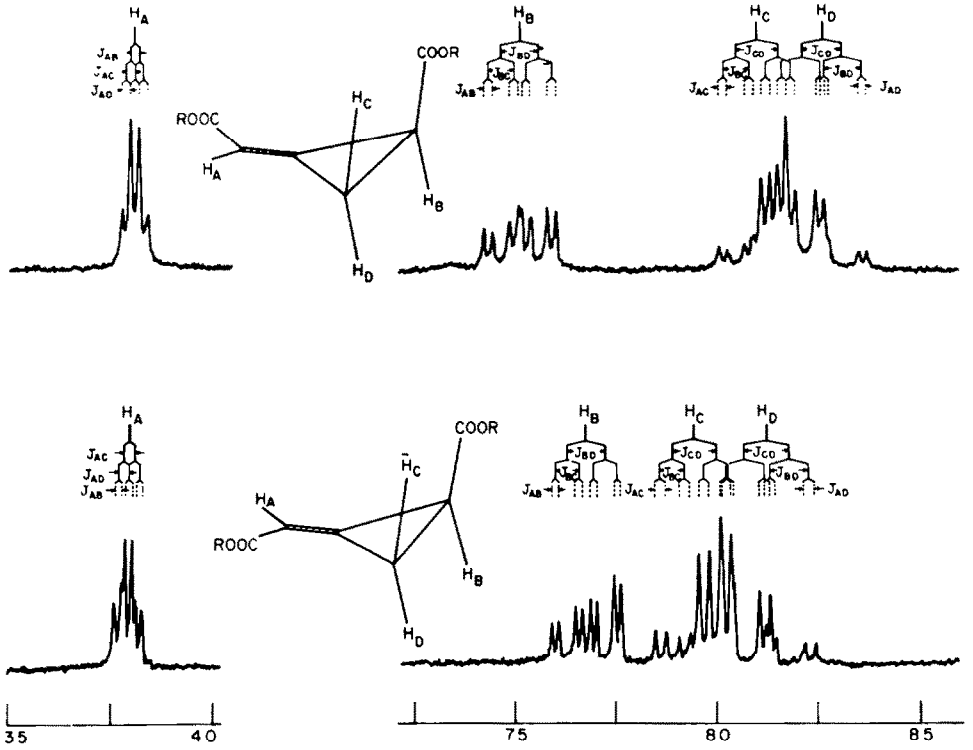


FIG. 1. The NMR spectra in ppm on the τ scale of methyl *syn*- and *anti*- carbomethoxycyclopropylideneacetate (*syn*-II and *anti*-II)

Catalytic hydrogenation of optically active dimethyl ester of Feist's acid. The same procedure employed by Ullman[5] in the hydrogenation of rac. Feist acid is used here. Optically active *trans* diester (300 mg of mp 32·5–33·5°; $[a]_{546}^{25} = +145°$) was hydrogenated with 93 mg Pd/C (5% Pd) in 2 ml EtOAc. The catalyst was removed by filtration, the solvent evaporated *in vacuo* and the resulting liquid separated by GLPC [3 m column of 20% diethyleneglycol succinate on kieselguhr, 120° (column B)].

Two products were isolated. The first (retention time 24 min; 11% of the mixture) was dimethyl 2-ethylsuccinate which was repassed to yield material of $[a]_{589}^{25} - 8·6°$ ($c = 0·5$ g in EtOH). Berner and Leonardsen[32] report $[a]_{589} - 14·89°$ for optically pure material, presumably in EtOH. The second product (retention time 31 min; 89% of the mixture) was dimethyl 3-methylcyclopropane-1,2-dicarboxylate with $[a]_{546}^{25} = +124·5°$ ($c = 0·9 \pm 0·2$ in CCl_4).

Catalytic hydrogenation of optically active methyl syn-*carbomethoxycyclopropylideneacetate* (syn-*II*). A sample of *syn*-II (80 mg of $[a]_{546}^{25} + 67°$; $c = 0·9$ g in CCl_4) was hydrogenated with 40 mg prereduced PtO_2 in 2 ml AcOH. The solvent was frozen and the hydrogenation products removed by centrifugation. Separation by GLPC (column B) gave impure methyl *cis*-2-(carbomethoxycyclopropyl)acetate ($[a]_{546}^{25} = +44°$; $c = 0·6$ g in CCl_4) and dimethyl 2-methylglutarate of $[a]_{546}^{25} = +10°$. Berner and Leonardsen[32] report $[a]_{589}^{25} = +24·46°$ for optically pure dimethyl ester of 2-methylglutaric acid.

Catalytic hydrogenation of optically active methyl anti-*carbomethoxycyclopropylideneacetate* (anti-*II*). A sample of *anti*-II (125 mg of $[a]_{546}^{25} - 49°$; $c = 0·7 \pm 0·1$ g in CCl_4) was hydrogenated with 100 mg prereduced PtO_2 in 2·50 ml AcOH and the products separated as before.

Dimethyl 2-methylglutarate showed $[a]_{589}^{25} + 19°$ ($c = 0·5 \pm 0·1$ g/100 ml EtOH) while impure methyl *cis*-2-carbomethoxycyclopropylacetate had $[a]_{546}^{25} + 74°$ ($c = 0·5 \pm 0·1$ g/100 ml CCl_4).

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