731. *Epimeric Dihydroaromatic Hydrocarbons: Stereospecific Syntheses of* cis- *and* trans-1,2-*Dihydro*-1,2-*dimethylnaphthalenes and* 9,10-*Dihydro*-9,10-*dimethylanthracenes.*

By L. M. Jackman and J. W. Lown.

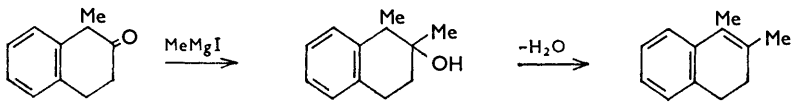
cis- and *trans*-αβ-Dimethylcinnamic acid have been prepared and their configurations established. The acids have been converted by stereospecific reactions into *cis*- and *trans*-1,2-dihydro-1,2-dimethylnaphthalene, respectively.

cis- and *trans*-9,10-Dihydro-9,10-dimethylanthracene have been synthesised by stereospecific routes, and it has been shown that a compound previously believed to be the *trans*-isomer is a mixture containing a compound possessing an ethyl group.

In connection with certain stereochemical studies on the mechanism of the dehydrogenation of hydroaromatic compounds by quinones, epimeric pairs of hydrocarbons were required as hydrogen donors. Suitable systems were 1,2-dihydro-1,2-dimethylnaphthalene and 9,10-dihydro-9,10-dimethylanthracene, and the stereospecific syntheses of these compounds are now described.

cis- *and* trans-1,2-*Dimethyl*-1,2-*dihydronaphthalene.*—Conversion of tetralins and

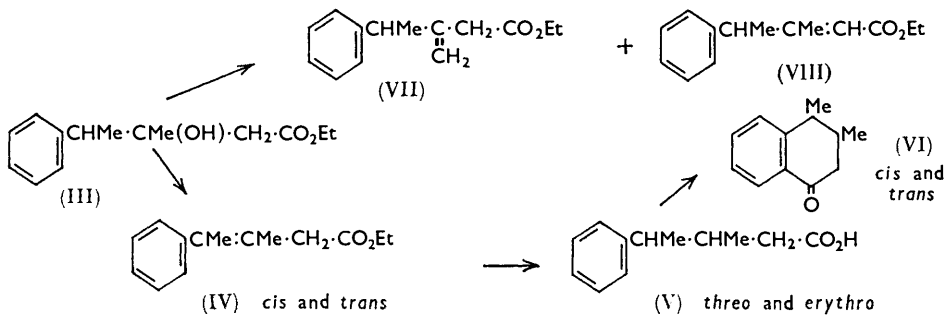
1-tetralones into the corresponding dihydronaphthalenes provides no difficulty,[1] so that the essential problem was the stereospecific synthesis of the epimeric 1,2-dimethyltetralins or 3,4-dimethyltetral-1-ones. The most direct approach to the former involves stereospecific reductions of 3,4-dihydro-1,2-dimethylnaphthalene (II) and this route was first investigated. Hückel and Vevera [2] have described the preparation of 3,4-dihydro-1,2-dimethylnaphthalene by the treatment of naphthalene dianion with methyl iodide. In



(I) (II)

our hands this method gave a complex mixture of hydrocarbons. An alternative synthesis [(I) ⟶ (II)] based on 1-methyltetral-2-one (I) was more satisfactory. Hydrogenation of the dihydronaphthalene (II) over Adams platinum gave *cis*-1,2-dimethyltetralin (see below), but attempts to reduce the double bond under conditions favouring the formation of the *trans*-isomer were unsuccessful.

An alternative approach [(III) ⟶ (VI)] involving the synthesis and stereospecific reduction of one or both geometric isomers of 3-methyl-4-phenylpent-3-enoic acid (IV) was next investigated. The hydroxy-acid (III) was obtained in good yield by a

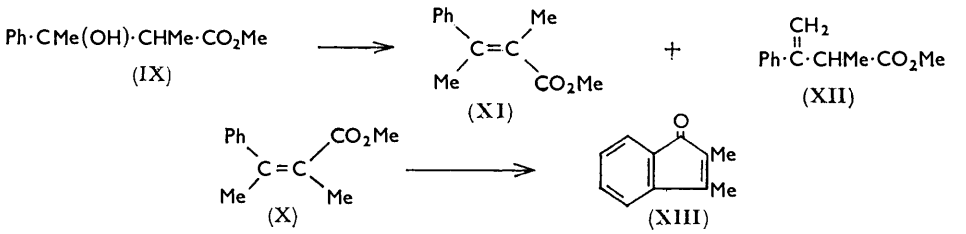


Reformatsky reaction between 3-phenylbutan-2-one and ethyl bromoacetate but its subsequent dehydration yielded a mixture of the methylene ester (VII) and the αβ-unsaturated ester (VIII) from which 3-methyl-4-phenylpent-2-enoic acid was isolated after hydrolysis. Hydrolysis of this mixture of esters and catalytic hydrogenation of the resulting acids gave a mixture of the diastereoisomeric 3-methyl-4-phenylpentanoic acids, cyclisation of which afforded a mixture of the epimeric 3,4-dimethyltetral-1-ones (VI). Fractional crystallisation of the 2,4-dinitrophenylhydrazone of the epimeric mixture of ketones led to the isolation of a pure compound which was subsequently shown to be *cis*-3,4-dimethyltetral-1-one 2,4-dinitrophenylhydrazone.

Attention was next directed towards preparation of *cis*- and *trans*-αβ-dimethylcinnamic acid as precursors for the diastereoisomeric 3-methyl-4-phenylpentanoic acids. The conversion of methyl β-hydroxy-α-methyl-β-phenylbutyrate (IX) into mixtures of the dimethylcinnamic acids has been described by several groups of workers,[3-7] some of whom isolated small quantities of an allegedly pure isomer. In particular Burton and Shoppee [5] obtained an acid, m. p. 112—113°, to which they assigned the *trans*-configuration on the

[1] Jackman and Thompson, *J.*, 1961, 4794.
[2] Hückel and Vevera, *Chem. Ber.*, 1956, **89**, 2105.
[3] Rupe, Steiger, and Fiedler, *Ber.*, 1914, **47**, 65.
[4] von Braun and Nelles, *Ber.*, 1933, **66**, 1464.
[5] Burton and Shoppee, *J.*, 1935, 1160.
[6] Kloetzel, *J. Amer. Chem. Soc.*, 1940, **62**, 1708.
[7] Hauser and Puterbaugh, *J. Amer. Chem. Soc.*, 1953, **75**, 1068.

basis of its melting point. The presence of the *cis*-isomer in the crude mixture was clearly demonstrated by the isolation of 2,3-dimethylinden-1-one from the reaction mixture with concentrated sulphuric acid.[5] However, the second isomer was not isolated in a pure form, nor was the solid acid subjected to treatment with sulphuric acid. We first



examined the dehydration of the methyl ester (IX) with phosphorus oxychloride. The nuclear magnetic resonance spectrum of the product showed the presence of three unsaturated acids in roughly equal proportions. The spectrum further showed that one of these esters was the α-substituted styrene (XII) and that the other two components were the desired cinnamic esters (X) and (XI). A systematic study of the dehydration with a number of reagents was carried out. Many reagents gave the methylene ester in theoretical yield, but it was ultimately established that prolonged treatment of the mixture of esters with iodine in refluxing benzene produced an equilibrium mixture of methyl *cis*- and *trans*-dimethylcinnamate (X) and (XI), and the methylene ester (IX) in the proportions 6 : 3 : 1. Hydrolysis of this mixture yielded a solid from which pure *cis*- and *trans*-dimethylcinnamic acid were isolated. Their melting points are almost identical so that it is not possible to assign configurations to products of previous workers. The configurations of the two acids followed from the fact that the *cis*- but not the *trans*-acid underwent cyclisation to 2,3-dimethylindenone (XIII). Confirmatory evidence was provided by the nuclear magnetic resonance data summarised in Table 1. The absorption of the β-methyl group shows the characteristic shift to lower fields in the spectrum of the isomer in which it is *cis* to the methoxycarbonyl group. The constitution of the methylene acid (XII) follows from its nuclear magnetic resonance spectrum (Table 1) and from its ozonolysis to formaldehyde and propiophenone.

TABLE 1.

Proton magnetic resonance data (τ-values) for the products of the dehydration of methyl β-hydroxy-α-methyl-β-phenylbutyrate.

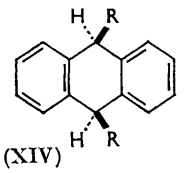
Me ester	Ester-OMe	α-Me	β-Me	Olefinic protons	Aryl protons
(i) *trans*-αβ-Dimethyl cinnamate ...	6·28	8·29	7·75	—	2·86
(ii) *cis*-α,β-Dimethyl cinnamate	6·815	8·05	8·05	—	2·98
(iii) 2-Methyl-3-phenylbut-3-enoate ...	6·35	8·53 *	—	4·58, 4·71	2·80

* Doublet, J = 7 c./sec.; 2-methyl.

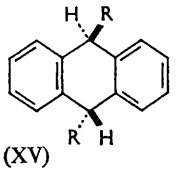
Hydrogenation of the *cis*-acid over palladium black in glacial acetic acid afforded an acid, m. p. 132°.[3] Under the same conditions the *trans*-isomer gave a liquid. However, the nuclear magnetic resonance spectra of the two dihydro-acids indicated that hydrogenation was stereospecific in each case, and we assume the *cis*-addition of hydrogen. Both isomers were homologised by the Arndt–Eistert reaction to the required pentanoic acids (V) which in turn were converted into *cis*- and *trans*-3,4-dimethyltetral-1-one by cyclisation with anhydrous hydrogen fluoride. It is noteworthy that cyclisation of the isomer derived from the *trans*-1,2-dimethylcinnamic acid gave an 80% yield of pure 2,4-dinitrophenylhydrazone of *trans*-3,4-dimethyltetral-1-one, thus confirming the stereochemical purity of the liquid dihydrocinnamic acid.

The epimeric ketones, which were purified through their 2,4-dinitrophenylhydrazones, were converted into the 3,4-dihydro-3,4-dimethylnaphthalenes by reduction and acid-catalysed dehydration.

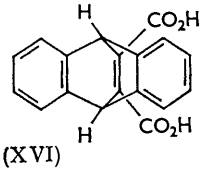
cis- *and* trans-9,10-*Dihydro*-9,10-*dimethylanthracene.*—At the commencement of this study, two ostensibly stereoisomeric compounds had been described [8-12] and assigned configurations on somewhat tenuous evidence. We therefore prepared the two isomers by stereospecific routes from the epimeric 9,10-dihydroanthracene-9,10-dicarboxylic acids (XIV; R = CO_2H) and (XV; R = CO_2H). The configurations of the acids had been established by Mathieu [13] who showed that only one isomer formed a cyclic anhydride.



(XIV)



(XV)



(XVI)

We have further confirmed this assignment by preparing the *cis*-diacid (XIV; R = CO_2H) by low-temperature ozonolysis of the Diels–Alder adduct (XVI) of anthracene and dimethyl acetylenedicarboxylate. Routes to the dimethyldihydroanthracene involved reduction of the dimethyl esters (which incidentally have the same melting point) by lithium aluminium hydride to the corresponding glycols (XIV and XV; R = CH_2·OH) (the *cis*-glycol was also prepared by reduction of the *cis*-anhydride), conversion of the glycols into the ditoluene-*p*-sulphonates, and reduction thereof with lithium aluminium hydride to the hydrocarbons (XIV and XV; R = Me). After this work was complete, Beckett and Lingard [14] described the preparation of the *cis*-hydrocarbon by the same method. They were, however, unsuccessful in obtaining the *trans*-epimer in this way. Our *trans*-9,10-dihydro-9,10-dimethylanthracene (XV; R = Me) had the melting point (101°) reported for one of the hydrocarbons derived from methyl iodide and the dianion of anthracene by the method of Beckett and Lingard, but in fact admixture of the two caused a substantial depression. Examination of the proton magnetic resonance spectrum of the latter hydrocarbon showed that it was a mixture of one of the epimeric 9,10-dihydro-9,10-dimethylanthracenes and another hydrocarbon in approximately equal proportion. The second component of the mixture gave rise to absorption very similar to, but displaced from, the characteristic absorption of the ethyl group in 9-ethyl-9,10-dihydroanthracene. It is possible that this hydrocarbon is 9,10-diethyl-9,10-dihydro- or 9-ethyl-9,10-dihydro-10-methyl-anthracene, the ethyl residues being derived by cleavage of diethyl ether which was used as a solvent. Badger, Goulden, and Warren [8] also obtained a hydrocarbon, m. p. 101°, by this reaction but without the use of ether as a solvent. There seems little doubt that their material is pure *cis*-9,10-dihydro-9,10-dimethylanthracene as they established its identity with a compound, m. p. 101°, obtained by direct reduction of 9,10-dimethylanthracene.

Experimental

Microanalyses were carried out in the Microanalytical Laboratory (Miss J. Cuckney), and ultraviolet and infrared spectra were measured in the Spectrographic Laboratory (Mrs. A. I. Boston and Dr. R. L. Erskine) of this Department. Unless otherwise stated, ultraviolet spectra refer to ethanol solutions. Nuclear magnetic resonance spectra were determined at

[8] Badger, Goulden, and Warren, *J.*, 1945, 18.
[9] Mikhailov, *Bull. Akad. Sci. U.R.S.S.*, 1945, 619.
[10] Mikhailov, *Bull. Akad. Sci., U.R.S.S.*, 1948, 420.
[11] Sisido and Isida, *J. Amer. Chem. Soc.*, 1948, **70**, 1289.
[12] Beckett and Mulley, *J.*, 1955, 4159.
[13] Mathieu, *Ann. Chim. (France)*, 1945, **20**, 2152.
[14] Beckett and Lingard, *J.*, 1959, 2409.

40 or 56·4 Mc./sec. with a Varian spectrometer for ~5% solutions in carbon tetrachloride. The spectra were calibrated by the side-band technique, with a Muirhead-Wigan D-695-A decade oscillator.

cis- *and* trans-1,2-*Dihydro*-1,2-*dimethylnaphthalene*.—1,2-*Dihydro*-3,4-*dimethylnaphthalene*. Methyl bromide (577 g.) was added to a solution of the sodio-derivative of naphthalene [prepared from naphthalene (390 g.) and sodium (150 g.)] in liquid ammonia. Addition of water, extraction with ether, and fractional distillation afforded an oil (82 g.), b. p. 100—105°/14 mm., from which unchanged naphthalene separated on cooling. Examination of the distillate fractions by gas–liquid chromatography showed the product to be a complex mixture of hydrocarbons which could not be separated by distillation. Hückel and Vevera [2] claim yields of 91·5% of 1,2-dihydro-3,4-dimethylnaphthalene.

(*b*) A solution of 1-methyltetral-2-one [15] (12·3 g.) in dry ether (50 ml.) was added dropwise to a stirred solution of methylmagnesium iodide [from methyl iodide (40 g.) and magnesium (0·85 g.) in dry ether (125 ml.)]. The mixture was refluxed for 3½ hr., cooled, treated with aqueous ammonium chloride, and extracted with ether (8 × 50 ml.). The solvent was removed from the dried ($MgSO_4$) extract, and the residual oil distilled from freshly fused potassium hydrogen sulphate (0·8 g.). Treatment of the product with Girard P reagent and refractionation afforded pure 1,2-dihydro-3,4-dimethylnaphthalene (5·97 g., 50%), b. p. 128°/20 mm. to 143°/25 mm., $n_D^{21·5}$ 1·5510—1·5585 (lit.,[16] 114—116°/15 mm., n_D^{20} 1·5763).

1,2-*Dimethyltetralin*. 1,2-Dihydro-3,4-dimethylnaphthalene (2·87 g.) was hydrogenated over Adams platinum catalyst (43 mg.) in ethanol (30 ml.) at 1 atm. Removal of the solvent from the filtered solution, and fractionation of the residual oil afforded 1,2-dimethyltetralin (2·73 g., 94%), b. p. 155—156°/25 mm. (lit.,[17] b. p. 235°/760 mm.).

3,4-*Dimethyltetral*-1-*one*. 1,2-Dimethyltetralin (2·73 g.) was treated with a solution of chromium trioxide (4·4 g.) in acetic acid (16·3 ml.) and water (2·5 ml.). After addition of water, the product was isolated by extraction with ether. Evaporation of the extract afforded an oil which was treated with 2,4-dinitrophenylhydrazine (3·5 g.) in concentrated sulphuric acid (25 ml.) and ethanol (87 ml.). The resulting orange precipitate was collected, washed with water, and dried. Chromatography on kieselguhr–bentonite (1 : 4) followed by fractional crystallisation from ethyl acetate gave cis-3,4-*dimethyltetral*-1-*one* 2,4-*dinitrophenylhydrazone* (0·48 g., 8%), m. p. 220—222° alone or mixed with the derivative (m. p. 219—220°) described below (Found: C, 61·3; H, 5·4; N, 15·9. $C_{18}H_{18}N_4O_4$ requires C, 61·0; H, 5·1; N, 15·8%).

Synthesis of 1,2-*Dihydro*-1,2-*dimethylnaphthalenes from* 3-*Phenylbutan*-2-*one*.—3-*Phenylbutan*-2-*one*. This was prepared in 50% yield by the action of methyl-lithium on α-phenylpropionic acid (cf. Tegner [18]) and had b. p. 89°/110 mm. to 90°/13 mm., $n_D^{22·5}$ 1·5100 (lit.,[18] b. p. 106—107°/22 mm., n_D^{20} 1·5092). α-Methyl-α-phenylpropionic acid (19·3%), m. p. 77°, was obtained as a by-product (lit.,[19] m. p. 80°) (Found: C, 73·5; H, 7·5. Calc. for $C_{10}H_{12}O_2$: C, 73·2; H, 7·3%).

Ethyl β-*hydroxy*-β-*methyl*-γ-*phenylvalerate*. A mixture of 3-phenylbutan-2-one (17·5 g.), ethyl bromoacetate (20 g.), and benzene (50 ml.) was added dropwise with gentle warming to zinc wool (7 g.). The mixture was refluxed with stirring for an hour, cooled, and hydrolysed by addition of ice-cold 20% sulphuric acid (55 ml.). The product was extracted with benzene. Evaporation and fractionation of the residue afforded the *valerate* (11·3 g.), b. p. 166—170°/12 mm., n_D^{23} 1·5090 (Found: C, 71·4; H, 8·5. $C_{14}H_{20}O_3$ requires C, 71·2; H, 8·5%).

Dehydration, etc., of ethyl β-*hydroxy*-β-*methyl*-γ-*phenylvalerate*. The hydroxy-ester (42 g.), benzene (150 ml.), and phosphorus oxychloride (35 g.) were refluxed together for 3½ hr., diluted with water, and extracted with benzene. Evaporation of the extract and fractionation of the residue afforded unsaturated esters (28·6 g., 74%), b. p. 144°/11 mm. to 154°/12 mm., n_D^{23} 1·5130—1·5175, $\nu_{max.}$ 1732 (conjugated ester), (1640 conjugated C=C), 1600 (aromatic), 1772 cm.$^{-1}$ (lactone), $\lambda_{max.}$ 210, 400 mμ (ε 4350, 871) (Found: C, 77·2; H, 8·4%).

This mixture (28·6 g.) was heated under reflux with water (2 ml.) and a solution of sodium ethoxide [from sodium (3·8 g.) in absolute ethanol (70 ml.)] for 3 hr. After removal of the solvent, the residue was dissolved in water and extracted with ether. The aqueous layer was

[15] Cornforth, Cornforth, and Robinson, *J.*, 1942, 689.
[16] Schroeter, Lichtenstadt, and Irineu, *Ber.*, 1918, **51**, 1587.
[17] Roblin, Davidson, and Bogart, *J. Amer. Chem. Soc.*, 1935, **57**, 151.
[18] Tegner, *Acta Chem. Scand.*, 1952, **6**, 782.
[19] Wallach, *Chem. Zentr.*, 1899, II, 1047.

covered with ether (50 ml.), cooled to 0°, and neutralised by 2N-hydrochloric acid with rapid stirring. The aqueous layer was removed and extracted with ether, and the extracts were dried ($MgSO_4$) and evaporated, affording an oil (28·2 g., 77·5%) which on cooling deposited a small quantity of crystals. Repeated recrystallisation of the solid acid from light petroleum (b. p. 40—60°) afforded *3-methyl-4-phenylpent-2-enoic acid*, plates, m. p. 101° (Found: C, 75·6; H,.7·8. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·5%).

Ozonolysis of 3-methyl-4-phenylpent-2-enoic acid. (i) 3-Methyl-4-phenylpent-2-enoic acid (0·8 g.) in glacial acetic acid (50 ml.) was subjected to ozonolysis at room temperature for 4 hr., at a flow rate of *ca.* 0·01 mole of ozone per hour. The mixture was steam-distilled from zinc dust (2 g.). The product was isolated as its 2,4-dinitrophenylhydrazone which was chromatographed on bentonite–kieselguhr (1 : 4), to give acetophenone 2,4-dinitrophenylhydrazone (0·77 g., 63%), m. p. and mixed m. p. 246° (lit.,[20] m. p. 249°, 237°).

(ii) Ozonolysis of 3-methyl-4-phenylpent-2-enoic acid (0·137 g.) in carbon tetrachloride (35 ml.) was carried out at −15° for 3½ hr. The carbon tetrachloride was replaced by acetic acid, and the product worked up as described above, yielding 3-phenylbutan-2-one 2,4-dinitrophenylhydrazone (10 mg., 40%), m. p. and mixed m. p. 167° (lit.,[21] m. p. 171—172°, 141—142°), and acetophenone-2,4-dinitrophenylhydrazone (7 mg., 2·5%), m. p. 239—242°.

β-Methyl-γ-phenylvaleric acid. The mixture of unsaturated acids obtained as above (17 g.) was hydrogenated at 1 atm. in ethanol (60 ml.) over Adams platinum catalyst. The solution was filtered through kieselguhr. Removal of the solvent and fractionation of the residual oil afforded the valeric acid (17 g., 100%), b. p. 174—177°/13 mm., n_D^{22} 1·5153 (lit.,[6] b. p. 124—125°/0·2 mm., 175°/13 mm.).

3,4-Dimethyltetral-1-one. A mixture of β-methyl-γ-phenylvaleric acid (12·43 g.) and anhydrous hydrogen fluoride (30 ml.) was kept in a Polythene vessel for 24 hr. After evaporation, the residue was neutralised with sodium hydroxide and extracted with ether. Evaporation of the dried ($MgSO_4$) extract and distillation of the residue afforded a mixture of *cis-* and *trans-*3,4-dimethyltetral-1-one (11·1 g., 88%), b. p. 153—157°/21 mm. (lit., b. p. 96—97°/0·3 mm.,[6] 142—143/13 mm.[4]). The ketones were converted into their 2,4-dinitrophenylhydrazones (16·6 g., 70·5%), and separation of the epimeric forms was attempted by systematic fractional recrystallisation from nitromethane. Twelve successive recrystallisations afforded (*a*) red plates (2·62 g., 15·7%), m. p. 219—220°, and (*b*) ill-defined crystals (14·2 g., 85%), m. p. 185—187°. Fraction (*b*) is regarded as a eutectic.

Synthesis of cis- *and* trans-*1,2-Dihydro-1,2-dimethylnaphthalene from* cis- *and* trans-*αβ-Dimethylcinnamic Acid.—Methyl β-hydroxy-α-methyl-β-phenylbutyrate.* A mixture of acetophenone (92 g.), methyl α-bromopropionate (124·1 g.), and benzene was added dropwise to zinc wool (60 g.). After 18 hours' refluxing, the mixture was worked up as described for ethyl β-hydroxy-β-methyl-γ-phenylvalerate, to yield *methyl β-hydroxy-α-methyl-β-phenylvalerate* (105·5 g., 69%), b. p. 82°/0·19 mm. to 89°/0·22 mm., $n_D^{18·5}$ 1·5096 (Found: C, 69·4; H, 8·0. $C_{13}H_{18}O_3$ requires C, 70·3; H, 8·1%).

This ester (99·8 g.) and iodine (9·6 g.) in dry benzene (400 ml.) were refluxed for 14 days, then cooled, washed with, successively, saturated sodium hydrogen carbonate solution, aqueous sodium thiosulphate, and water, and dried ($MgSO_4$). Removal of the solvent and fractionation under reduced pressure afforded a mixture of unsaturated esters (66·5 g., 76%), b. p. 71—73°/0·5—0·6 mm., n_D^{20} 1·5335. An estimate of the product composition made from the intensities of the methoxyl bands in the nuclear magnetic resonance spectrum (Table 1) gave *cis*-ester (X) 60%, *trans*-ester (XI) 30%, methylene ester (XII) 10%.

Dehydration of the hydroxy-ester was carried out with a variety of reagents and reaction conditions. Working up was similar to that described above, and the products were analysed by nuclear magnetic resonance spectroscopy. Substantially only the ester (XII) was obtained by use of: P_2O_5 in boiling C_6H_6, 9 hr.; $KHSO_4$ at 150°, 9 or 4 hr.; $H{\cdot}CO_2H$ at 100°, 40 min.; 85% $H{\cdot}CO_2H$, b. p. 7 hr.; $SOCl_2$ in boiling pyridine, 80 min. Boiling $POCl_3$ (9 hr.) gave (X) 30, (XI) 30, (XII) 40%. Ac_2O–AcCl at the b. p. gave (X) 5, (XII) 95%. Iodine (2 mg. per g. of ester) in boiling C_6H_6 had no effect; 100 mg. gave in 3½ days (X) 48, (XI) 22, (XII) 35%, changing to (X) 60%, (XI) 30, (XII) 10% in 7½ or 9½ days.

cis- *and* trans-*αβ-Dimethylcinnamic acid.* Methyl αβ-dimethylcinnamate (70 g.) and potassium

[20] Linstead and Weedon, "A Guide to Qualitative Organic Chemical Analysis" Butterworths, London, 1956.

[21] Takeshima, *J. Sci. Res. Inst.* (*Tokyo*), 1954, **48**, 113.

hydroxide (36 g.) in water (225 ml.), and dioxan (75 ml.) were refluxed for 6 hr., then cooled and extracted with ether, and the aqueous layer was acidified with ice-cold 10N-sulphuric acid. The neutral fraction (5 g., 7%) consisted largely of acetophenone. The precipitated acidic fraction (63·9 g., 93%) slowly solidified. Fractional crystallisation of the mixed acids from light petroleum (b. p. 80—100°) afforded cis- (20·7 g., 30%), m. p. 112—113°, needles (Found: C, 75·1; H, 7·0. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·9%), and trans-αβ-*dimethylcinnamic acid* (2·2 g., 32%), rhombs, m. p. 109—110° (mixed with the *cis*-acid 75—95°) (Found: C, 74·8; H, 6·7%).

The acids were converted by diazomethane into their *methyl esters*, cis-, b. p. 81°/1·5 mm., n_D^{20} 1·5278 (Found: C, 75·5; H, 7·4. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%), and trans-, b. p. 84·5°/1·0 mm., $n_D^{19·5}$ 1·5318 (Found: C, 75·0; H, 7·5%).

Cyclodehydration of cis-αβ-*dimethylcinnamic acid.* The powdered *cis*-acid (50 mg.) was added in portions to concentrated sulphuric acid (1 ml.) at 0°. The deep blue mixture was stirred for 5 min., poured on crushed ice, and extracted with ether. Removal of the solvent afforded a yellow oil (0·4 g.) which on crystallisation from ethanol gave 2,3-dimethylinden-1-one (19 mg., 43%), m. p. 78—79·5° (lit.,[5] m. p. 80°).

Ozonolysis of methyl 2-methyl-3-phenylbut-3-enoate. The unsaturated ester (0·658 g.) produced by dehydration of methyl β-hydroxy-α-methyl-β-phenylvalerate with thionyl chloride and pyridine and consisting largely of the suspected methylene ester was subjected to ozonolysis in acetic acid (45 ml.) at 0° for 55 min. at a flow rate of ozone of *ca.* 0·01 mole/hr. The product was steam-distilled from zinc dust (2·0 g.), the distillate (400 ml.) neutralised with 40% sodium hydroxide solution (70 ml.), and a solution of dimedone (3 g.) in 50% aqueous ethanol (50 ml.) added. The resulting precipitate was collected and recrystallised from ethanol, to yield formaldehyde dimedone derivative (0·68 g., 0·71 mol.), m. p. and mixed m. p. 189—190°. The filtrate from the dimedone treatment was steam-distilled and the distillate treated with 2,4-dinitrophenylhydrazine (2 g.) in ethanol (50 ml.) and concentrated sulphuric acid (20 ml.). Chromatography of the resulting 2,4-dinitrophenylhydrazones in chloroform on kieselguhr–bentonite (1 : 4) afforded acetophenone 2,4-dinitrophenylhydrazone (30 mg.), m. p. 235—237°, mixed m. p. 239—241°, and propiophenone 2,4-dinitrophenylhydrazone (5·0 mg.), m. p. and mixed m. p. 191—193°.

erythro- *and* threo-α-*Methyl*-β-*phenylbutyric acid.* *cis*-αβ-Dimethylcinnamic acid (20 g.) was catalytically hydrogenated at 1 atm. in glacial acetic acid (50 ml.) over palladium black (0·2 g.). Evaporation afforded *erythro*-α-methyl-β-phenylbutyric acid (17·5 g., 87%), m. p. 132—133° (lit., 131—132°,[6] 137—138° [3]), $\lambda_{max.}$ 258 mμ (ε 2670). Similarly, *trans*-αβ-dimethylcinnamic acid (3·94 g.) yielded threo-α-*methyl*-β-*phenylbutyric acid* (3·36 g., 83%), b. p. 120—125°/0·5 mm., $\lambda_{max.}$ 285, 264 mμ (ε 2470, 1900) (Found: C, 74·1; H, 7·9. $C_{11}H_{14}O_2$ requires C, 74·4; H, 7·8%). The nuclear magnetic resonance spectra of the two acids indicated that they were stereochemically pure.

erythro- *and* threo-γ-*Methyl*-γ-*phenylvaleric acid.* Pure *erythro*-α-methyl-β-phenylbutyric acid (4 g.) was converted by the Arndt–Eistert method, as described by Kloetzel,[6] into erythro-β-*methyl*-γ-*phenylvaleric acid* (2·5 g., 15%), b. p. 120°/0·01 mm. (Found: C, 75·1; H, 8·3. $C_{12}H_{16}O_2$ requires C, 74·9; H, 8·5%). Simiarly the pure *threo*-acid (3·36 g.) was converted into threo-β-*methyl*-γ-*phenylvaleric acid* (1·20 g., 30%), b. p. 124—126°/0·01 mm. (Found: C, 74·4; H, 8·5%). A β-methyl-γ-phenylvaleric acid of unknown stereochemistry has been described previously.[4,6]

cis- *and* trans-3,4-*Dimethyltetral*-1-*one* 2,4-*dinitrophenylhydrazone.* *erythro*-α-Methyl-β-phenylbutyric acid (0·1 g.) in anhydrous hydrogen fluoride (8 ml.) was kept in a Polythene container for 24 hr. The reagent was allowed to evaporate, the residue neutralised with potassium hydroxide solution and extracted with ether, and the extract dried ($MgSO_4$). Removal of the solvent afforded *cis*-3,4-dimethyltetral-1-one (0·1 g.). The 2,4-dinitrophenylhydrazone had m. p. 222° alone or mixed with the derivative obtained by another route. Treatment of the 2,4-dinitrophenylhydrazone (2·4 g.) by the method of Demaecker and Martin [22] yielded *cis*-3,4-dimethyltetral-1-one (1·11 g.), b. p. 104—105°/1 mm., n_D^{22} 1·5414. Similarly *threo*-α-methyl-β-phenylbutyric acid (1·2 g.) with anhydrous hydrogen fluoride afforded *trans*-3,4-dimethyltetral-1-one (1·5 g.) which was converted into its 2,4-*dinitrophenylhydrazone* (1·78 g., 80·5%), m. p. 202—204° (mixed with the *cis*-isomer 178—179°) (Found: C, 61·0; H, 4·9; N, 15·8. $C_{18}H_{18}N_4O_4$ requires C, 61·0; H, 5·1; N, 15·8%). Treatment of the 2,4-dinitrophenylhydrazone by the method of Demaecker and Martin [22] afforded pure *trans*-3,4-dimethyltetral-1-one (0·49 g.), b. p. 104°/1 mm., n_D^{26} 1·5455.

[22] Demaecker and Martin, *Nature*, 1954, **173**, 1266.

cis- *and* trans-1,2-*Dihydro*-1,2-*dimethylnaphthalene*. *cis*-3,4-Dimethyltetral-1-one (1·11 g.) in dry ether (25 ml.) was added dropwise to a stirred suspension of lithium aluminium hydride (1·0 g.) in ether (45 ml.). After 10 min., water (3 ml.) and then 2N-sulphuric acid (50 ml.) were added. Evaporation of the dried ($MgSO_4$) organic layer afforded a viscous oil (1·2 g.). The oil was distilled twice from freshly fused and powdered potassium hydrogen sulphate. The distillate, dissolved in light petroleum (b. p. 40—60°), was passed through a column of alumina. Evaporation of the eluate and distillation of the residue afforded cis-1,2-*dihydro*-1,2-*dimethylnaphthalene* (0·42 g., 40%), b. p. 67—70°/1·2 mm., $n_D^{22\cdot5}$ 1·5528—1·5530 (Found: C, 90·9; H, 9·2. $C_{12}H_{14}$ requires C, 91·1; H, 8·9%), $\lambda_{max.}$ 263, 296, 223, 216 mμ (ε 8700, 316, 15,320, 22,000). Similar reduction of *trans*-3,4-dimethyltetral-1-one with lithium aluminium hydride and distillation of the alcohol from fused potassium hydrogen sulphate afforded trans-1,2-*dihydro*-1,2-*dimethylnaphthalene* (0·25 g., 11·2%), b. p. 80°/1 mm. (Found: C, 90·8; H, 9·1%), $\lambda_{max.}$ 264, 297, 223, 216 mμ (ε 9480, 458, 16,410, 22,400).

cis- *and* trans-9,10-*Dihydro*-9,10-*dimethylanthracene*.—cis-9,10-*Dihydroanthracene*-9,10-*dicarboxylic acid*. 9,10-Dihydro-9,10-ethanoanthracene-11,12-dicarboxylic anhydride [23] (0·15 g.) was ozonised in ethyl acetate (30 ml.) at −75°. The solution was extracted with saturated aqueous sodium hydrogen carbonate (4 × 10 ml.). The alkaline extract was acidified with 2N-hydrochloric acid and extracted with ethyl acetate (10 × 10 ml.). Removal of the solvent from the dried ($MgSO_4$) extract afforded a viscous oil (30 mg.) which crystallised from glacial acetic acid, to yield *cis*-9,10-dihydroanthracene-9,10-dicarboxylic acid (8 mg., 5·5%), m. p. 265° (lit.,[12] m. p. 265—266°).

cis- *and* trans-9,10-*Dihydro*-9,10-*bishydroxymethylanthracene*. A slurry of dimethyl *trans*-9,10-dihydroanthracene-9,10-dicarboxylate [prepared from the pure *trans*-diacid [13] (7·5 g.) and diazomethane (*ca.* 5 g.) in ether (200 ml.)] was added to a stirred suspension of lithium aluminium hydride (3 g.) in ether (100 ml.). After 1 hr. water (15 ml.) was added cautiously. 2N-Sulphuric acid (120 ml.) was added and the mixture extracted with ether. Evaporation of the dried ($MgSO_4$) extract afforded a yellow oil (14·3 g.); crystallisation from benzene–light petroleum gave trans-9,10-*dihydro*-9,10-*bishydroxymethylanthracene* as needles, m. p. 107—107·5° (mixed with the *cis*-glycol 97°) (Found: C, 80·3; H, 6·8. $C_{16}H_{16}O_2$ requires C, 80·2; H, 6·7%). Similar reduction of dimethyl *cis*-9,10-dihydroanthracene-9,10-dicarboxylate (0·62 g.) [prepared from the pure *cis*-diacid (1 g.) and diazomethane (*ca.* 0·5 g.)] afforded *cis*-9,10-dihydro-9,10-bishydroxymethylanthracene (0·43 g., 85%), m. p. 164—165° (lit.,[14] 166—168°). Reduction of the *cis*-9,10-dihydroanthracene-9,10-dicarboxylic anhydride yielded the same glycol, m. p. 164—165° (Found: C, 80·1; H, 6·7%).

Treatment of *trans*-9,10-dihydro-9,10-bishydroxymethylanthracene (3 g.) with toluene-*p*-sulphonyl chloride (5·5 g.) in pyridine (22 ml.) at 0° for 5 days yielded the trans-*ditoluene*-p-*sulphonate* (4·42 g., 65%), m. p. 189° (Found: C, 65·7; H, 5·4; S, 11·7. $C_{30}H_{28}O_6S_2$ requires C, 65·7; H, 5·2; S, 11·7%). The *cis*-glycol afforded the *cis*-ester (47%), m. p. 183° (lit.,[14] 177—177·5°) (Found: C, 65·2; H, 5·4%).

cis- *and* trans-9,10-*Dihydro*-9,10-*dimethylanthracene*. The *trans*-ditoluene-*p*-sulphonate (4·0 g.) was extracted with ether from a Soxhlet apparatus into a suspension of lithium aluminium hydride (4·0 g.) in ether (400 ml.) and tetrahydrofuran (36 ml.), and worked up in the usual way to give a white solid (1 g.). Chromatography in hexane on alumina and recrystallisation from methanol gave cis-9,10-*dihydro*-9,10-*dimethylanthracene* (0·75 g., 50%), m. p. 101—101·5° (Found: C, 92·0; H, 8·0. $C_{16}H_{16}$ required C, 92·3; H, 7·7%).

TABLE 2.

Proton magnetic resonance data (τ-values).

	9-Me	9-Et CH_2	9-Et CH_3	9,10-Protons	Aryl protons
cis-9,10-Dihydro-9,10-dimethylanthracene	8·52			6·13	2·90
trans-9,10-Dihydro-9,10-dimethylanthracene	8·50			6·06	2·90
9-Ethyl-9,10-dihydroanthracene	—	9·17	8·41	~6·4	2·91
Molecular compound, m. p. 101—102°	8·48	9·02	8·31	6·3—5·8	2·96
1 : 1 *cis*–*trans*-Mixture	8·53	9·16	8·30	6·3—5·8	2·96

[23] Diels and Alder, *Annalen*, 1931, **486**, 191.

Similar hydrogenolysis of the *cis*-ester (58 mg.) gave pure *cis*-9,10-dihydro-9,10-dimethylanthracene (5·8 mg., 26·5%), m. p. 129—130° (Found: C, 92·1; H, 7·5%).

Reaction of Methyl Iodide and Disodioanthracene.—A suspension of pure anthracene (40 g.) and powdered sodium (20 g.) in dry ether (400 ml.) was shaken for 48 hr. Dry methyl iodide (65 g.) was added to the cooled mixture to decolorise the blue suspension. Evaporation of the filtered mixture and fractionation of the residue gave a colourless oil (8·2 g.) which, crystallised from ethanol (yield 3·08 g., 6·6%), had m. p. 101—102° (lit.,[14] m. p. 101—102°) (mixed with the *trans*-isomer, 9,10-dihydro-9,10-dimethylanthracene, 75—77°). Table 2 summarises the nuclear magnetic resonance data obtained for the *cis*- and *trans*-9,10-dihydro-9,10-dimethylanthracene and related 9-substituted dihydroanthracenes.

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