780. *A Revision of the Structural Assignments for the Geometrical Isomers of 3-Methyl-5-phenylpentadienoic Acid.*

By RICHARD H. WILEY.

Re-investigation of the geometrical isomers of 3-methyl-5-phenylpentadienoic acid has shown that the compound, m. p. 125°, formerly assigned the *cis*-2 : *trans*-4-structure is a molecular complex of the isomers of m. p.s 158° and 160°. On the basis of their physical properties and their infrared and ultraviolet absorption characteristics these two isomers are now assigned the *cis*-2 : *trans*-4- (II) and the *trans*-2 : *trans*-4-structure (I) respectively. This reassignment makes possible a new interpretation of the steric course of the Reformatsky reaction and of the mechanism of the decarboxylation by which the isomers are prepared as well as the clarification of several inconsistencies and apparent abnormalities previously noted.

THE assignment of *cis-trans*-structures to the known isomers of 3-methyl-5-phenylpentadienoic acid has recently been re-examined [1] in detail and used [2] as a basis, with some qualifications and reservations, for assigning structures to intermediates in the synthesis of vitamin A. The *trans*-2 : *trans*-4-structure has been assigned to the isomer of m. p. 160° on the basis that it is the most stable product and is obtained by iodine-catalysed isomerisations of the other two forms. The isomer, m. p. 125°, has been assigned the *cis*-2 : *trans*-4-structure because it is obtained in a Reformatsky reaction with benzylideneacetone and ethyl bromoacetate under conditions which with other carbonyl compounds give lower-melting acids isomerisable to, and often accompanied by, their higher melting forms. The isomer, m. p. 158°, being isomerisable to the 160° form, was assumed to be of necessity a *cis*-form also and has, therefore, been assigned the *trans*-2 : *cis*-4 structure even though the ultraviolet absorption data require an improbable coplanar hindered *cis*-structure. It is also necessary to postulate a rather improbable formation of this hindered *trans*-2 : *cis*-4-structure by opening of the lactone ring in 5 : 6-dihydro-4-methyl-6-phenyl-2-pyrone (III) which has been reported [3, 4] as a product of the Reformatsky reaction between benzaldehyde and ethyl γ-bromosenecioate.

In addition to these considerations which cast some doubt on the reliability of the assignments, problems have also been encountered in assigning probable structures to the apparent isomers obtained with cinnamylidene analogues [5] of the phenyl structures and with the isoprenoid structure, β-methyl-γ-*iso*pentylideneglutaconic acid [6] and in explaining the course of the decarboxylation of γ-arylidene-β-methylglutaconic acids.[7] To explain the stereochemical course of the decarboxylation it has been necessary to postulate that with the arylidene derivatives no inversion takes place while with the ionylidene, and presumably other alkylidene types, inversion occurs at both of the double bonds. Inversion at the double bond from which the carboxyl is removed can be explained but there appears to be no precedent for the accompanying inversion at the adjacent centre of unsaturation.

It has now been observed that the " isomer," m. p. 125°, is actually a molecular complex of the 158° and 160° isomers. In these studies the 160° isomer has been obtained as previously described [1] by the iodine-catalysed isomerisation of the 158° isomer and from the mixture of products obtained from the Reformatsky reaction of ethyl bromoacetate with benzylideneacetone. The 158° isomer has been obtained from the Reformatsky reaction

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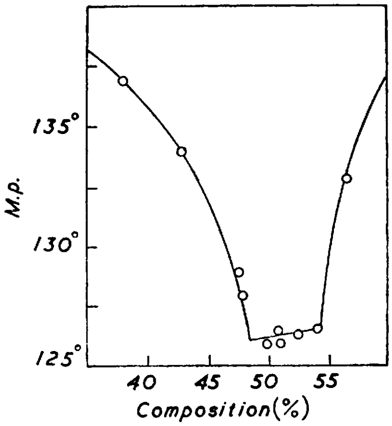
[1] Cawley and Nelan, *J. Amer. Chem. Soc.*, 1955, **77**, 4130.
[2] Robeson, Cawley, Weisler, Stern, Eddinger, and Chechak, *ibid.*, p. 4111.
[3] Fuson and Southwick, *ibid.*, 1944, **66**, 679.
[4] Harper and Oughton, *Chem. and Ind.*, 1950, 574.
[5] Petrow and Stephenson, *J.*, 1950, 1310.
[6] Wiley and Ellert, *J. Amer. Chem. Soc.*, 1957, **79**, 2266.
[7] Cawley, *ibid.*, 1955, **77**, 4125.

of ethyl γ-bromosenecioate with benzaldehyde and by decarboxylation of γ-benzylidene-β-methylglutaconic acid. The 125° complex has been obtained from the mixture obtained from the benzylideneacetone Reformatsky reaction and, now for the first time, by recrystallisation of a mixture of equal amounts of the 158° and 160° isomers. The 125° complex has also been obtained from the mother-liquors as the more soluble product of the iodine-catalysed isomerisation of the 158° isomer to the 160° isomer. The 125° sample prepared from the two isomers shows no depression of melting point on admixture with a sample isolated from the Reformatsky reaction and gives an infrared spectrum identical with that of the Reformatsky product. Esterification of the 125° isomer with diazomethane gives a mixture of dimethyl esters, liquid at room temperature as is also the mixture of the dimethyl esters, m. p.s 42° and 37°, obtained by esterification of the 158° and 160° isomers.

Further evidence for the existence of a molecular complex, m. p. 125—126°, is available from the melting point–composition diagram (see Figure) for mixtures of the isomers, which shows that the 50% composition is not a simple, single eutectic point. The existence of a maximum in the curve is not clearly shown by the available data. It appears that the depression in melting point produced by either of the isomers on the complex is too slight to be detected by the usual melting-point measurements. This is consistent with the fact that no previous report of a depression in melting point for the complex on admixture with either isomer has been recorded.



Phase diagram for (left) cis-2 : trans-4- *and (right)* trans-2-trans-4-*forms of* 3-*methyl*-5-*phenylpentadienoic acid.*

With the information that the " isomer," m. p. 125°, is a molecular complex, it is now possible to assign structures to the two isomers which eliminate most, if not all, of the above-mentioned difficulties as well as certain other apparent contradictions in the literature describing the preparations of these compounds. The complex, m. p. 125°, has been described as the initial product obtained from the Reformatsky reaction of ethyl bromoacetate with benzylideneacetone. Three laboratories [1, 8, 9] have reported that this reaction gives the 125° complex: three others [10, 11, 12] that it gives the 160° isomer. The 160° isomer has also been prepared by the iodine-catalysed isomerisation of either the 125° or the 158° isomer. This indicates an isomerisation under conditions used by those who failed to obtain the 125° isomer caused either by the use of excess of hot mineral acid, as has been previously suggested,[1] or by the iodine added to initiate the Reformatsky reaction. However, the benzylideneacetone is certainly in the *trans*-configuration [13] and the

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[8] Kuhn and Hoffer, *Ber.*, 1932, **65**, 651.

[9] Heilbron, Jones, Julia, and Weedon, *J.*, 1949, 1823.

[10] Shchukina and Rubstov, *Zhur. obshchei Khim.*, 1948, **18**, 1645.

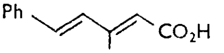
[11] Kohler and Heritage, *Amer. Chem. J.*, 1910, **43**, 475.

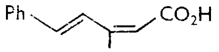
[12] von Auwers and Heyna, *J. prakt. Chem.*, 1923, **105**, 361.

[13] Lutz and Jordan, *J. Amer. Chem. Soc.*, 1950, **72**, 4090.

Reformatsky reaction may be assumed to give a mixture of the *cis*-2- and *trans*-2-isomers. It has been recorded [8] that this type of Reformatsky reaction does in fact give mixtures of isomers. In this event the normal product of this reaction is a mixture of the *trans*-2 : *trans*-4- (I) and the *cis*-2 : *trans*-4-isomer (II) which is isolated as the 125° molecular complex. If, however, conditions are such that the *cis*-2 : *trans*-4-isomer is isomerised to an appreciable extent the only product which can be isolated pure will be the more insoluble *trans*-2 : *trans*-4-isomer.

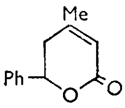
(I)



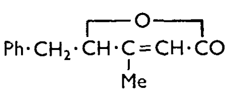


(II)

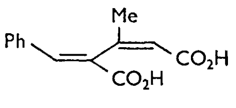
This explanation requires that the 158° isomer has the *cis*-2 : *trans*-4 configuration (II). This is not inconsistent with the available information about its formation as the product of the benzaldehyde-γ-bromosenecioate Reformatsky reaction.[3,4,14] This gives a mixture of unsaturated esters which has been separated into two fractions before saponification to the acids. The lower-boiling ester has been reported [3,4] to give the 160° isomer: it seems likely that it consists of one or both of the *cis*-4-isomers which are readily isomerised to the *trans*-*trans*-form during isolation. The higher-boiling ester is reported [3] to give the 158° isomer and this is apparently correct but only partly so as it has now been observed that it is possible to obtain impure samples of the 125° complex from the mother-liquors. The δ-lactone (III) that has previously been obtained [3,4] as a by-product of this Reformatsky reaction can now be viewed as undergoing ring opening to the *cis*-2 : *trans*-4-structure which is more readily understandable than it was on the previous structural assignment which required a rather improbable ring opening to the hindered *trans*-2 : *cis*-4-structure. Unsaturated lactones are known to open with double-bond inversion at the $\alpha\beta$-position to give the *trans*-2 unsaturated acid but the *cis*-orientation is retained under favourable conditions.[15] The $\gamma\delta$-double bond would be expected to be formed in the *trans*-configuration by analogy with the base-catalysed β-elimination of a β-acetoxy-group which forms the *trans*-product.[16] It appears that the most probable product of such a ring opening would be the *cis*-2 : *trans*-4-structure in keeping with the present revised structure of the product. Although this lactone has not been isolated in the present studies of this reaction, there does occur in all of the ester fractions a carbonyl band at 1764 cm.$^{-1}$ indicative of an unsaturated γ-lactone-carbonyl group. This, coupled with the failure to achieve δ-lactonisation of the dicarboxylic acid, under conditions which readily give δ-lactonisation in the alkylidene series, indicates that the structure of this lactone is that of the γ-lactone (IV). There is no clear-cut evidence of terminal methylene groupings in the infrared spectra for the products of this reaction. This confirms the previous report [4] that no α-alkylation occurs with the senecioate reaction although it does [17] with the analogous γ-bromocrotonate.



(III)


$\mathrm{Ph{\cdot}CH_2{\cdot}\overbrace{CH{\cdot}\underset{Me}{C}{=}CH{\cdot}CO}^{O}}$

(IV)



(V)

The 158° isomer has also previously been obtained [1] by decarboxylation of γ-benzylidene-β-methylglutaconic acid (V) catalysed by lutidine-copper acetate. This has also been confirmed. If the *cis*-2 : *trans*-4-structure is correct for the decarboxylated product, the glutaconic acid is most likely to be either *cis*-2 : *trans*-4- or *cis*-2 : *cis*-4-compound (V) and in the latter case undergoes inversion on decarboxylation. The *trans*-4-structure for the glutaconic acid can be eliminated with some assurance as the ultraviolet

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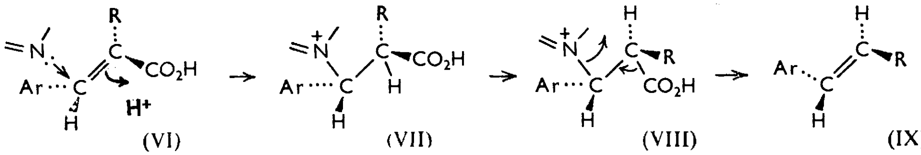
[14] Ziegler, Schumann, and Winkelmann, *Annalen*, 1942, **551**, 120.
[15] Eisner, Elvidge, and Linstead, *J.*, 1953, 1372.
[16] Linstead, Owen, and Webb, *J.*, 1953, 1211.
[17] Jones, O'Sullivan, and Whiting, *J.*, 1949, 1415.

absorption ($\lambda_{max.}$ 276; ε 17,600) is typical of a *trans*-cinnamic acid structure which is present in the *cis*-4-acid (V). The inversion of the *cis*-4- to the *trans*-4-form is consistent with the formation of the more stable *trans*-form during the reaction and with the addition-elimination mechanism postulated for the decarboxylation of arylidenemalonic acids[18] provided that the initial addition of base and acid gives a *trans*-product. The mechanism is shown in (VI—IX). This involves *trans*-addition of the base and acid (VI to VII); rotation to bring the carboxyl *trans* to the lutidine before elimination (VIII); and *trans*-elimination to (IX) in which the phenyl group is *trans* to the residual carbon chain.



(VI) (VII) (VIII) (IX)

The assignment of the *cis*-2-structure to the benzylideneglutaconic acid is consistent with the known ease[6] with which alkylideneglutaconic acids are converted into δ-lactones and with their conversion into anhydrides. The failure of the cinnamylidene analogue to form an anhydride, previously taken[7] as indicating a *trans*-2-structure is apparently not determining. Models show that lactonisation and anhydride formation are equally favoured structurally. The phenyl analogue fails to lactonise with acetic acid under conditions successfully used with the alkylidene analogues. It is decarboxylated to *trans*-3-methyl-1-phenylbutadiene rather than to the lactone when the potassium salt of the dicarboxylic acid is heated with acetic acid. On this basis the β-methyl-γ-*iso*-pentylideneglutaconic acid isomers previously described[6] are probably the *cis*-2 : *cis*-4-isomer and the *trans*-2 : *cis*-4-isomer formed with excess of alkali. It is known that alkali converts *cis*- into *trans*-β-methylglutaconic acid.[19] Also it is not unusual that the *cis*-2-form which, by analogy with β-methylglutaconic acid itself, would be the higher-melting, more insoluble form is the form isolated from the condensation starting with either the *cis*- or *trans*-form of dimethyl β-methylglutaconate.

Further confirmation of the *cis*-2 : *trans*-4-structure for the 158° isomer is to be found in the ultraviolet absorption data. The ultraviolet absorption maxima for the 125° molecular complex (306 mμ; ε 30,400) shows its characteristics to be approximately the mean of those of the 158° (308 mμ; ε 27,700) and the 160° (307 mμ; ε 33,800) isomer. The non-existence of a third isomer with identical absorption characteristics removes the necessity of postulating that one of these is a 4-*cis*-structure which, because it absorbs at the same wavelength as the 4-*trans*-forms, must be coplanar. Models indicate that such a coplanar form for the 4-*cis*-structure is so highly hindered as to be quite improbable. The ultraviolet absorption data for the methyl esters prepared from the acids with diazomethane are consistent with those for the acids. The ester from the 125° complex is a liquid with $\lambda_{max.}$ 310 mμ (ε 32,000), intermediate in intensity and wavelength maximum between the ester, m. p. 36°, from the 160° isomer ($\lambda_{max.}$ 308; ε 37,600) and the ester, m. p. 42°, from the 158° isomer ($\lambda_{max.}$ 312; ε 28,300). There are isosbestic points at 242 and 332 mμ, again evidence that the 125° product is a complex of the other two. One and possibly two isosbestic points at 245 and 328 mμ are to be seen in the ultraviolet absorption data for the acids.[1] The ultraviolet absorption data for the methyl hexa-2 : 4-dienoates also show[20] an isosbestic point in the curves for the *cis*-2 : *trans*-4-, the *cis*-*cis*-, and the

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[18] Corey and Fraenkel, *J. Amer. Chem. Soc.*, 1953, **75**, 1168.
[19] Feist, *Annalen*, 1906, **345**, 79.
[20] Allan, Jones, and Whiting, *J.*, 1955, 1862.

trans-trans-acids which indicates that the supposed *cis*-2 : *trans*-4-acid of m. p. 31—34° is a complex of the *cis-cis*-, m. p. 82°, and the *trans-trans*-acid, m. p. 134°.

It is to be noted that the principal absorption maximum for the *cis*-2 : *trans*-4-ester occurs at significantly longer wavelengths than that for the *trans-trans*-ester. This is the third such sorbic acid type in which such effects have been observed. Methyl *cis*-2 : *cis*-4-sorbate [20] and the *cis*-2 : *trans*-4-dienoate [21] both absorb at longer wavelengths than do their respective *trans-trans*-isomers. *cis*-Crotonic acid also absorbs at a longer wavelength than does the *trans*-isomer. This is true even though the length of the chromophore in the *cis-trans*-isomer (5·45 Å) is less than that of the *trans-trans*-isomer (6·0 Å). These observations indicate that such shifts are not exclusively associated with terminal *cis-trans*-isomers as has been suggested [22] to account for a similar shift in the position of the maximum for terminal *cis*-, as compared with all-*trans*-, vitamin A which does not occur in the related aldehydes in which the *cis*-bond is not the terminal bond of the chromophore.

The infrared absorption spectra for the three substances show few differences and again confirm the existence of a complex. The 125° complex shows absorption maxima at 1490, 976, 933, and 885 cm.$^{-1}$ which are present in the spectrum of the 158° isomer but are not present in that of the 160° isomer, and maxima at 1353 and 916 cm.$^{-1}$ which are present in the spectrum of the 160° isomer but not in that of the 158° isomer. With the exception of the 956 cm.$^{-1}$ maximum in the 160° isomer, there is no significant maximum in the spectra for the 158° and 160° isomers which is not present in the spectrum of the 125° complex and *vice versa*. Some of the principal bands are appreciably shifted. The statement that [1] the 158° isomer shows no absorption in the 962 cm.$^{-1}$ region is perhaps misleading since it shows a very pronounced maximum at 966 cm.$^{-1}$ with a weaker maximum at 976 cm.$^{-1}$. The 160° isomer shows maxima at 963 and 956 cm.$^{-1}$, as previously noted, indicating the presence of a *trans*-ethylenic bond. Finally, the spectra of the 125° complex as isolated and as prepared by recrystallisation of a mixture of its components are identical over the entire range. Minute traces of the component isomers present as impurities in the 125° complex are readily detected by the appearance of a maximum at 1613 cm.$^{-1}$ characteristic of the 160° isomer and an increase in the intensity of the 885 cm.$^{-1}$ band characteristic of the 158° isomer.

This reassignment of the configurations substantiates the suggested re-interpretation [23] of the data for the product obtained from *cis*- and *trans*-β-ionylideneacetaldehyde.[1,2] The product from the *trans*-aldehyde and β-methylgutaconate has, by analogy, the *cis*-2 : *cis*-4 : *trans*-6-structure; that from the *cis*-aldehyde, the *cis*-2 : *cis*-4 : *cis*-6-structure. Decarboxylation with inversion will give the *cis*-2 : *trans*-4 : *trans*-6- and the *cis*-2 : *trans*-4 : *cis*-6-structure respectively. Iodine-isomerisations of these give the previously identified all-*trans*- and *trans*-2 : *trans*-4 : *cis*-6-vitamin A acids. This structural assignment avoids postulating that the decarboxylation of the ionylidene derivatives takes place with simultaneous inversion of the configuration at both 2- and 4-double bonds and that the decarboxylation of other alkylidene and arylidene types takes place without inversion at either double bond. It is true that slightly different reaction conditions are required for the decarboxylation of the arylidene and alkylidene types but no fundamental difference of mechanism is indicated. The inversion is further confirmed by evidence now presented that complete decarboxylation of the dicarboxylic acid gives 3-methyl-1-phenylbutadiene, m. p. 33—35°, which shows a principal ultraviolet maxima at 282 mμ (ε 41,800) corresponding to that at 280 mμ (ε 28,300) for *trans*-1-phenylbutadiene [24] and is probably, therefore, *trans*. The structures previously assigned [2] to *neo*vitamin A as the *cis*-2-isomer and the *cis*-2 : *cis*-6-vitamin A are not changed by this reconsideration of the intermediates from which they have been prepared. The basis for the assignment is, however, clarified.

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[21] Crombie, *J.*, 1955, 1007.
[22] Hubbard, *J. Amer. Chem. Soc.*, 1956, **78**, 4666.
[23] Heilbron and Weedon, *Bull. Soc. chim. France*, 1958, 83.
[24] Braude, Jones, and Stern, *J.*, 1947, 1087.

EXPERIMENTAL

M. p.s were taken in capillary tubes cleaned with chromic–sulphuric acid, washed with distilled water and with acetone, and dried in an oven. They were observed with a calibrated thermometer partially immersed in a stirred oil-bath and may be considered to be corrected. Precision in the reproducibility of the m. p.s of the acids is difficult to obtain since rate of heating is significant particularly with the substituted glutaconic acid which is decarboxylated at its m. p. Mixed m. p.s were run simultaneously with determinations on the separate components.

Reformatsky Reaction of Benzylideneacetone with Ethyl Bromoacetate.—This reaction was repeated by following the detailed directions given previously [1] on a 0·05-molal basis, to give as a first fraction [precipitated from boiling ligroin (b. p. 40—60°)–benzene] 1·4 g. of crystals, m. p. 124—152°, and 2·6 g. of m. p. 124—126°. Recrystallisation of the former from benzene or, preferably, ethanol gave the *trans-trans*-acid, m. p. 159—160°, mixed m. p. 127—135° with a sample of the *cis*-2 : *trans*-4 acid, m. p. 157—158°, obtained by decarboxylation. The molecular complex, purified by recrystallisation from ligroin, or ligroin with 5% of added benzene, had m. p. 125—126°. The relative amounts of the two products vary unpredictably.

Reformatsky Reaction of Benzaldehyde with Ethyl γ-Bromosenecioate.—This reaction was repeated on a 0·14-molal basis by the procedure given previously.[3] The γ-bromosenecioate, n_D^{24} 1·4995, was prepared from ethyl senecioate [25] and *N*-bromosuccinimide. No iodine was added to initiate the reaction. The distilled unsaturated ester (15·14 g.) was separated into eight fractions, b. p. 115°/3 mm. to 166°/1·5 mm. The seventh fraction, b. p. 160—166°/1·5 mm. (2 g.), was treated with saturated alcoholic potassium hydroxide (20 ml.). Acidification of the ether-extracted, diluted reaction mixture precipitated a solid which recrystallised from ethanol at room temperature to give 0·8 g. of product, m. p. 158—158·5°, which gave no depression in m. p. on mixture with a sample of the *cis*-2 : *trans*-4-acid, m. p. 157—158°, obtained by decarboxylation, and melted at 125—145° when mixed with the *trans-trans*-acid, m. p. 156—158°, obtained by the iodine-catalysed rearrangement. Further cooling of the mother-liquors gave second and third fractions of crystals. Recrystallisation of the second fraction (0·1 g.) from benzene–ligroin (b. p. 40—60°) gave crystals, m. p. 124—125°. On admixture with a sample of the molecular complex, m. p. 126—127°, obtained from the Reformatsky reaction with benzylideneacetone, a m. p. of 126—127° was observed.

The infrared absorption spectra for four of the ester fractions showed a pronounced band at 1764 cm.$^{-1}$ indicative of a γ-lactone. The band was most prominent in the seventh fraction used for the hydrolysis and least prominent in the third fraction (2·64 g.), b. p. 148—154°/2 mm. Attempts to isolate a γ-lactone by more careful fractionation were unsuccessful.

Decarboxylation of γ-Benzylidene-β-methylglutaconic Acid.—The *cis*-2 : *trans*-4-acid, m. p. 157—158°, was obtained by following the procedure given previously.[1] The lutidine solution was not evaporated before being poured into dilute aqueous acid to precipitate the crude product. 7·0 g. of γ-benzylidene-β-methylgutaconic acid gave 3·55 g. of the product, m. p. 157—158°, as the first fraction of crystals from ethanol. Recrystallisation from nitromethane gave long needles, m. p. 158—158·5°, mixed m. p. 125—135° with the *trans-trans*-acid, m. p. 156—158°, obtained by the iodine-catalysed isomerisation.

Dipotassium γ-benzylidene-β-methylglutaconate was warmed with glacial acetic acid according to the procedure given previously [6] for the conversion of γ-alkylidene-β-methylglutaconic acids into their δ-lactones. Evaporation of the ether solution of the neutral fraction deposited crystals. Fractionation gave a fraction, b. p. 76—81°/3—5 mm., m. p. 33—35°. The m. p. previously recorded [11] for 3-methyl-1-phenylbutadiene is 37° (Found: C, 90·9; H, 8·5%; *M*, 138·8. Calc. for $C_{11}H_{12}$: C, 91·6; H, 8·4%; *M*, 144·8). The ultraviolet spectrum shows maxima at 218 (ε 17,850), 225 (ε 17,400), 232 (ε 11,300), and 282 mμ (ε 41,800). 1-Phenylbutadiene [24] shows maxima at 223 (ε 12,000), 233 (ε 8500), 271 (ε 28,000), 280 (ε 28,300), 290 (ε 27,000), 305 (ε 6000). The infrared absorption spectrum shows, as the most prominent band, a maximum at 962 cm.$^{-1}$ characteristic of the *trans*-disubstituted ethylenes.

Iodine-catalysed Isomerisations of the cis-2 : trans-4- *and the Molecular Complex to the* trans-2 : trans-4-*Acid.*—Either the *cis*-2 : *trans*-4-acid, m. p. 156—158°, obtained by decarboxylation, or the molecular complex, m. p. 125—126°, when treated with iodine according to the procedure

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[25] The author is indebted to Mr. P. Veeravagu for preparing this compound.

given previously [1] gives as the fraction insoluble in boiling ligroin (b. p. 40—60°) the *trans-trans*-acid, m. p. 156—157°. The mother-liquors from the isomerisation of the *cis*-2 : *trans*-4-acid gave crystals of the molecular complex, m. p. 125—126°.

Phase Diagram.—The data for the phase diagram (Figure) were obtained by the usual procedure.[26] Samples of the *trans-trans*-acid obtained from the iodine-catalysed isomerisation and the *cis-trans*-acid obtained by decarboxylation were used.

Preparation of the Molecular Complex from the Component Acids.—A mixture of equal amounts (0·6005 g.) of the *trans-trans* obtained from the Reformatsky reaction and the *cis*-2 : *trans*-4-acid obtained by decarboxylation were fused together and recrystallised from benzene to give the molecular complex, m. p. 125—126°. The infrared absorption spectrum for this sample of the complex is identical with, and superimposable on, that of the complex, m. p. 125—126°, obtained from the Reformatsky reaction with benzylideneacetone. The complex can also be obtained by recrystallisation, without previous fusion, of equal amounts of these two acids. It is necessary, however, to recrystallise the mixture with care in order to avoid contamination with traces of the components which are readily detected by the appearance of a band at 1613 cm.$^{-1}$ not present in the spectrum of the complex but characteristic of the *trans-trans*-isomer, and by an increase in intensity of the 885 cm.$^{-1}$ band which is more intense in the spectrum for the *cis*-2 : *trans*-4-isomer than it is in that of the complex. With such care the spectra are identical; otherwise they are superimposable over the entire range with the two exceptions stated. By far the most convenient procedure for obtaining crystals of the molecular complex free from excess of either component is to evaporate a benzene solution of a mixture of the components on a watch-glass. The crystals which separate at the periphery of the evaporating solution remain moist with the solution and grow as the evaporation proceeds. The liquid is replenished with additional solution or solvent to keep the growing crystals moist.

*Methyl 3-Methyl-5-phenyl-*cis-2 : trans-4-*pentadienoate.*—An ether solution of 3-methyl-5-phenyl-*cis*-2 : *trans*-4-pentadienoic acid (0·93 g.), m. p. 158°, prepared by the decarboxylation of γ-benzylidene-β-methylglutaconic acid, was treated with a slight excess of diazomethane in ether. The ether solution was washed with dilute aqueous alkali, dried, and evaporated. The residue crystallised on cooling. Trituration twice with cold ligroin (b. p. 40—60°) gave a residue (0·67 g.) of white crystals, m. p. 41·5—42·5°. The m. p. was not raised by recrystallisation from ligroin (Found: C, 77·0, 77·4; H, 7·0, 7·2. $C_{13}H_{14}O_2$ requires C, 77·2; H, 7·0%). $\lambda_{max.}$ were 232 (ε 14,350), 238 (ε 11,500) and 312 mμ (ε 28,300).

*Methyl 3-Methyl-5-phenyl-*trans-2 : trans-4-*pentadienoate.*—This was prepared from the *trans-trans*-acid, m. p. 160°, isolated from the mixture of products obtained in the Reformatsky reaction of benzylideneacetone with ethyl bromoacetate. A solution of the acid (0·45 g.) in ether (15 ml.) treated with ethereal diazomethane gave, after isolation as described for the *cis-trans*-ester, white crystals (0·41 g.), m. p. 35—36°. The m. p. was not raised by recrystallisation from ligroin (Found: C, 77·25, 77·43; H, 7·12, 6·90. $C_{13}H_{14}O_2$ requires C, 77·2; H, 7·0%). $\lambda_{max.}$ were at 308 (ε 37,600), 238 (ε 9900), and 232 mμ (ε 11,900). A mixture of this *ester* with the *cis-trans*-ester liquefied at room temperature.

*Mixture of Methyl 3-Methyl-4-phenyl-*trans-2 : trans-4- *and* cis-2 : trans-4-*pentadienoate.*—This was prepared from the molecular complex, m. p. 125°, isolated from the mixture of products obtained in the Reformatsky reaction of benylideneacetone with ethyl bromoacetate. Prepared and isolated as described for the component ester, a liquid product was obtained. A solution of this in ligroin (b. p. 40—60°), cooled at −78°, precipitated crystals which were separated by decantation. The liquid residue after thorough evacuation was analysed (Found: C, 77·27; H, 7·1. Calc. for $C_{13}H_{14}O_2$: C, 77·2; H, 7·0%) and had $\lambda_{max.}$ 310 (ε 32,000), 238 (ε 10,600), and 232 mμ (ε 13,800).

The infrared absorption spectra of the acids were determined as Nujol mulls, and those of the esters as liquid films, on a Grubb-Parsons DB1 double-beam recording infrared spectrometer with a type S4 monochromator and sodium chloride optics. The author is indebted to Mr. R. L. Erskine for assistance with these observations.

The ultraviolet absorption spectra were determined for ethanol solution in 1 cm. silica cells in a Perkin-Elmer recording ultraviolet spectrometer. The author is indebted to Mrs. A. I. Boston for assistance with these measurements. The carbon and hydrogen determinations were done by the micro-analytical laboratory at the Imperial College.

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[26] Vogel, " A Text-book of Practical Organic Chemistry," Longmans, Green and Co., London, 2nd edn., 1951, p. 28.

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DEPARTMENT OF CHEMISTRY, IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, LONDON, S.W.7.

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