Amides of Vegetable Origin. Part V. Stereochemistry of Conjugated Dienes.*

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Essentially stereospecific syntheses of the four methyl deca-2 : 4-dienoates are described. This is the first preparation of a compound

$R\cdot CH{=}CH\cdot CH{=}CH\cdot R'$

in all four forms. The four forms of the corresponding acids, *iso*butylamides, *p*-bromophenacyl esters, and *S*-benzylthiuronium salts are also described, together with the deca-2 : 4-dienols obtained by lithium aluminium hydride reduction. *N-iso*Butyldeca-*trans*-2 : *trans*-4-dienamide, a component of pellitorine, is one of the amides prepared. Methyl stillingate, from stillingia oil, is reinvestigated; it is identical with synthetic methyl deca-*trans*-2 : *cis*-4-dienoate.

The steric stability, properties, and physiological action of the compounds are discussed. Their ultra-violet spectra possess characteristic features, and regularities in the infra-red spectra, particularly in the C=C stretching region and the unsaturated C–H out-of-plane deformation region, are observed. An explanation for the spectroscopical results is suggested.

During structural and synthetical investigations of certain natural lipids (aliphatic polyene *iso*butylamides † of plant origin and acids derived from natural fats) at present in progress in these laboratories, the paucity of fundamental information on geometrical isomerism in conjugated systems has hindered progress. An investigation of the systems $\cdot CH{=}CH\cdot CH{=}CH\cdot$ and $\cdot CH{=}CH\cdot CH{=}CH\cdot CO_2R$ is described in this communication. The four theoretically possible stereoisomers were prepared by methods which are largely or entirely stereospecific and are believed to be generally applicable to compounds of a similar type. The geometrical isomers have been examined in the hope of finding satisfactory methods for diagnosis of configuration in stereochemically unknown systems and some progress has been made, particularly by spectroscopical methods.

In Parts I and II (Crombie, *J.*, 1952, 2997, 4338), *trans*-2 : *trans*-6-, *trans*-2 : *cis*-6- and *cis*-2 : *trans*-6-stereoisomers of the amide (I), together with *trans*-2 : *trans*-8- and *cis*-2 : *trans*-8-stereoisomers of (II) were prepared. The remaining stereoisomers of these amides were already known, so these have become the first two cases in which, for a structure of the non-conjugated type (III; R ≠ R′), all four isomers are available.

(I) $Me\cdot[CH_2]_2\cdot CH{=}CH\cdot CH_2\cdot CH_2\cdot CH{=}CH\cdot CO\cdot NHBu^i$

(II) $Me\cdot[CH_2]_2\cdot CH{=}CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH{=}CH\cdot CO\cdot NHBu^i$

(III) $R\cdot CH{=}CH\cdot[CH_2]_n\cdot CH{=}CH\cdot R'$

$R\cdot CH{=}CH\cdot CH{=}CH\cdot R'$ (IV)

$Me\cdot[CH_2]_4\cdot CH{=}CH\cdot CH{=}CH\cdot CO_2H$ (V)

$Me\cdot[CH_2]_4\cdot CH{=}CH\cdot CH{=}CH\cdot CH_2\cdot OH$ (VI)

The three theoretically possible isomers of the conjugated system (IV; R = R′) are known for 1 : 4-diphenylbutadiene (for references see Pinckard, Wille, and Zechmeister, *J. Amer. Chem. Soc.*, 1948, **70**, 1938) and muconic acid (Elvidge, Linstead, Sims, and Orkin, *J.*, 1950, 2235; cf. also αα′-dimethylmuconic acid, Elvidge, Linstead, and Smith, *J.*, 1952, 1026). However, for the general type (IV; R ≠ R′) the four theoretically possible geometrical isomers have not hitherto been synthesised. In the case of sorbic acid, only two isomers (*trans*-2 : *trans*-4 and *cis*-2 : *trans*-4) are known * (Eisner, Elvidge, and Linstead, *J.*, 1953, 1372). Syntheses of three of the stereoisomers of piperic acid are claimed (Ott and Eichler, *Ber.*, 1922, **55**, 2653; Lohaus, *J. pr. Chem.*, 1928, **119**, 235;

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* Part IV, preceding paper.

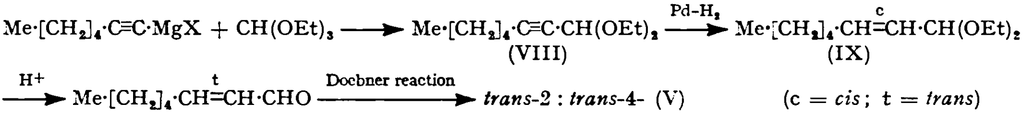
† Little attention has been paid to the classification of this group of amides but occasional references are to be found in treatises on the alkaloids (*e.g.*, Winterstein and Trier, "Die Alkaloide," Borntraeger, 1931, p. 159; Henry, "The Plant Alkaloids," Churchill, 1942, p. 2; Manske and Holmes, "The Alkaloids," Academic Press, 1950, Vol. I, p. 171). They have no basic properties and are more satisfactorily considered in the lipid group.

Annalen, 1934, **513**, 219; 1936, **525**, 312; Lohaus and Gall, *ibid.*, 1935, **517**, 278) but re-investigation of some aspects of this subject seems desirable.

The compounds of type (IV; $R \neq R'$) selected for detailed examination in the present investigation are the deca-2 : 4-dienoic acids (V) and related compounds (methyl esters, *iso*butylamides, and standard crystalline derivatives). In addition the four stereoisomers of the deca-2 : 4-dienols have been prepared and examined. This choice was made because a number of natural *iso*butylamides have the structural feature $\cdot CH_2\cdot CH{=}CH\cdot CH{=}CH\cdot CO\cdot NHBu^i$ or $R\cdot CH{=}CH\cdot CH{=}CH\cdot CH_2\cdot$, *e.g.*, anacyclin (preceding paper), the sanshoöls (Aihara, *J. Pharm. Soc. Japan*, 1950, **70**, 43, 47), and affinin (Acree, Jacobson, and Haller, *J. Org. Chem.*, 1945, **10**, 236, 449; 1947, **12**, 731). A major component of the pellitorine complex (preceding paper) is *N*-*iso*butyldeca-*trans*-2 : *trans*-4-dienamide and its synthesis is described below. During the investigation, a stereospecific synthesis of stillingic acid, which occurs as a glyceride in stillingia oil, was effected.

*Synthesis of the Stereoisomeric Deca-*2 : 4*-dienoic Acids and Deca-*2 : 4*-dienols.*—At the outset of this investigation none of the deca-2 : 4-dienoic acids or their derivatives had been prepared. In connection with the nature of pellitorine, an interim account of the *trans*-2 : *trans*-4-acid and its *iso*butylamide was given (Crombie, *Chem. and Ind.*, 1952, 1034). A synthesis of this compound by a slightly different route has been reported by Jacobson (*J. Amer. Chem. Soc.*, 1953, **75**, 2584).

*Deca-*trans-2 : trans-4*-dienoic acid.* This was prepared from hept-1-yne. Heptynylmagnesium bromide was converted into 1 : 1-diethoxyoct-2-yne (VIII) by treatment with ethyl orthoformate. Semihydrogenation with palladium–calcium carbonate or –barium sulphate (palladium–charcoal is less selective) gave 1 : 1-diethoxyoct-2-ene (IX; presumably *cis*) which on acidic hydrolysis gave *trans*-oct-2-enal. The complete stereochemical inversion is induced by the acidic conditions (Raphael and Sondheimer, *J.*, 1951, 2693; Crombie, Harper, and Thompson, *J.*, 1951, 2906; Crombie and Tayler, unpublished work). *trans*-Octenal had the expected light absorption, gave a 2 : 4-dinitrophenylhydrazone, and when condensed with malonic acid in the presence of pyridine yielded deca-*trans*-2 : *trans*-4-dienoic acid. (For evidence that a *trans*-linkage is formed under Doebner conditions see Crombie, *Quart. Reviews*, 1952, **6**, 101, and Part I.) It was characterised, as were the other stereoisomers described below, by its *p*-bromophenacyl ester and *S*-benzylthiuronium salt. Spectroscopical and other data are discussed later.



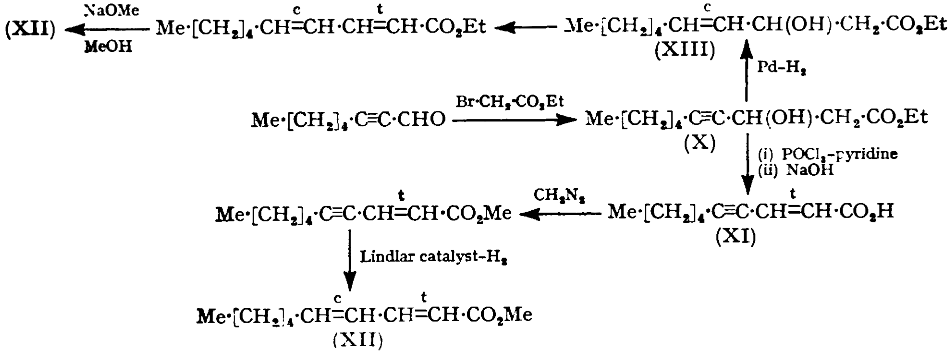
$$\mathrm{Me{\cdot}[CH_2]_4{\cdot}C{\equiv}C{\cdot}MgX + CH(OEt)_3 \longrightarrow \underset{(VIII)}{Me{\cdot}[CH_2]_4{\cdot}C{\equiv}C{\cdot}CH(OEt)_2} \xrightarrow{Pd\text{-}H_2} \underset{(IX)}{Me{\cdot}[CH_2]_4{\cdot}CH\overset{c}{=}CH{\cdot}CH(OEt)_2}}$$

$$\mathrm{\xrightarrow{H^+} Me{\cdot}[CH_2]_4{\cdot}CH\overset{t}{=}CH{\cdot}CHO \xrightarrow{Doebner\ reaction} \mathit{trans}\text{-}2 : \mathit{trans}\text{-}4\text{-}\ (V) \qquad (c = \mathit{cis};\ t = \mathit{trans})}$$

*Deca-*trans-2 : cis*-dienoic acid.* A Reformatski reaction between oct-2-ynal [derived from (VIII) above] and ethyl bromoacetate is the basis of the preparation. This is the first instance of such a reaction involving an αβ-acetylenic aldehyde (cf. Shriner, " Organic Reactions," Wiley, Vol. I, 1942, p. 1). At first the preparation was conducted in benzene with activated zinc dust, but the reaction sometimes had a long induction period and then proceeded with violence. In tetrahydrofuran, with etched zinc wool, the reaction was smooth and easily controlled. Initially, difficulty was encountered in the dehydration (X) ⟶ (XI). Treatment with potassium hydrogen sulphate or toluene-*p*-sulphonic acid gave products with ultra-violet absorption of much longer wavelength than was expected, even under conditions which effected only partial dehydration. This seems to be due to isomerisation, during the reaction, to a triene. The difficulty was overcome by use of phosphorus oxychloride–pyridine (Isler *et al.*, *Helv. Chim. Acta*, 1949, **32**, 489; Hamlet, Henbest, and Jones, *J.*, 1951, 2652) and pure enyne ester was obtained in good yield : no extraneous long-wavelength absorption was detected. Hydrolysis and crystallisations gave pure enynoic acid. Subsequent hydrogenation was carried out on methyl ester derived from this, and not on ester isolated directly from the dehydration because this last step is not necessarily stereospecific (although no evidence to the contrary was observed).

• Professor E. R. H. Jones, F.R.S., and Dr. M. C. Whiting have recently informed the author that they have now synthesised the two remaining stereoisomers (personal communication).

The pure enyne ester showed strong absorption at 961 cm.$^{-1}$, confirming the expected *trans*-2-configuration. Attempts to prepare deca-*trans*-2-en-4-ynoic acid by Doebner reaction with oct-2-ynal gave only black tars.



When methyl deca-*trans*-2-en-4-ynoate is shaken with hydrogen in presence of lead-poisoned palladium–calcium carbonate and quinoline (Lindlar, *Helv. Chim. Acta*, 1952, **35**, 446), absorption does not cease when only 1 mol. of hydrogen is absorbed. But if the process is artificially interrupted at this point, or a little earlier, methyl deca-*trans*-2 : *cis*-4-dienoate can be isolated in reasonable yield. The hydrogenation is stereospecific as far as can be judged by infra-red spectroscopy, but total selectivity (*i.e.*, hydrogenation of triple to double bond only) is not entirely achieved. Small amounts of more saturated and unchanged enyne esters need to be removed by distillation. Hydrolysis of purified ester gave the *trans*-2 : *cis*-4-acid.

An alternative synthesis involved semihydrogenation of the hydroxy-ester (X) to the *cis*-ethylene (XIII), followed by dehydration with phosphorus oxychloride–pyridine, and ester interchange to give methyl deca-2 : 4-dienoate. Infra-red examination showed that the product was the expected *trans*-2 : *cis*-4-compound considerably contaminated with the *trans*-2 : *trans*-4-stereoisomer. This was confirmed by hydrolysis and preparation of derivatives. The *p*-bromophenacyl ester when fractionally crystallised yielded pure *trans*-*trans*-material as the least soluble component, whereas the *S*-benzylthiuronium salt gave, after repeated crystallisations, pure deca-*trans*-2 : *cis*-4-dienoic acid derivative. It is likely that the *trans*-*trans*-impurity arises by stereomutation during the dehydration stage.

Deca-cis-2 : trans-4-*dienoic acid*. Synthesis of this isomer involved non-1-yn-4-ol (XIV) which was prepared both by interaction of propargylmagnesium bromide with hexanal (Prevost, Gaudemar, and Honiberg, *Compt. rend.*, 1950, **230**, 1186; Gaudemar, *ibid.*, 1951, **233**, 64) and, better, by a Reformatski reaction between propargyl bromide and hexaldehyde (Zeile and Meyer, *Ber.*, 1942, **75**, 356; Henbest, Jones, and Walls, *J.*, 1949, 2696). 4-Hydroxynon-1-yne was converted into its tetrahydropyranyl ether, largely to increase solubility of the acetylenic Grignard reagent formed in the next step. If this was not done and the hydroxyl allowed to form a BrMg·O· derivative, poor yields ensued on carboxylation. After carboxylation, the product was heated with methanolic sulphuric acid to esterify and remove the tetrahydropyranyl residue.

Attempts to dehydrate the acetylenic hydroxy-ester (XV) by phosphorus oxychloride–pyridine were discouraging. At room temperature a chloro-derivative was obtained and on heating extensive decomposition set in. The pure ethylenic hydroxy-ester (XVI) was therefore refluxed in acid solution to give dec-2-eno-5-lactone (XVII).* On treatment with sodium methoxide in methanol for 1 hr. at 25°, according to a method used to make *cis*-2 : *trans*-4-sorbic acid (Eisner, Elvidge, and Linstead, *loc. cit.*), this lactone yielded sodium deca-*cis*-2 : *trans*-4-dienoate by stereospecific ring opening.

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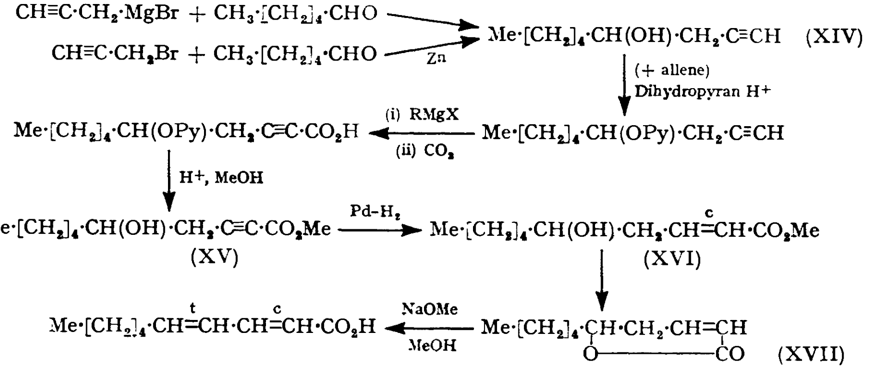
* This is the (±)-form of the structure proposed for massoialactone from *Cryptocarya massoia* bark oil (Meijer, *Rec. Trav. chim.*, 1940, **59**, 191) and recently confirmed by Abe and Sato (*Chem. Abs.*, 1954, 14126). Direct comparison with a natural specimen has not yet been possible.

Deca-cis-2 : cis-*4-dienoic acid.* As there is no established method for the synthesis of *cis-cis*-stereoisomers of this type, semihydrogenation of methyl deca-2 : 4-diynoate was examined. Semireductions of diynes have been attempted before, though the results have not been very encouraging from the point of view of either stereospecificity or selectivity. Information in the literature relates largely to symmetrical diacetylenes. Thus, diphenyldiacetylene gives, on catalytic semihydrogenation in the presence of palladium–barium sulphate in ethanol, a mixture of the three possible geometrical isomers together with products of non-selective additions. The *cis-cis*-isomer can be isolated by crystallisation or chromatography (Pinckard, Wille, and Zechmeister, *loc. cit.*; Ott and Schröter, *Ber.*, 1927, **60**, 624; Kelber and Schwarz, *Ber.*, 1912, **45**, 1946; Strauss, *Annalen*, 1905, **342**, 190). Other symmetrical diacetylenes generally give poor results (Kuhn and Wallenfels, *Ber.*, 1938, **71**, 1889; Sargent, Thesis, London, 1948; Salkind and Gverdsiteli, *J. Gen. Chem. U.S.S.R.*, 1939, **9**, 971; *Chem. Abs.*, 1939, **33**, 8569). Riley (*J.*, 1953, 2193) recently reported that docosa-10 : 12-diynedioate gives only insignificant amounts of conjugated diene at any stage during its reaction with hydrogen in the presence of Raney nickel. On the other hand, Anet, Lythgoe, Silk, and Trippett (*J.*, 1953, 309) obtained significant increases in light absorption when oenanthotoxin (a conjugated enediynediene) absorbs 2 mols. of hydrogen in the presence of Lindlar catalyst. The products could not be isolated.



$$CH{\equiv}C\cdot CH_2\cdot MgBr + CH_3\cdot[CH_2]_4\cdot CHO \longrightarrow Me\cdot[CH_2]_4\cdot CH(OH)\cdot CH_2\cdot C{\equiv}CH \quad (XIV)$$

$$CH{\equiv}C\cdot CH_2Br + CH_3\cdot[CH_2]_4\cdot CHO \xrightarrow[Zn]{} Me\cdot[CH_2]_4\cdot CH(OH)\cdot CH_2\cdot C{\equiv}CH \quad (XIV)$$

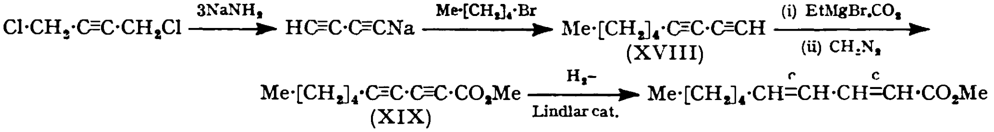
$$(XIV) \xrightarrow[\text{Dihydropyran } H^+]{(+\text{ allene})} Me\cdot[CH_2]_4\cdot CH(OPy)\cdot CH_2\cdot C{\equiv}CH \xrightarrow[\text{(ii) } CO_2]{\text{(i) } RMgX} Me\cdot[CH_2]_4\cdot CH(OPy)\cdot CH_2\cdot C{\equiv}C\cdot CO_2H$$

$$\xrightarrow{H^+,\ MeOH} \underset{(XV)}{Me\cdot[CH_2]_4\cdot CH(OH)\cdot CH_2\cdot C{\equiv}C\cdot CO_2Me} \xrightarrow{Pd\text{-}H_2} \underset{(XVI)}{Me\cdot[CH_2]_4\cdot CH(OH)\cdot CH_2\cdot CH\overset{c}{=}CH\cdot CO_2Me}$$

$$\longrightarrow Me\cdot[CH_2]_4\cdot \underset{O\text{———————}CO}{CH\cdot CH_2\cdot CH{=}CH} \quad (XVII) \xrightarrow[MeOH]{NaOMe} Me\cdot[CH_2]_4\cdot CH\overset{t}{=}CH\cdot CH\overset{c}{=}CH\cdot CO_2H$$

(Py = tetrahydro-2-pyranyl; c = *cis*; t = *trans*)

In the present case methyl deca-2 : 4-diynoate was shaken with Lindlar catalyst and quinoline in ethyl acetate. When 2 mols. of hydrogen had been absorbed (absorption showed no signs of ceasing), the reaction was interrupted and the product worked up and distilled. Examination of refractive index, ultra-violet light absorption, and microhydrogenation data of the series of fractions showed that reaction, as in the case of the enyne, was not entirely selective. Even with an allowed absorption of 1·8 mol., some ester, more saturated than diene, was isolated in the fore-runs. Nevertheless, ultra-violet light absorption shows that the major product is the diene ester, and the contaminants can be largely removed by careful distillation since acetylenic ester becomes concentrated in the later fractions and " saturated " material in the earlier. On hydrolysis, the purified ester gave a liquid acid which yielded pure crystalline derivatives, different from those of the other three acids. Spectroscopical data confirm that this is the fourth deca-2 : 4-dienoic acid (see below) and the hydrogenation is usefully stereospecific as judged from the infra-red data. The ester may still contain a little impurity.



$$Cl\cdot CH_2\cdot C{\equiv}C\cdot CH_2Cl \xrightarrow{3NaNH_2} HC{\equiv}C\cdot C{\equiv}CNa \xrightarrow{Me\cdot[CH_2]_4\cdot Br} \underset{(XVIII)}{Me\cdot[CH_2]_4\cdot C{\equiv}C\cdot C{\equiv}CH} \xrightarrow[\text{(ii) } CH_2N_2]{\text{(i) } EtMgBr,CO_2}$$

$$\underset{(XIX)}{Me\cdot[CH_2]_4\cdot C{\equiv}C\cdot C{\equiv}C\cdot CO_2Me} \xrightarrow[\text{Lindlar cat.}]{H_2\text{-}} Me\cdot[CH_2]_4\cdot CH\overset{c}{=}CH\cdot CH\overset{c}{=}CH\cdot CO_2Me$$

Methyl deca-2 : 4-diynoate (XIX), needed as the intermediate, was prepared as shown from nona-1 : 3-diyne, itself synthesised according to a general method (Armitage, Jones, and Whiting, *J.*, 1951, 44). Diynes of this type can be readily carboxylated as their

Grignard complexes in the usual way (personal communication, Dr. M. C. Whiting) and deca-2 : 4-diynoic acid was obtained crystalline. After the preparation had been completed, Skattebol and Sörensen (*Acta Chem. Scand.*, 1953, **7**, 1388) reported the diyne acid and its methyl ester. Their preparative method was similar to ours.

Incidentally, opportunity was taken to compare some aspects of the infra-red and ultra-violet light absorption data of oct-2-ynal, oct-*trans*-2-enal, and octanal (Table 1). The lower carbonyl-stretching frequency of an αβ-unsaturated, compared with a saturated aldehyde is well known, but the still further decrease on conjugation with an acetylene linkage does not seem to have been recorded. Data for the 2 : 4-dinitrophenylhydrazones are consistent with values in the literature for the general classes to which they belong. The ultra-violet light absorptions for aldehydes were measured in hexane to avoid hemi-acetal formation (Ashdown and Kletz, *J.*, 1948, 1454) : previous values for the extinction coefficients of αβ-acetylenic aldehydes in ethanol solution may be low for this reason (Lunt and Sondheimer, *J.*, 1950, 3361).

TABLE 1.

	Aldehyde			2 : 4-Dinitrophenylhydrazone		
	C=O (cm.$^{-1}$)	$\lambda_{max.}$ (mμ) [a]	ε	M. p.	$\lambda_{max.}$ (mμ) [b]	ε
$CH_3\cdot[CH_2]_4\cdot C{\equiv}C\cdot CHO$ [c]	1674	227	8000	80°	365	25,500
$CH_3\cdot[CH_2]_4\cdot CH\overset{t}{=}CH\cdot CHO$	1695	[e] 225, 320	[d] 9000, 27	128	374	29,000
$CH_3\cdot[CH_2]_6\cdot CHO$	1732	295	13	106	359	14,500

[a] In hexane. [b] In $CHCl_3$. [c] Lunt and Sondheimer (*loc. cit.*) give $\lambda_{max.}$ 227 mμ (ε 3200) for hept-2-ynal and $\lambda_{max.}$ 363 mμ (ε 25,000) for tetrolaldehyde 2 : 4-dinitrophenylhydrazone. [d] Other αβ-ethylenic aldehydes prepared in related work had $\lambda_{max.}$ 218 mμ (ε ~11,000). [e] Inflexion.

Deca-2 : 4-dienols. The four possible stereoisomers were prepared, in good yields, by lithium aluminium hydride reduction of the corresponding methyl decadienoates. Three of these were characterised as α-naphthylurethanes (Table 5).

Synthesis and Stereochemistry of Stillingic Acid.—Stillingia oil (from the seeds of *Sapium sebiferum* Roxb.) contains, as a mixed glyceride, a fatty acid with an unusually short chain (Hilditch, *J. Oil Col. Chem. Ass.*, 1949, **32**, 18; Crossley and Hilditch, *J.*, 1949, 3353). Crossley and Hilditch showed it to be an *n*-deca-2 : 4-dienoic acid as it yielded *n*-decanoic acid on hydrogenation, was oxidised to *n*-hexanoic acid by permanganate, and had its light-absorption maximum in the expected position. As they were not able to obtain satisfactory analytical data for either the liquid acid or its methyl ester and no crystalline derivatives were reported, a re-examination was undertaken.

Methyl stillingate was obtained in 3·0% yield from commercial stillingia oil. It gave excellent analytical figures for $C_{11}H_{18}O_2$ and even after storage at 0° for 12 months in a stoppered vessel the majority could be recovered pure by distillation. The acid was much less stable and gave persistently low analyses for carbon. It was characterised as the *S*-benzylthiuronium salt and *p*-bromophenacyl ester : the former was stable at 0° but the latter became resinous in a few days (after 6 hr. in air at 25° its m. p. fell by 5°). Comparison of these derivatives with those from the four stereoisomeric deca-2 : 4-dienoic acids showed that stillingic acid is deca-*trans*-2 : *cis*-4-dienoic acid (Table 2); and the infra-red spectra of the two methyl esters were identical. As methyl stillingate is readily available from natural sources, good supplies of a *trans*-2 : *cis*-4-dienoic acid and dienol are easily obtainable. The data in Tables 3—9 relate to naturally derived *trans*-2 : *cis*-4-compounds.

TABLE 2. *Identification of the stereochemistry of stillingic acid.*

	Me ester				*p*-Bromophenacyl ester			*S*-Benzyl-thiuronium salt
	B. p./mm.	n_D (20°)	$\lambda_{max.}$ (mμ)	ε	M. p.	$\lambda_{max.}$ (mμ)	ε	M. p.
Stillingic acid ...	72°/0·15	1·4884	264	22,000	71°	263	38,000	135—136°
Deca-*trans*-2 : *cis*-4-dienoic acid	75°/0·1	1·4854	265	21,000	71	263	37,500	137—138

Properties of the Deca-2 : 4-dienoic Acids, Deca-2 : 4-dienols, and Their Derivatives.—The skeleton of all four methyl deca-2 : 4-dienoates was established by hydrogenation to methyl decanoate which was identified as the *p*-bromophenacyl ester. On microhydrogenation 2 mols. of hydrogen were absorbed: light absorption data confirmed the sorbic chromophore (though the intensity fluctuations have stereochemical significance). The gross structure is thus established for each. Data on derivatives, and infra-red spectra, show without doubt that the four compounds are different homogeneous individuals. This in itself provides strong evidence that the reactions chosen in the four syntheses have led to the predicted stereoisomers. Only the *trans-trans*-isomer (as *N*-*iso*butylamide) forms an adduct with maleic anhydride under mild conditions, as expected from other recorded observations (for a summary see Crombie, *Quart. Reviews, loc. cit.*).

Steric stability. All of the stereoisomers show considerable resistance to stereomutation. Thus although thermal treatment (160—180° for 45 min.) led to some decomposition of the *cis*-2 : *cis*-4- and the *cis*-2 : *trans*-4- (and to a lesser extent the *trans*-2 : *cis*-4-)methyl ester, no stereomutation was detected by infra-red methods. Similarly, iodine-catalysed irradiation with ultra-violet light for 8 hr. caused no change. The esters were not isomerised by boiling dilute alcoholic potassium hydroxide, and no particular sensitivity to dilute mineral acid was noticed. Preparation of the four *iso*butylamides involved treatment with oxalyl chloride with liberation of hydrogen chloride, but again four different (infra-red spectra), and apparently pure, derivatives having the expected properties were obtained. Reduction of the methyl decadienoates with lithium aluminium hydride also caused no inversion (derivatives and infra-red spectra).

TABLE 3. *Stereoisomeric methyl deca-2 : 4-dienoates.*

	B. p./mm.	n_D	d_4	R_D (obs.)	Exaltation [a]	Unsatn. [b]	$\lambda_{max.}$ (mμ) [c]	ε
trans-2 : *trans*-4	69—70°/0·25	1·4918 (22°)	0·9082 (22°)	58·21	4·49	2·0	260	28,500
trans-2 : *cis*-4...	71°/0·15	1·4874 (22°)	0·9128 (22°)	57·47	3·75	2·0	265	22,000
cis-2 : *trans*-4...	73°/0·35	1·4876 (23°)	0·9131 (23°)	57·47	3·75	1·9	263	23,800
cis-2 : *cis*-4 ...	74°/0·4	1·4830 (23°)	0·9095 (23°)	57·24	3·52	2·0	263	17,300

[a] Calc. mol. refractivity, 53·72 (data from Gilman, " Organic Chemistry," Wiley, 1943, Vol. II, p. 1751). [b] No. of double bonds, determined by microhydrogenation. [c] Unicam photoelectric instrument.

TABLE 4. *Derivatives of stereoisomeric deca-2 : 4-dienoic acids.*

	S-Benzylthiuronium salt.	*p*-Bromophenacyl esters					*N*-*iso*Butylamides			
	M. p.	M. p.	$\lambda_{max.}$ (mμ) [a]	ε	$\lambda_{max.}$ (mμ) [b]	ε	B. p./mm.	n_D (temp.)	$\lambda_{max.}$ (mμ) [c]	ε
trans-2 : *trans*-4	175°	125°	263	52,200	268	39,500	(M. p. 90°)	—	258	29,500
trans-2 : *cis*-4...	136	72	264	43,000	272	33,800	142°/0·1	1·5062 (20°)	258	26,000
cis-2 : *trans*-4...	129	82	263	39,200	270	27,500	130°/0·07	1·5088 (19°)	259	23,500
cis-2 : *cis*-4 ...	141	82	263	35,300	270	24,300	140°/0·3	1·4985 (13°)	258	17,500

[a] Unicam instrument. [b] Calc. by subtraction of the absorption curve of the *p*-bromophenacyl ester of decanoic acid [$\lambda_{max.}$ 256 mμ, ε 19,700] from that of the appropriate stereoisomer. [c] Hilger medium quartz instrument.

TABLE 5. *Stereoisomeric deca-2 : 4-dienols.*

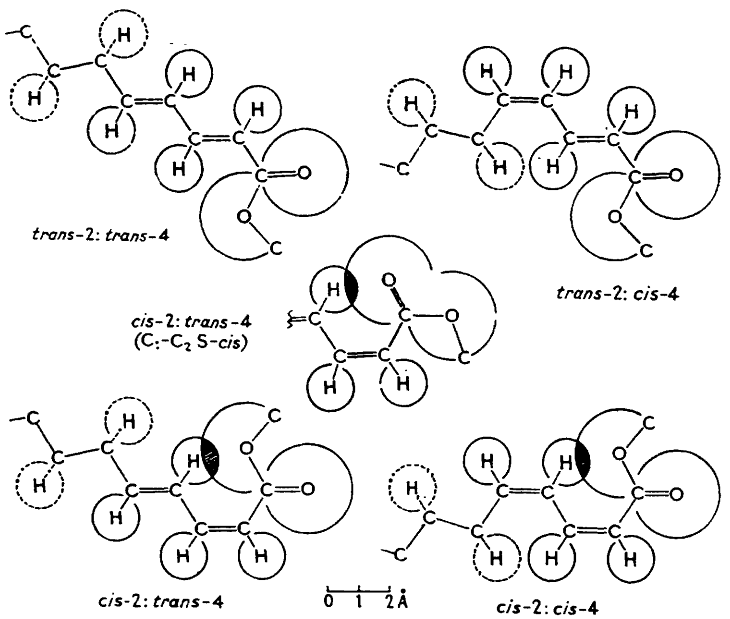
	B. p./mm.	n_D	d_4	R_D (obs.)	Exaltation [a]	$\lambda_{max.}$ (mμ) [b]	ε	α-Naphthylurethane. M. p.
trans-2 : *trans*-4	84°/0·5	1·4857 (23°)	0·8608 (23°)	51·42	2·44	230	30,600	95°
trans-2 : *cis*-4...	86°/0·6	1·4870 (23°)	0·8666 (23°)	51·21	2·23	232	22,100	61
cis-2 : *trans*-4...	84°/0·6	1·4892 (21°)	0·8672 (21°)	51·35	2·37	232	24,000	Gum
cis-2 : *cis*-4 ...	87°/0·6	1·4852 (22°)	0·8690 (22°)	50·88	1·90	233	20,000	71

[a] Calc. mol. refractivity (Gilman, *op. cit.*), 48·98. [b] Unicam instrument.

Physiological properties. The stereoisomeric methyl deca-2 : 4-dienoates have very similar odours though, when familiarity is gained, it is possible to distinguish between them. Similar remarks apply to the decadienols, but identification is less easy in this case. Of the four *N-iso*butylamides, only the *trans*-2 : *trans*-4-compound has considerable sialogogue activity, but it is not as powerful as *neo*herculin or *N-iso*butyl-*trans*-2 : *trans*-4-*cis*-8 : *cis*-10-tetradecatetraenamide : the others have a bitter taste and a slight emetic effect. Only the *trans*-2 : *trans*-4- and the *trans*-2 : *cis*-4-amides have yet been tested as insecticides : both are inactive against adult *Tenebrio molitor* L., but the former is about one-third as active as the pyrethrins against adult *Musca domestica*. The *trans*-2 : *cis*-4- is less than one-tenth as active as the *trans*-2 : *trans*-4-amide and the latter is two-fifths as active as the fraction A and B mentioned in Part IV. In the author's experience so far, sialogogue effect is always associated with insecticidal activity in this group of amides.

Physical properties. The four methyl esters and the alcohols are liquid : all the acids and *iso*butylamides are liquid except the *trans-trans*-isomers. Similarly, when the derivatives are crystalline, the *trans-trans*-compound has the highest m. p. This is to be associated with linear character which allows tight packing in the crystal lattice (see Parts I and II). The stereoisomer with the next highest m. p. is usually the *cis-cis*-compound and examination of models suggests that this is because the *cis-cis*- is more nearly linear than the *trans-cis*-chain.

FIG. 1. *Planar projection diagrams of the chromophores of stereoisomeric methyl deca-2 : 4-dienoates.*



The following values are used for bond lengths : C=C 1·34; *s*-C–C 1·44; C–C 1·54; C–H 1·09; C=O 1·20 Å (cf. Lonsdale, Robertson, and Woodward, *Proc. Roy. Soc.*, 1941, *A*, **178**, 43). Bond angles : C–C=C 123°; C–C=O 120°. The van der Waals radius for oxygen is taken as 1·40 and for hydrogen 0·75 Å.

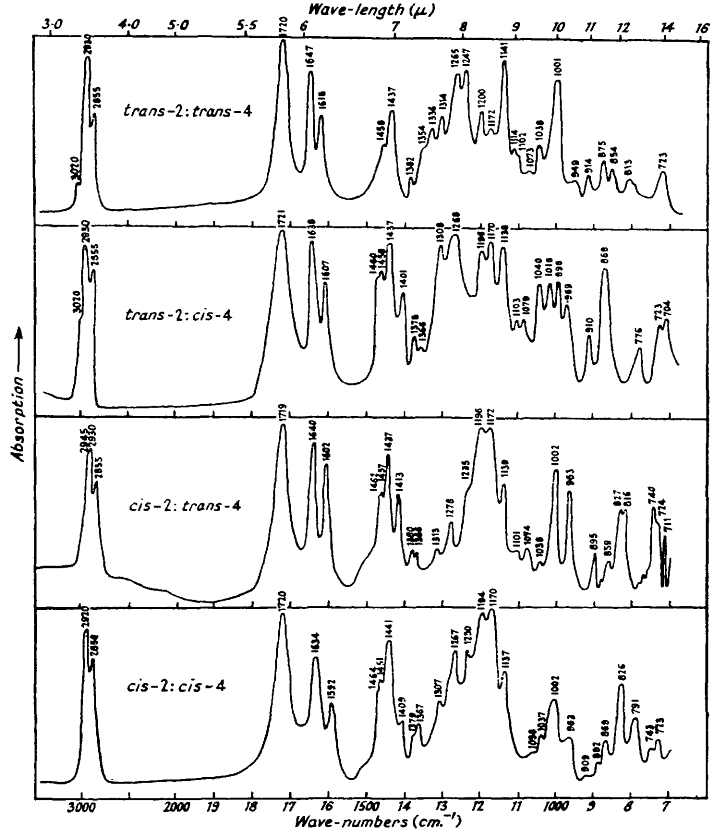
Exaltations of molecular refractivities of the methyl decadienoates decrease in the order *trans*-2 : *trans*-4 > *cis*-2 : *trans*-4 ≈ *trans*-2 : *cis*-4 > *cis*-2 : *cis*-4. In the decadienols the sequence is similar. If exaltation is taken as a measure of conjugation then it too follows the above order.

Ultra-violet light absorption data. These are recorded for the deca-2 : 4-dienoic acids, their methyl esters, *p*-bromophenacyl esters, and *iso*butylamides, and the deca-2 : 4-dienols (Tables 3 and 4). The stereochemistry of the diene system has only slight influence on the position of maximal absorption. Nevertheless, it is perhaps just significant that for the *trans-trans*-dienols and methyl esters, $\lambda_{max.}$ lies at a measurably lower position than for the other stereoisomers (cf. Celmer and Solomons, *J. Amer. Chem. Soc.*, 1953, **75**, 3430;

Nichols, Herb, and Riemenschneider, *ibid.*, 1951, **73**, 247). The alteration indicates a small change in electronic transition energy : this is noticeable in passing from a *trans-trans-trans-* ($\lambda_{max.}$ 268 mμ) to a *trans-trans-cis*-triene ($\lambda_{max.}$ 271 mμ; see Crombie and Tayler, *J.*, 1954, 2816).

The extinction coefficients of the methyl deca-2 : 4-dienoates decrease in the same order as molecular exaltation and, presumably, the conjugation. The change from methyl deca-*trans*-2 : *trans*-4- to -*trans*-2 : *cis*-4-dienoate will first be examined. The lower ε of the *trans*-2 : *cis*-4-isomer is unlikely to be associated with contamination caused by over-hydrogenation as the values for the synthetic and the natural specimen agree well (Table 2).

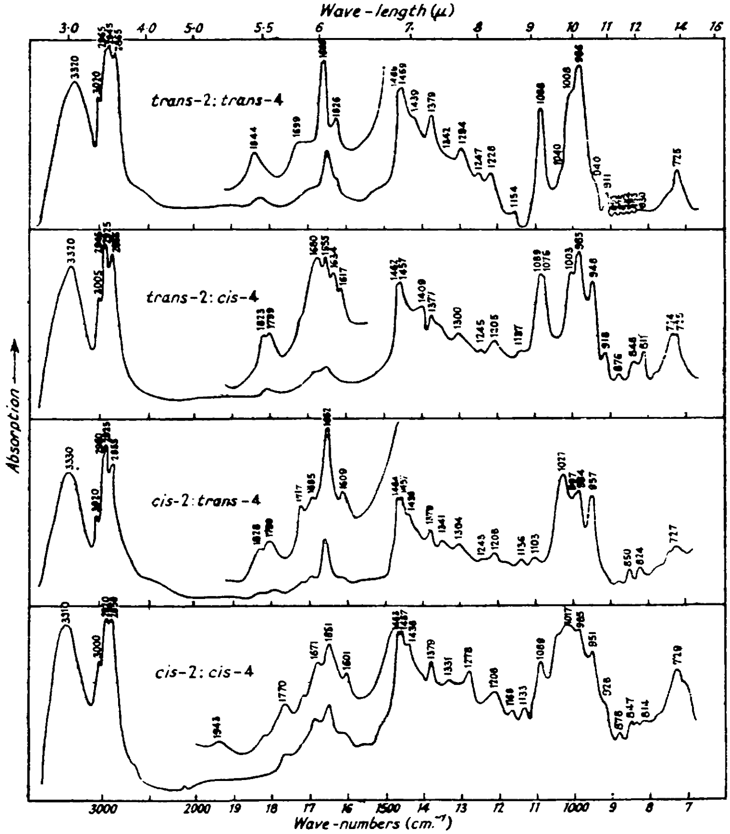
FIG. 2. *Infra-red spectra of methyl deca-2 : 4-dienoates (pure liquid films).*



The chromophore length ($C_{(5)}$ to the centre of the O of the C=O) is the same (6·0 Å) in each case, if the reasonable assumption is made that linkages joining the double bonds are in the *s*-*trans*-configuration (Fig. 1). Static models can be constructed (even using Courtauld atomic models : these over-accentuate steric hindrance for many spectroscopic purposes), which allow complete planarity of the chromophore without any considerable hindrance effects. However, the *trans*-2 : *cis*-4 model makes it clear that there must be repulsion between the two *cis*-substituents and that rotation of the *n*-pentyl residue will meet with considerable hindrance from the hydrogen atom on $C_{(3)}$. The two effects are related. Neither operates for the *trans*-2 : *trans*-4-compound and this may explain spectroscopical differences as follows.

Possible consequences of the repulsion are opening of the bond angles with retention of coplanarity of the four substituents attached to the *cis*-double bond, or movement of one substituent to above and of another to below the formal plane of the carbon–carbon double bond. The latter state of affairs can be regarded as due to rotation of the double bond through a small angle (the energy required for this limited rotation is likely to be small, though quantitative data are difficult to obtain; see Mulliken and Roothaan, *Chem. Reviews*, 1947, **41**, 219). As a consequence, there is a decrease in overlap of the two *p*-electrons in the π-orbital and this is reflected in the infra-red spectrum (see below). The departure from planarity and opening of bond angles will also help to lower the energy barrier to free rotation of the alkyl group. It can be still further reduced by rotation on the $C_{(3)}$–$C_{(4)}$ *s*-bond, which decreases resonance energy and partly destroys coplanarity of the chromophore. The effect is again to decrease $\varepsilon_{max.}$ (Braude, Jones, Koch, Richardson, Sondheimer, and Toogood, *J.*, 1949, 1890; Braude, Sondheimer, and Forbes, *Nature*, 1954, 173, 117; see also Brooker, White, Sprague, Dent, and Van Zandt, *Chem. Reviews*, 1947, **41**, 325; Ferguson, *ibid.*, 1948, **43**, 385).

FIG. 3. *Infra-red spectra of deca-2 : 4-dienols (pure liquid films; upper curve, ~150 micron film).*



The case of the *cis*-2 : *trans*-4-stereoisomer is more complicated. The chromophore length defined as above is shorter (5·45 Å) on the assumption of an all *s-trans*-structure (Fig. 1). Furthermore, an *s-cis*-bond for the $C_{(1)}$–$C_{(2)}$ linkage is acceptable as it results in somewhat reduced interaction with the $C_{(4)}$-hydrogen atom (chromophore length 3·85 Å). This chromophore-length effect could be the cause of a reduced extinction coefficient, as the latter depends on dipole moment and is proportional to the square of the distance between the ends of the conjugated system (Zechmeister, Le Rosen, Schroeder, Polgar, and Pauling, *J. Amer. Chem. Soc.*, 1943, **65**, 1940). Apart from this, there is steric hindrance between the $C_{(4)}$-hydrogen and an oxygen atom in both conformations. Finally, in the *s-trans*-form, the $C_{(4)}$-hydrogen atom presents a barrier to rotation of the methoxyl of the methoxycarbonyl grouping which could be relieved only by rotation of single or double carbon–

carbon linkages as discussed above. Chromophore lengths in the two possible conformations of the *cis-cis*-isomer ($C_{(1)}$–$C_{(2)}$ *s-trans* or *s-cis*) are the same as for the *cis*-2 : *trans*-4-compound and the same remarks apply. In addition there are the effects caused by the *cis*-$C_{(4)}$–$C_{(5)}$ double bond and referred to in the discussion of the *trans*-2-*cis*-4-compound. It is not surprising that the extinction coefficient is lowered still more.

The four deca-2 : 4-dienols are of interest as the diene chromophore length is formally the same in all four cases, if $C_{(3)}$–$C_{(4)}$ is assumed to be *s-trans* (there is, however, probably some hyperconjugation involving the oxygen). On a static model there is no severe inhibition of coplanarity. But again there is the characteristic sequence of decreasing $\varepsilon_{\max.}$ found in the methyl esters, which can be explained by applying repulsion and hindrance to rotation in *cis*-forms, as outlined above. The *trans-trans*-isomer is completely free from such effects, which are greatest in the *cis-cis*-form. In the *p*-bromophenacyl esters, an approximate correction for the absorption of the *p*-bromophenacyl residue has been made by subtraction of the extinction curve for *p*-bromophenacyl decanoate from that of the appropriate diene derivative. The values are listed in Table 4 and indicate some conjugative effect between the two chromophoric systems separated by a methylene grouping; strictly speaking, the procedure is not valid. The extinction coefficients obtained in this series and in the *iso*-butylamides and acids are explicable on the general ideas developed above.

Infra-red absorption data. An isolated *trans*-olefinic linkage of the type $-CH_2\cdot CH{=}CH\cdot CH_2-$ gives rise to a strong absorption band at 966 cm.$^{-1}$, whilst a *cis*-linkage has little or no absorption at this frequency (for references, see Crombie, *Quart. Reviews*, *loc. cit.*). The cause of the absorption is believed to be an out-of-plane deformation vibration of the two hydrogen atoms attached *trans* to the double bond. Conjugative influences with carboxyl, phenyl, or other double bonds cause a shift to higher frequencies (Table 6). In contrast, conjugation with an acetylenic linkage causes a shift to lower frequencies. The positions of the absorption seem little influenced by the physical state of the specimen (mull, liquid film, or solution). Whilst the present work was in progress, Jackson, Paschke, Boyd, Tolberg, and Wheeler (*J. Amer. Oil Chem. Soc.*, **1952**, **229**)

TABLE 6. *Dependence of out-of-plane unsaturated* C–H *vibrations* (*cm.*$^{-1}$) *on conjugation.*

$Pr^n\cdot CH{=}CH\cdot[CH_2]_2\cdot OH$ [a]	968	$Me\cdot CH{=}CH\cdot CH{=}CH\cdot CO\cdot NHBu^i$ [b]	990
$Me\cdot CH{=}CH\cdot[CH_2]_2\cdot COMe$ [a]	967	$Me\cdot[CH_2]_3\cdot[CH{=}CH]_3\cdot[CH_2]_7\cdot CO_2H$ [b,f]	998
$Me\cdot[CH_2]_6\cdot CH{=}CH\cdot CO_2Me$ [a]	978	$Pr^n\cdot C{\equiv}C\cdot CH{=}CH\cdot CH_2\cdot CO_2Me$ [a,g]	950
$Me\cdot[CH_2]_6\cdot CH{=}CH\cdot CO\cdot NHBu^i$ [b,c]	977	$Pr^n\cdot C{\equiv}C\cdot CH{=}CH\cdot CH_2Br$ [a,g]	950
$Me\cdot[CH_2]_4\cdot CH{=}CH\cdot CHO$ [a]	978	$Me\cdot[CH_2]_4\cdot C{\equiv}C\cdot CH{=}CH\cdot CO_2Et$ [a]	961
$Ph\cdot CH{=}CH\cdot CO_2H$ [b,d]	980	$Me\cdot[CH_2]_5\cdot CH{=}CH\cdot C{\equiv}C\cdot[CH_2]_7\cdot CO_2Me$ [a,h]	955
$Me\cdot CH{=}CH\cdot CH{=}CH\cdot[CH_2]_2\cdot CO_2H$ [b,e]	988		

See also Table 3, Part I. All double bonds in the above compounds are *trans*. [a] Liquid film. [b] Paraffin mull. [c] Part I. [d] Flett, *J.*, 1951, 963. [e] Crombie and Shah, unpublished work. [f] Crombie and Tayler, *loc. cit.* [g] Celmer and Solomons, *loc. cit.* [h] Ahlers and Ligthelm, *J.*, 1952, 5039. For stereoisomeric dienes see Tables 7, 8, and 9.

TABLE 7. *Infra-red assignments* (*cm.*$^{-1}$) *for stereoisomeric methyl deca*-2 : 4-*dienoates and deca*-2 : 4-*dienols.*[a]

	Methyl decadienoates						Decadienols					
	$\nu C{=}C_{I}$	$\nu C{=}C_{II}$	Mean $\nu C{=}C$	$\Delta C{=}C$	δ' $[CH{=}CH]_2$		$\nu C{=}C_{I}$	$\nu C{=}C_{II}$	Mean $\nu C{=}C$	$\Delta C{=}C$	δ' $[CH{=}CH]_2$	
trans-2 : *trans*-4	1647	1618	1633	29	1001	—	1660	1626	1643	34	986	—
	(1648)	(1620)	(1634)	(28)	(1000)	—						
trans-2 : *cis*-4...	1639	1607	1623	32	996	969	1655	1616	1635	39	983	948
	(1642)	(1610)	(1626)	(32)	(995)	(969)						
cis-2 : *trans*-4...	1640	1602	1621	38	1002	963	1652	1609	1630	43	984	952
	(1642)	(1603)	(1622)	(39)	(1001)	(963)						
cis-2 : *cis*-4 ...	1634	1592	1613	42	1002[b]	963[b]	1651	1601	1626	50	985[b]	951[b]
	(1637)	(1594)	(1616)	(43)	(1002)[b]	(963)[b]						

[a] All liquid films, but figures in parentheses represent measurements on a 10% solution in CCl_4. The suffixes I and II denote the bands of higher and lower frequency respectively. [b] Relevance uncertain: may be due to impurity.

suggested that in *cis-trans*-dienes a band at 942 cm.$^{-1}$, as well as one at 982 cm.$^{-1}$, was characteristic of the configuration. Some support for this is found in the report by Celmer and Solomons (*loc. cit.*); they find that nona-*trans*-3 : *cis*-5-dienoic acid and trideca-*trans*-3 : *cis*-5-dienoic acid have bands at 1020, 985, and 950 cm.$^{-1}$.

The position of the stretching frequency of a C=C (unconjugated with other olefinic linkages) and geometrical configuration were correlated in Part I. *cis*-Isomers absorb at some 10—15 cm.$^{-1}$ lower than the *trans*-forms. A similar effect is found in the Raman spectra of monoethenoid geometrical isomers (see references cited in Part I) and its implications regarding the spectra of dienes are examined below. The infra-red data obtained in this investigation are discussed broadly under three headings: (i) the olefinic C–H deformation region; (ii) the C=C and C=O stretching region; and (iii) other regions.

(i) The olefinic C–H out-of-plane deformation region. Table 7 shows that in the deca-2 : 4-dienols the *trans-trans*-isomer has a band only at 986 cm.$^{-1}$ whilst the two *cis-trans*-compounds have a second band at 950 cm.$^{-1}$. The position of the second band agrees better with the results of Celmer and Solomons than those of Jackson *et al.*, possibly because the diene system, in the two cases cited by the latter authors, was seated deeply in a long chain, remote from polar influences. The *cis-cis*-stereoisomer also has absorption at 984 and 950 cm.$^{-1}$ but because of difficulties in purification further information is required before these are accepted as characteristic: *cis-trans* impurity could be responsible, as also for the *cis-cis* methyl ester.

In the methyl deca-2 : 4-dienoates and the *iso*butylamides both bands are shifted to higher frequencies, presumably because of conjugation. Such shifts must be taken into account for determinations of configuration. Intensity measurements in this region may be valuable; in particular, the two bands in the *cis-cis*-isomer are weak but it has not yet been possible to undertake quantitative extinction measurements. A band at 1016 cm.$^{-1}$ is present for methyl deca-*trans*-2 : *cis*-4-dienoate but not for the other stereoisomers and may correspond with the band at 1020 cm.$^{-1}$ noted by Celmer and Solomons.

For the decadienols, a $CH_2{\cdot}OH$ group would normally have a C–O stretching vibration at 1060 cm.$^{-1}$ but the group is influenced by electronic effects, and unsaturation causes the band to move to lower frequencies because of the decreased C–O force constant (Zeiss and Tsutsui, *J. Amer. Chem. Soc.*, 1953, **75**, 897), though in no case so far observed does it fall below 1000 cm.$^{-1}$. It is therefore likely that the assignment can be made to the strong band lying between 1003 and 1027 cm.$^{-1}$ and that major interference with the 986-cm.$^{-1}$ vibration is not experienced.

(ii) The C=C and C=O stretching region. An isolated olefinic linkage in a compound of the type CHR=CHR′ where R and R′ are alkyl, has a weak stretching vibration at 1660—1670 cm.$^{-1}$. On conjugation with a second double bond, vibrational interaction occurs and two weak bands appear, unless one is forbidden by molecular symmetry, at ~1635—1650 and 1600 cm.$^{-1}$ (Rasmussen, " Fortschritte der Chemie Organischer Naturstoffe, 1948, Vol. V, p. 331; Sheppard and Simpson, *Quart. Reviews*, 1952, **6**, 1). The influence of geometrical configuration on these vibrations has not hitherto been studied. The methyl decadienoates will be considered first as the two diene bands ($C{=}C_I$ refers to the band of higher and $C{=}C_{II}$ to that of lower frequency) are strong and easily recognisable because of the proximity of the groups to the methoxycarbonyl group. There is a movement of both bands (particularly $C{=}C_{II}$) to lower frequencies as one passes from the *trans-trans*- through the two *cis-trans*- to the *cis-cis*-isomer. At the same time, the separation constant Δ increases also. The position of the carbonyl stretching vibration is constant within experimental error and all the bands are hardly affected on remeasurement in **5** or 10% solution in carbon tetrachloride. Similar results are obtained for the *p*-bromophenacyl esters, though the $C{=}C_{II}$ vibration seems to lie, as would be expected, under the phenyl$_I$ vibration in the case of the *cis-cis*-compound. This characteristic behaviour of the double-bond vibrations should prove useful for recognition of the geometrical configurations of dienes.

The *N*-*iso*butyldeca-2 : 4-dienamides present a more complex problem. Here, the amide A (C=O type) lies close to the $C{=}C_I$ and the $C{=}C_{II}$ vibration, and the arguments for the assignments presented in Table 9 are as follows. *N*-*iso*Butyldecanamide has its amide A vibration, unequivocally, at 1642 cm.$^{-1}$. *N*-*iso*Butyldeca-*trans*-2-enamide has two strong vibrations at 1629 and 1671 cm.$^{-1}$. On conjugation, the amide A carbonyl vibration must fall to lower frequencies, so the band at 1629 cm.$^{-1}$ is assigned to this. In conformity *N-iso*butyldec-*cis*-2-enamide has strong bands at 1631 and 1660 cm.$^{-1}$, *i.e.*, the shift due to *cis*-configuration (mentioned above and known from other examples in the infra-red and Raman spectra : see Parts I and II) has occurred on the other band (C=C), as expected. We thus also expect the amide A vibration to fall a little further by conjugation with a second double bond (comparison of methyl dec-*trans*-2-enoate with methyl deca-*trans*-2 : *trans*-4-dienoate indicates about 6 cm.$^{-1}$). In *N-iso*butyldeca-*trans*-2 : *trans*-4-dienamide the band at 1625 cm.$^{-1}$ is therefore identified as amide A vibration, and the two bands at 1654 and 1614 cm.$^{-1}$ are assigned to the C=C$_I$ and the C=C$_{II}$ vibration respectively.

TABLE 8. *Infra-red assignments* (*cm.*$^{-1}$) *for stereoisomeric* p-*bromophenacyl deca*-2 : 4-*dienoates.* [a, b]

	Ester νC=O	Keto νC=O	νC=C$_I$ [c]	νC=C$_{II}$ [c]	Mean νC=C	ΔC=C	Ph$_I$ [a]	Ph$_{II}$ [a]
trans-2 : *trans*-4	1719	1702	1640	1617	1628	23	1586	1483
trans-2 : *cis*-4	1711	1694	1631	1602	1617	29	1588	1486
cis-2 : *trans*-4	1714	1696	1640	1600	1620	40	1588	1486
cis-2 : *cis*-4	1714	1694	1636	— [d]	—	—	1587	1485

[a] *p*-Bromophenacyl decanoate had ester C=O 1741, keto C=O 1701, Ph$_I$ 1588, Ph$_{II}$ 1485 cm.$^{-1}$ [b] Paraffin mulls. [c] For the meaning of the suffixes see note to Table 7. [d] Obscured by Ph$_I$ vibration

TABLE 9. *Infra-red assignments* (*cm.*$^{-1}$) *for stereoisomeric* N-iso*butyldeca*-2 : 4-*dienamides.*

	νNH		Amide A νC=O	νC=C$_I$ [f]	νC=C$_{II}$ [f]	Mean νC=C	ΔC=C	Amide B νC=O	δ' [CH=CH]$_2$	
trans-2 : *trans*-4 [a]	3295	3075	1625 [c]	1654 [c]	1614 [c]	1634	40	1550	994 [c]	—
trans-2 : *cis*-4 [b] ...	3285	3075	1623	1653	1609 [d]	1631	44	1549	993	963
cis-2 : *trans*-4 [b] ...	3285	3090	1632 [e]	1650 [e]	1605 [e]	1627	45	1544	998 [e]	961 [e]
cis-2 : *cis*-4 [b]	3285	3075	1628	1649	1595 [d]	1622	54	1546	994	962

Paraffin mull. [b] Liquid film. [c] *trans*-2 : *trans*-4-Sorbic *iso*butylamide (paraffin mull) had the corresponding bands at 1629, 1655, 1618, and 990 cm.$^{-1}$. [d] Incompletely resolved. [e] *cis*-2 : *trans*-4-Sorbic *iso*butylamide (paraffin mull) had the corresponding bands at 1634, 1652, 1605, 991, and 961 cm.$^{-1}$ [prepared by Miss U. Eisner (Eisner, Elvidge, and Linstead, *loc. cit.*]. [f] See note to Table 7.

The values for the double bond vibrations (Table 9) in the four stereoisomers then show regular shifts similar to those just mentioned. Further, the amide A vibration has slightly higher values in the two compounds with *cis*-2 double bonds. Models indicate that this may be due to a steric effect, the C$_{(4)}$-hydrogen atom forcing the carbonyl of the bulky amide group sufficiently out of planarity to have slight effects on the frequency.

The C=C$_I$ and C=C$_{II}$ vibrations of the four deca-2 : 4-dienols are weak compared with those discussed above but, if thick films are used, they are readily recognised, though unidentified bands, probably overtones and combination tones, intrude. Because there is no conjugation with a carboxylic function, all the frequencies are higher. The characteristic general fall of frequencies and increase in Δ values on passing from *trans-trans*- to *cis-cis*-amide agrees with the other cases.

(iii) Other regions. A few other features may be useful for stereochemical identification in related cases. In the deca-2 : 4-dienoic esters a band at 1401—1413 cm.$^{-1}$ is absent only from the *trans*-2 : *trans*-4-form though it lies at shorter wave-lengths in the *trans*-2 : *cis*-4-isomer. All the esters have moderately strong bands at 1137—1141 cm.$^{-1}$ (possibly an ester C–O vibration); the very weak character, relative to it, of the band at 1172 cm.$^{-1}$ is worthy of note for the *trans*-2 : *trans*-4-compound. Only the *cis*-2 : *trans*-4-decadienol has no strong vibration near 1089 cm.$^{-1}$. The O–H stretching band lies at 3310—3330 cm.$^{-1}$, and the band between 720 and 730 cm.$^{-1}$ is probably an alkyl-chain bending vibration.

Results (Tables 7, 8, and 9) for the C=C$_I$ and C=C$_{II}$ stretching frequencies require further comment. If hindrance, reflected in the ultra-violet spectra for systems containing *cis*-linkages, caused only an adjustment of the diene system from coplanarity by rotation on *s*-bonds, then, so far as the C=C stretching vibrations are concerned one would expect the effects of conjugation to be decreased, *i.e.*, they would move to higher frequencies on passing through the series *trans-trans*, *cis-trans*, and *trans-cis*, to *cis-cis*. In fact they move to lower frequencies. This can be explained if hindrance is relieved, or repulsion reduced, by angular twisting of the carbon–carbon double bond, with decrease in its force constant and a marked shift to lower frequencies: this effect might well overpower an opposing shift due to the *s*-bond adjustment. Such an explanation agrees with the fact mentioned above that the more hindered *cis*-mono-olefins absorb at lower frequencies than the *trans*-forms, in both infra-red and Raman spectra.

In the light of the synthetical work reported here, it is believed that essentially stereospecific synthesis of compounds of the type R·CH=CH·CH=CH·R′ containing any of the four stereochemical possibilities is feasible, and in this respect synthetical methods are ahead of diagnostic ones.

EXPERIMENTAL

For general remarks see preceding paper. For many physical data see Tables.

1 : 1-*Diethoxyoct-2-yne*.—Methylmagnesium bromide was prepared in ether (700 ml.) from magnesium (24 g.). Hept-1-yne (96 g.) was added slowly and the mixture then refluxed for 6 hr. Ethyl orthoformate (163 g., 1·1 mol.) was added to the cooled acetylenic Grignard reagent and refluxing continued for 6 hr. more. Ice and water were added, the ether layer was removed, and the aqueous phase treated with acetic acid (100 ml.) and extracted twice with ether. The ethereal solutions were united, washed with sodium hydrogen carbonate, and dried (Na_2SO_4). Evaporation and distillation yielded 1 : 1-diethoxyoct-2-yne (150 g., 77%), b. p. 120—123°/18 mm., n_D^{15} 1·4382 (Moureu and Delange, *Bull. Soc. chim.*, 1904, **31**, 1333, give b. p. 118—125°/20 mm., n_D^{15} 1·438).

cis-1 : 1-*Diethoxyoct-2-ene*.—1 : 1-Diethoxyoct-2-yne (26·0 g.) was hydrogenated in ethyl acetate (10 ml.) with palladium–calcium carbonate (5%; 1·0 g.) until 3·10 l. of gas had been absorbed at 16°/740 mm. (required for semihydrogenation, 2·94 l.). Kieselguhr was added and the catalyst removed by filtration. Evaporation and distillation gave cis-1 : 1-*diethoxyoct-2-ene* (18·3 g., 70%), b. p. 116—118°/30 mm., n_D^{21} 1·4292 (Found: C, 71·7; H, 11·8. $C_{12}H_{24}O_2$ requires C, 71·95; H, 12·05%).

trans-*Oct-2-enal*.—1 : 1-Diethoxyoct-2-ene (14·5 g.) was refluxed with 5% sulphuric acid (100 ml.) for 3 hr. The brown upper layer was removed with ether, dried, and distilled, giving *trans*-oct-2-enal (7·3 g., 80%), b. p. 84—86°/19 mm., n_D^{24} 1·4485 (Found: C, 76·1; H, 11·25. $C_8H_{14}O$ requires C, 76·15; H, 11·2%). The 2 : 4-*dinitrophenylhydrazone* crystallised from ethanol as orange needles, m. p. 128° (Found: C, 54·8; H, 5·85. $C_{14}H_{18}O_4N_4$ requires C, 54·9; H, 5·9%). Van Romburgh (*Rec. trav. chim.*, 1938, **57**, 494) records that an oct-2-enal (b. p. 83°/14 mm.) occurs in the essential oil of *Achasma walang* Val.

Deca-trans-2 : trans-4-*dienoic Acid*.—Pyridine (12 ml.) and *trans*-octenal (16·8 g.) were mixed, and malonic acid (13·8 g.) was added slowly, with shaking. After 2 days at 20°, all the solid material had dissolved and the orange yellow liquid was heated to 100° for 30 min., then cooled and poured into ice-cold, dilute sulphuric acid. The crude product was extracted with ether, and the acid extracted from this with 10% aqueous sodium hydroxide. *Deca*-trans-2 : trans-4-*dienoic acid* was liberated at 0° with dilute sulphuric acid, collected with ether, and purified by distillation (8·15 g., 37%), having b. p. 121—124°/0·3 mm., n_D^{31} 1·5058. It rapidly crystallised in plates. Recrystallisation from light petroleum gave the acid, m. p. 49—50° (Found: C, 71·55; H, 9·8. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%). Light absorption: max. at 257 mμ (ε 28,500) (by the photographic method, a subsidiary maximum or inflexion can be observed at 264 mμ in many of the measurements on the dienoic acids and their derivatives: it is not observed by the photoelectric method; cf. Parts IV and V). The p-*bromophenacyl ester* crystallised as needles from ethanol (Found: C, 59·0; H, 5·85. $C_{18}H_{21}O_3Br$ requires C, 59·2; H, 5·8%). The S-*benzylthiuronium salt* was readily formed (Found: C, 64·8; H, 7·8. $C_{18}H_{26}O_2N_2S$ requires C, 64·65; H, 7·85%). As in the case of the *S*-benzylthiuronium salts mentioned below, the m. p. is somewhat dependent on the rate of heating (cf. Berger, *Acta Chem. Scand.*, 1954, **8**, 427). *Methyl deca*-trans-2 : trans-4-*dienoate*, prepared by use of diazomethane (0·61 g. of acid gave 0·43 g. of ester), had b. p. 69—70°/0·25 mm., n_D^{20} 1·4928, or, prepared by use of methanol containing a trace of sulphuric acid (0·97 g. of acid gave 0·85 g. of ester), had b. p. 87—89°/13 mm., n_D^{17} 1·4937 (Found: C, 72·45; H, 10·1. $C_{11}H_{18}O_2$ requires C, 72·5; H, 10·0%).

n-*Oct-2-ynal.*—1 : 1-Diethoxyoct-2-yne (31·2 g.) was refluxed with 4% sulphuric acid (100 ml.) for 4 hr., cooled, and extracted with ether. Evaporation and distillation of the brown extract gave oct-2-ynal (14·2 g., 73%), b. p. 74—76°/15 mm., 86—88°/27 mm., n_D^{20} 1·4499 (Found : C, 77·4; H, 9·85. Calc. for $C_8H_{12}O$: C, 77·4; H, 9·75%). The 2 : 4-*dinitrophenylhydrazone* crystallised from ethanol in orange laths, m. p. 80° (Found : C, 55·2; H, 5·4; N, 17·9. $C_{14}H_{16}O_4N_4$ requires C, 55·25; H, 5·3; N, 18·4%).

Ethyl 3-*Hydroxydec*-4-*ynoate.*—Activated zinc dust (4·0 g.) was covered with benzene (80 ml.), and ethyl bromoacetate (9·0 g.) mixed with oct-2-ynal (6·2 g.) was added in portions, with refluxing, until reaction commenced. When all of the reagents had been added, the mixture was heated on the steam-bath for 90 min. The benzene layer was decanted and unchanged zinc washed with benzene. These benzene solutions were united and washed with dilute hydrochloric acid and aqueous sodium hydrogen carbonate, and then dried. Removal of solvent and two distillations yielded *ethyl* 3-*hydroxydec*-4-*ynoate* (5·0 g., 47%), b. p. 103—104°/0·2 mm., $n_D^{22·5}$ 1·4556 (Found : C, 68·35; H, 9·55. $C_{12}H_{20}O_3$ requires C, 67·9; H, 9·5%). Microhydrogenation required 2·52H_2 (triple bond and partial hydrogenolysis of the hydroxyl grouping). Light absorption : none having $E_{1\,cm.}^{1\%}$ >30 observed. Infra-red absorption : strong wide band at 3450 cm.$^{-1}$ (hydroxyl) and medium-weak band at 2224 cm.$^{-1}$ (C≡C).

Methyl 3-*Hydroxydec*-4-*ynoate.*—Zinc wool (6·0 g.) was activated by treatment with dilute acid, washed, dried, and covered with tetrahydrofuran (10 ml.). A little mercuric chloride was added and the mixture heated to the b. p. Oct-2-ynal (10 g.) and methyl bromoacetate (14 g.) were mixed in tetrahydrofuran, and a small amount was added to the zinc. A smooth reaction soon began. The mixture was removed from the bath, and the remaining reactants were added at such a rate as to maintain gentle refluxing. After 1 hour's heating the product was cooled and poured into ice and acetic acid. This mixture was saturated with sodium chloride and extracted with ether (4 times). The extracts were washed with aqueous sodium hydrogen carbonate, dried, and distilled, to give methyl 3-hydroxydec-4-ynoate (8·2 g., 52%), b. p. 94—100°/0·4 mm., n_D^{18} 1·4665. Dehydration by phosphorus oxychloride–pyridine (see below) gave methyl dec-2-en-4-ynoate, b. p. 86—92°/0·5 mm., n_D^{20} 1·4868.

Ethyl Dec-2-*en*-4-*ynoate.*—Ethyl 3-hydroxydec-4-ynoate (2·1 g.) was mixed with pyridine (3·0 ml.), and phosphorus oxychloride (3·5 ml.) in pyridine (10 ml.) was added with ice-cooling. The product was heated to 100° for 3½ hr.; it darkened considerably. It was poured into ice-water and extracted with ether. The extract was washed with dilute hydrochloric acid and sodium hydrogen carbonate solution, dried, and distilled, to give *ethyl dec*-2-*en*-4-*ynoate* (1·30 g.), b. p. 85—87°/0·2 mm., n_D^{22} 1·4819 (Found : C, 74·2; H, 9·3. $C_{12}H_{18}O_2$ requires C, 74·15; H, 9·35%). Microhydrogenation required 2·85H_2. Light absorption : max. at 251, 258, 264 mμ ($E_{1\,cm.}^{1\%}$ 780, 870, 870; ε 15,200, 16,800, 16,800). The vibrational spectrum showed bands (*inter alia*) at 2212 (C≡C), 1720 (C=O), and 1619 (C=C) cm.$^{-1}$. Methyl dec-*trans*-2-enoate has bands at 1726 (C=O) and 1655 (C=C) whilst methyl decanoate has one strong band at 1744(C=O) cm.$^{-1}$ (all liquid films.).

Dehydration with potassium hydrogen sulphate or toluene-*p*-sulphonic acid gave mixtures.

Ethyl 3-*Hydroxydec*-cis-4-*enoate.*—Ethyl 3-hydroxydec-4-ynoate (4·6 g.) was hydrogenated in ethyl acetate (5 ml.) with 5% palladium–calcium carbonate. When 510 ml. of hydrogen had been absorbed (511 ml. at 19°/772 mm. for semi-hydrogenation), kieselguhr was added and the catalyst filtered off. Evaporation and distillation yielded *ethyl* 3-*hydroxydec*-cis-2-*enoate* (3·3 g.), b. p. 98—100°/0·4 mm., n_D^{20} 1·4504 (Found : C, 67·7; H, 10·4. $C_{12}H_{22}O_3$ requires C, 67·25; H, 10·35%). Light absorption : no maximum of $E_{1\,cm.}^{1\%}$ >10.

Dehydration of Ethyl 3-*Hydroxydec*-cis-4-*enoate.*—The *cis*-hydroxy-ester (1·86 g.) was diluted with pyridine (2·5 ml.), and phosphorus oxychloride (3·0 g.) in pyridine (9 ml.) was added. The mixture was heated on a steam-bath for 3½ hr., poured into water, and worked up as described for ethyl dec-2-en-4-ynoate. The *diene ester* (1·05 g.) had b. p. 90—91°/0·5 mm., n_D^{19} 1·4818 (Found : C, 72·8; H, 10·25. $C_{12}H_{20}O_2$ requires C, 73·4: H, 10·25%). Microhydrogenation 1·97H_2. Light absorption : max. at 264 mμ (ε 22,100). This ester was converted, by setting it aside in methanol containing a little sodium methoxide for 16 hr., into the *methyl ester*, b. p. 67—68°/0·13 mm., n_D^{25} 1·4855 (Found : C, 72·15; H, 10·1. $C_{11}H_{18}O_2$ requires C, 72·6 ; H, 9·9%). Microhydrogenation required 1·89H_2. Light absorption : max. at 265 mμ (ε 22,900).

Use of potassium hydrogen sulphate gave a mixture.

Hydrolysis of this ester (1·19 g.), as described below for methyl stillingate, yielded a deca-2 : 4-dienoic acid (0·93 g.), b. p. 130°/0·6 mm., n_D^{26} 1·5020 (Found : C, 70·45; H, 9·75%). Microhydrogenation required 1·87H_2. Light absorption : max. at 258 mμ (ε 20,200). The *p*-bromophenacyl ester initially melted unsharply at ~110° and after three recrystallisations from ethanol formed flat shining crystals, m. p. 121—122° which, when admixed with an authentic specimen of the *trans-trans*-ester (m. p. 124·5°), had m. p. 122—124°. The acid gave an *S*-benzylthiuronium salt, m. p. 132—137° (crude). When crystallised from ethyl acetate, a derivative of m. p. 134° was obtained, undepressed on admixture with the authentic *trans*-2 : *cis*-4-derivative.

Dec-trans-*2-en-4-ynoic Acid*.—The ethyl ester (2·6 g.) was hydrolysed with potassium hydroxide (1·0 g.) in methanol (5 ml.). Working up in the usual way gave the crude acid (2·15 g., 97%) which solidified. Crystallisation from light petroleum gave pure *dec*-trans-*2-en-4-ynoic acid*, m. p. 46—47°, as needles (Found: C, 71·95; H, 8·6. $C_{10}H_{14}O_2$ requires C, 72·25; H, 8·5%). Microhydrogenation required 2·85H_2. Light absorption: max. at 257 mμ (ε 15,800). The p-*bromophenacyl ester* crystallised in plates (from ethanol), m. p. 114° (Found: C, 59·5; H, 5·5. $C_{18}H_{19}OBr$ requires C, 59·5; H. 5·3%). Light absorption: max. at 264 mμ (ε 36,300). The *methyl ester* was prepared by esterification with diazomethane and had n_D^{28} 1·4852 (Found: C, 72·7; H, 9·1. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·95%).

Methyl Deca-trans-2 : cis-4-*dienoate*.—The above enyne ester (0·959 g.) was dissolved in methanol (5 ml.), and lead-poisoned palladium catalyst, prepared according to Lindlar (*loc. cit.*), was added together with quinoline (0·15 ml.). The whole was shaken with hydrogen until 135 ml. had been absorbed at 25°/763 mm. ($1H_2 = 130$ ml.). There was no sign of the absorption's halting at this stage. Kieselguhr was added, the mixture filtered, the solvent evaporated, and the residue twice distilled, to give *methyl deca*-trans-2 : cis-4-*dienoate* (712 mg.). The best fraction had b. p. 75°/0·07 mm., n_D^{20} 1·4854, whilst the others had the same b. p. but n_D^{20} 1·4816—1·4854 (Found: C, 72·55; H, 10·25%). See also Table 2. It had the odour characteristic of methyl stillingate. Hydrolysis as described above gave deca-*trans*-2 : *cis*-4-dienoic acid, b. p. 122°/0·5 mm. (Found: C, 70·05; H, 9·9%). Light absorption: max. at 259 mμ (ε 16,100). The p-*bromophenacyl ester* crystallised from ethanol in needles (Found: Br, 21·2. $C_{18}H_{21}O_3Br$ requires Br, 21·85%), undepressed in m. p. by *p*-bromophenacyl stillingate. The S-*benzylthiuronium salt* crystallised from ethyl acetate (needles) (Found: N, 8·0. $C_{18}H_{26}O_2N_2S$ requires N, 8·35%): it did not depress the melting point of the corresponding stillingic derivative. The *N*-*iso*butylamide (see below) was identical with that from stillingic acid (infra-red spectrum). Except for the data above and in Table 2, natural deca-*trans*-2 : *cis*-4-dienoic acid was used.

Non-1-*yn*-4-*ol*.—(*a*) A Grignard reagent was prepared in dry ether (60 ml.) from magnesium etched with mercuric chloride (5·65 g.), and propargyl bromide (29·2 g.). Ether (50 ml.) was added, the mixture cooled in an ice-bath, and hexanal (22·4 g.) added slowly so that refluxing did not occur. The product was stirred for 2 hr., set aside overnight, and then decomposed by water and dilute acid. The ether layer was collected, dried, and distilled. *Non*-1-*yn*-4-*ol* was isolated, and on redistillation the major portion (8·5 g., 27%) had b. p. 107—109°/32 mm., n_D^{25} 1·4458 (Found: C, 76·8; H, 11·55. $C_9H_{16}O$ requires C, 77·1; H, 11·5%). It probably contains allenic impurity as does the specimen described below (cf. Celmer and Solomons, *J. Amer. Chem. Soc.*, 1953, **75**, 3430). This is eliminated during the Grignard carboxylation step.

(*b*) Zinc wool (70 g.) was etched with 2N-hydrochloric acid, washed with ethanol and ether, and covered with tetrahydrofuran (100 ml.). Mercuric chloride (50 mg.) and then a few ml. of a mixture of propargyl bromide (120 g.) and hexanal (110 g.) were added. A reaction set in promptly and the remainder of the mixture was added dropwise. When addition was complete, the product was refluxed for 2 hr. and poured into 10% acetic acid (1 l.). Sufficient sodium chloride was added to saturate the solution which was then thoroughly extracted with ether. The extracts were dried, evaporated, and distilled. Non-1-yn-4-ol (58 g., 41%), b. p. 58—60°/0·1 mm., n_D^{21} 1·4509, was obtained, together with much higher-boiling material which was not further investigated.

4-*Tetrahydropyranyloxynon*-1-*yne*.—Non-1-yn-4-ol (32·9 g.) was mixed with dihydropyran (20 g.) and cooled in ice. Phosphorus oxychloride (0·2 ml.; Henbest, Jones, and Walls, *J.*, 1950, 3646) was added, and the product set aside for 12 hr. and then poured into water, extracted with ether, and distilled. The majority (32 g.) had b. p. 71—80°/0·08 mm., $n_D^{17.5}$ 1·4542—1·4598. The *ether* of b. p. 75—77°/0·08 mm., $n_D^{17.5}$ 1·4543, was used for analysis (Found: C, 74·65; H, 11·1. $C_{14}H_{24}O_2$ requires C, 74·95; H, 10·8%).

Methyl 5-*Hydroxydec*-2-*ynoate*.—A Grignard reagent was prepared from magnesium (12·5 g.) and ethyl bromide (55 g.) in anhydrous ether (250 ml.), 4-tetrahydropyranyloxynon-1-yne (55 g.) in anhydrous benzene (375 ml.) was added slowly, and the whole stirred for 3 hr. After 1 hour's refluxing the product was poured on solid carbon dioxide in an autoclave which was then kept sealed for 3 days. The resultant sludge was treated with methanol (500 ml.)

containing sulphuric acid (45 ml.) and set aside overnight (Henbest, Jones, and Walls, *loc. cit.*). Some ether and benzene were removed by azeotropic distillation, and the mixture was set aside for 24 hr. more. Sodium hydrogen carbonate was added and the excess removed by filtration. The filtrate was concentrated, poured into water, and extracted with ether. Evaporation and distillation gave *methyl 5-hydroxydec-2-ynoate* (27·7 g.), b. p. 112—115°/0·35 mm., n_D^{18} 1·4680 (Found : C, 66·35; H, 9·3. $C_{11}H_{18}O_3$ requires C, 66·6; H, 9·15%). Microhydrogenation required 2·0H$_2$. Light absorption : no max. >215 mμ. At 215 and 320 mμ, ε was 4950 and 500 respectively.

*Methyl 5-Hydroxydec-*cis*-2-enoate.*—The acetylenic ester (19·32 g.) was hydrogenated in ethyl acetate (20 ml.) in the presence of Lindlar catalyst (5 g.); quinoline was not added. After hydrogen (1·18 l.) had been absorbed, the uptake of gas almost ceased, so more catalyst (4 g.) was added. Gas absorption continued briskly and when a total of 2·265 l. of hydrogen (15°/765 mm.) was absorbed the reaction was stopped (calc. for semihydrogenation 2·37 l. at 15°/765 mm.). The catalyst was removed, the solvent evaporated *in vacuo*, and the residue distilled, to give *methyl 5-hydroxydec-*cis*-2-enoate* (17·7 g.), b. p. 102—106°/0·45 mm., n_D^{13} 1·4657. A portion redistilled for analysis had b. p. 104—106°/0·4 mm., n_D^{21} 1·4646 (Found : C, 66·3; H, 10·1. $C_{11}H_{20}O_3$ requires C, 66·1; H, 10·05%). Microhydrogenation required 1·1H$_2$. Light absorption : no max. >217 mμ. At 217 and 237 mμ, ε was 10,000 and 1000 respectively.

Dec-2-eno-5-lactone.—Methyl 5-hydroxydec-*cis*-2-enoate (16·4 g.) was refluxed with 2N-hydrochloric acid (150 ml.) for 80 min., cooled, and extracted with ether. The extracts were washed with sodium hydrogen carbonate solution and water, and dried (Na_2SO_4), and the *lactone* (12·25 g.) distilled (b. p. 86°/0·07 mm., n_D^{22} 1·4709) (Found : C, 71·4; H, 9·8. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%). Microhydrogenation required 1·1H$_2$. Light absorption : no max. >213 mμ. At 213, 230 mμ, ε was 5050 and 1200 respectively. αβ-Unsaturated, δ-lactonic C=O, 1723 cm.$^{-1}$ (liquid film).

*Deca-*cis*-2 :* trans*-4-dienoic Acid.*—Sodium (0·8 g.) was dissolved in anhydrous methanol (80 ml.), dec-2-eno-5-lactone (5·24 g.) added to the cooled reagent (20°), and the whole set aside for 90 min. The solvent was then removed *in vacuo*, water (100 ml.) added, the solution was extracted with ether, and the extracts were rejected. The solution was then acidified and the acid collected with ether. Evaporation and distillation gave deca-*cis*-2 : *trans*-4-dienoic acid as a refractive and rather viscous liquid, b. p. 112—114°/0·45 mm., n_D^{18} 1·5007 (Found : C, 70·4; H, 9·8%). Light absorption : max. at 258 mμ (ε 17,500). The p-*bromophenacyl ester* crystallised from ethanol–water in shining plates (Found : Br, 22·25%). The S-*benzylthiuronium salt* crystallised from ethyl acetate (Found : N, 8·0%). *Methyl deca-*cis*-2 :* trans*-4-dienoate* was prepared from the acid (2·8 g.) at 0° with a slight excess of diazomethane in ether; it distilled at 76—80°/0·5 mm. (2·10 g.) but was contaminated by a little volatile crystalline material. This was eliminated by cooling to 0°, pouring off the ester, and redistilling it (Found : C, 72·35; H, 10·05%). Microhydrogenation required 1·9H$_2$. A small quantity of material, b. p. 122°/0·5 mm., $n_D^{19.5}$ 1·4766, was also isolated.

Deca-2 : 4-diynoic Acid (with J. D. Shah).—Sodamide was prepared from liquid ammonia (2 l.) and sodium (69 g.) in the presence of ferric nitrate catalyst. The bath-temp. was adjusted to −70° and dichlorobut-2-yne (123 g.) added very slowly, to give sodiodiacetylene. Pentyl bromide (151 g.) was added and the mixture stirred overnight. Residual ammonia was allowed to evaporate and the product extracted with ether. After evaporation of the ether, crude nona-1 : 3-diyne (80 g.), b. p. 50°/2 mm., n_D^{21} 1·4745, was obtained.

The diyne (24 g.) in anhydrous ether (30 ml.) was added to a Grignard reagent prepared from magnesium (6·2 g.), ethyl bromide (40 g.), and ether (100 ml.), and the mixture refluxed for 3 hr. The product was poured on solid carbon dioxide in an autoclave and the whole kept sealed for 24 hr. Two similar preparations were carried out and the products united and treated with ice-cold 15% sulphuric acid. The dark syrup was extracted with ether, and the acid extracted from this with sodium hydrogen carbonate solution. After acidification under light petroleum (b. p. 40—60°; 250 ml.), the petroleum layer was removed and the aqueous phase further extracted with light petroleum. The combined extracts were washed and dried, the solvent was removed, and the residue crystallised at low temperature from light petroleum (b. p. 40—60°) to give deca-2 : 4-diynoic acid (25·1 g.), as plates, m. p. 37°. Treatment of the mother-liquors afforded further acid (7·1 g.), m. p. 35·5—37° (Found : C, 73·05; H, 7·55%; equiv., 166. Calc. for $C_{10}H_{12}O_2$: C, 73·2; H, 7·3%; equiv., 164). Microhydrogenation required 3·95H$_2$. The p-*bromophenacyl ester* crystallised in needles, m. p. 83° (Found : C, 59·8; H, 4·7; Br, 22·3. $C_{18}H_{17}O_3Br$ requires C, 59·85; H, 4·75; Br, 22·15%). Methyl deca-2 : 4-diynoate (11·6 g.), prepared by diazomethane from the acid (15 g.), had b. p. 86/0·15 mm., n_D^{19} 1·5018, d^{22} 0·9502

(Found: C, 74·3; H, 8·05. Calc. for $C_{11}H_{14}O_2$: C, 74·15; H, 7·85%). Microhydrogenation required 3·9H_2. Light absorption of the methyl ester: max. at 226, 237, 248, 262, 278 mμ (ε 1300, 2500, 4400, 5900, 3700) [Skattebol and Sorensen, *loc. cit.*, give $\lambda_{max.}$ 226, 236, 247, 261, 277 mμ (ε 1700, 3240, 6320, 7080, 5630), b. p. 40°/0·001 mm.]. Methyl deca-2 : 4-diynoate showed strong C≡C vibrations at 2242 and 2218 cm.$^{-1}$; C=O stretching 1714 cm.$^{-1}$. An absorption band is present at 991 cm.$^{-1}$ (liquid film).

Methyl Deca-cis-2 : cis-4-*dienoate*.—Methyl deca-2 : 4-diynoate (8·94 g.) was shaken in methyl acetate (25 ml.) with Lindlar catalyst (4·0 g.) and quinoline (1·6 ml.) under hydrogen until 2·20 l. at 18°/767 mm. had been absorbed (2 hr.; semihydrogenation required 2·36 l. at 18°/767 mm.). The catalyst was removed and washed with methyl acetate, and the filtrate plus washings evaporated under reduced pressure at 25°. The residue was dissolved in ether, washed with 2N-sulphuric acid and then water, and dried. Distillation gave the fractions: (1) b. p. 71—72°/0·4 mm., n_D^{18} 1·4734, microhydrogenation 1·7H_2, $\lambda_{max.}$ 263 mμ (ε 11,500) (0·75 g.); (2) b. p. 72—73°/0·4 mm., n_D^{18} 1·4769, microhydrogenation 1·87H_2, $\lambda_{max.}$ 263 mμ (ε 12,700) (3·00 g.); (3) b. p. 73—74°/0·4 mm., n_D^{18} 1·4810, microhydrogenation 2·01H_2, $\lambda_{max.}$ 263 mμ (ε 16,400) (1·97 g.); (4) 74—78°/0·4 mm., $n_D^{18\cdot5}$ 1·4865, microhydrogenation 2·06H_2, $\lambda_{max.}$ 263 mμ (ε 14,400) (1·47 g.); and (5) 78°/0·4 mm., $n_D^{18\cdot5}$ 1·4912, microhydrogenation 2·76H_2, $\lambda_{max.}$ 263 mμ (ε 14,400) (0·36 g.). Fractions (2), (3), and (4) were united (6·44 g.) and re-fractionated, the best specimen having b. p. 78°/0·6 mm., $n_D^{20\cdot5}$ 1·4848, $\lambda_{max.}$ 263 mμ (ε 16,400) (Found: C, 72·8; H, 9·85%). (All ε values are calculated by using *M* 182, though the first fraction contains some overhydrogenated material and the last underhydrogenated acetylenic materials: the presence of the latter was confirmed by infra-red spectroscopy.)

Deca-cis-2 : cis-4-*dienoic Acid*.—The ester (1·33 g.) was refluxed for 90 min. with a slight excess of alcoholic potassium hydroxide (the ester became yellow immediately on addition of the cold reagent), then poured into water, and the acid extracted and purified in the normal way. It had b. p. 112—114°/0·5 mm., n_D^{17} 1·4896 (0·98 g.) (Found: C, 70·4; H, 9·9%). Light absorption: max. at 260 mμ (ε 13,000). The p-*bromophenacyl ester* crystallised in plates from ethanol (Found: Br, 21·9%). The S-*benzylthiuronium salt* crystallised from ethyl acetate in plates (Found: N, 8·05%).

Hydrogenation of the Methyl Decadienoates.—The methyl ester was completely hydrogenated in methanol, in presence of palladium–barium sulphate. After filtration, the ester was hydrolysed with a slight excess of methanolic potassium hydroxide and then neutralised. *p*-Bromophenacyl bromide was added and the derivative prepared in the usual way. In all four cases *p*-bromophenacyl decanoate was obtained, having m. p. and mixed m. p. 65—66°.

Isolation of Methyl Stillingate from Stillingia Oil.—Stillingia oil ("Processed Oil," from Messrs. Couper, Friend and Co., London; raw oil has also been used) had the light absorption max. at 258, 266, 280 mμ ($E_{1\,cm.}^{1\%}$ 69, 69, 50). The oil (619 g.) was refluxed for 5 hr. with potassium hydroxide (135 g.) in methanol (700 ml.), and about half of the methanol removed by distillation. The residue was acidified with hydrochloric acid, diluted with water, and extracted with ether. These extracts were dried (Na_2SO_4) and evaporated and the crude fatty acids esterified by refluxing 1% methanolic sulphuric acid (500 ml.) for 4 hr. The product was poured into water and the mixed esters were isolated by ether-extraction, washed with dilute sodium hydroxide solution, and, after removal of the ether, fractionated. Methyl stillingate (18·6 g.) was obtained. For data see Table 2 (Found: C, 72·6; H, 10·1. Calc. for $C_{11}H_{18}O_2$: C, 72·5; H, 10·0%). Microhydrogenation required 2·05H_2. A second sample isolated by this procedure had $\lambda_{max.}$ 264 mμ (ε 21,000). Crossley and Hilditch (*loc. cit.*) give b. p. 86°/0·2 mm., $\lambda_{max.}$ 264 mμ (ε 24,000). The ester had a characteristic and rather unpleasant odour.

Stillingic Acid.—Methyl stillingate (4·17 g.) was refluxed with methanolic potassium hydroxide (45 ml.; 0·837N) for 60 min. The ester rapidly became yellow but not dark. Most of the methanol was distilled and an excess of water was added. The acid was isolated by acidification (Congo-red) and ether-extraction: it was purified by dissolution in sodium hydroxide solution (10%), the free acid being collected with ether after acidification. Drying (Na_2SO_4), evaporation in nitrogen, and distillation yielded stillingic acid (2·73 g.) as a viscous colourless liquid, b. p. 107°/0·2 mm., n_D^{18} 1·5078 (Found: C, 70·85; H, 9·65%). Microhydrogenation required 1·98H_2. Light absorption: max. at 257 mμ (ε 18,000). A second specimen had $\lambda_{max.}$ 257 mμ (ε 19,300). The acid was highly unstable, and in air at 25° during 12 hr. a film polymerised to gum. Its p-*bromophenacyl ester* crystallised in flat needles from ethanol–water (Found: Br, 21·8%). This had partly resinified after 14 days at 0°. The S-*benzylthiuronium salt* formed powdery prisms from ethyl acetate (Found: N, 8·3%).

Deca-2 : 4-*dienols*.—These were prepared by slowly adding a solution of lithium aluminium hydride in ether to a solution of the appropriate methyl ester in ether, at such a rate that ether did not reflux. Excess of reagent was decomposed by water, ice-cold dilute sulphuric acid was added, and the ether layer separated, evaporated, and distilled.

trans-2 : trans-4-*Dienol*. Methyl deca-*trans*-2 : *trans*-4-dienoate (0·47 g.) was reduced with lithium aluminium hydride (0·079 g.) to give *deca*-trans-2 : trans-4-*dienol* (0·34 g.) (Found : C, 77·65; H, 11·95. $C_{10}H_{18}O$ requires C, 77·85; H, 11·75%). The *α-naphthylurethane* formed fluffy needles from light petroleum (b. p. 40—60°) (Found : N, 4·35. $C_{21}H_{25}O_2N$ requires N, 4·35%).

trans-2 : cis-4-*Dienol*. The ester (0·96 g.) and lithium aluminium hydride (0·12 g.) gave the *dienol* (0·60 g.) (Found : C, 77·4; H, 11·9%). The *α-naphthylurethane* crystallised from light petroleum (b. p. 40—60°) as needles (Found : N, 4·35%). It was markedly more soluble in petroleum than the *trans*-2 : *trans*-4-isomer, as were the *cis*-2 : *trans*-4- and *cis*-2 : *cis*-4-compounds. The *p*-phenylazobenzoyl derivative was an oil.

cis-2 : *trans*-4-*Dienol*. The ester (1·06 g.) gave, with lithium aluminium hydride (0·15 g.), *deca*-cis-2 : trans-4-*dienol* (0·79 g.) (Found : C, 77·65; H, 11·85%).

cis-2 : *cis*-4-*Dienol*. Methyl deca-*cis*-2 : *trans*-4-dienoate (0·88 g.) and lithium aluminium hydride (0·11 g.) yielded *deca*-cis-2 : cis-4-*dienol* (0·58 g.) (Found : C, 77·9; H, 11·75%). The *α-naphthylurethane* was recrystallised three times from light petroleum (b. p. 40—60°) (Found : N, 4·45%).

Preparation of iso*Butylamides*.—The acid (1 mol.) in benzene was treated with excess of oxalyl chloride (usually 1·3 mol.) at 25°. After 2 hr., the mixture was heated under reflux for 1 hr., and the solvent and excess of reagent were removed *in vacuo*. The acid chloride was distilled and dissolved in anhydrous ether. *iso*Butylamine (2·5 mol.) in ether was added dropwise with cooling and shaking. After 1 hr. the product was poured into water, washed with N-sulphuric acid, then sodium hydrogen carbonate solution, dried, evaporated, and distilled. N-iso*Butyldeca*-trans-2 : trans-4-*dienamide* (0·964 g.), m. p. 90° (Found : C, 75·2; H, 11·6; N, 6·4. $C_{14}H_{25}ON$ requires C, 75·25; H, 11·3; N, 6·25%), was obtained from the acid (1·00 g.) by the above procedure but replacing the distillation by crystallisation at 0° from light petroleum (b. p. 40—60°) gave needles (microhydrogenation : 1·9H_2). See also Table 4. Deca-*trans*-2 : *cis*-4-dienoic acid (1·63 g.) gave the iso*butylamide* (1·62 g.) as an almost colourless viscous liquid (Found : C, 75·0; H, 11·25; N, 6·3%. Microhydrogenation : 2·0H_2). The *cis*-2 : *trans*-4-acid (0·91 g.) gave its iso*butylamide* (0·80 g.) according to the general method (Found : C, 75·5; H, 11·4; N, 6·0%. Microhydrogenation : 1·9H_2). Similarly the *cis*-2 : *cis*-4-acid (0·58 g.) gave the corresponding iso*butylamide* (0·49 g.) (Found : N, 6·1%).

N-iso*Butyldeca*-trans-2-*en*-4-*ynamide* (1·7 g. : Found : C, 75·65; H, 10·45; N, 6·5%. Microhydrogenation : 2·9H_2. $C_{14}H_{23}ON$ requires C, 75·95; H, 10·5; N, 6·35%) was prepared from the corresponding acid (1·53 g.). It was not distilled and after two recrystallisations (with charcoaling) from light petroleum (b. p. 40—60°) formed needles, m. p. 69°. Light absorption : max. at 258 mμ (ε 21,500).

N-iso*Butyl*-trans-2 : trans-4-*sorbamide* (Found : C, 71·8; H, 10·2; N, 8·2. Microhydrogenation : 1·95. $C_{10}H_{17}ON$ requires C, 71·8; H, 10·25; N, 8·35%) crystallised in short needles or plates, m. p. 112°, from light petroleum (b. p. 40—60°)–benzene. Light absorption : max. at 257 mμ (ε 31,500). *N-iso*Butyl-*trans*-2 : *trans*-4-sorbamide is inactive against adult *Tenebrio molitor* and *Musca domestica*. It is desirable to keep all unsaturated *iso*butylamides at 0° in sealed tubes. Those containing *cis*-linkages are the most unstable, but pure specimens of *N-iso*butyl-*trans*-2 : *trans*-4-sorbamide and *N-iso*butyldeca-*trans*-2 : *trans*-4-dienamide changed to a brown gum in air at 25° during about 14 days. The deterioration may happen overnight but in other cases may be long delayed.

Reaction Between Stereoisomeric iso*Butylamides and Maleic Anhydride*.—*N-iso*Butyldeca-*trans*-2 : *trans*-4-dienamide (100 mg.), maleic anhydride (40 mg.), and benzene (0·8 ml.) were sealed under nitrogen and heated at 100° for 90 min. On cooling to 25°, a solid product crystallised. Heating was continued for 5 hr. in all and, after cooling, the *adduct* was filtered off and crystallised (needles, m. p. 193° somewhat dependent on rate of heating) from benzene (Found : C, 66·95; H, 8·25; N, 4·4. $C_{18}H_{27}O_4N$ requires C, 67·25; H, 8·45; N, 4·35%). The three stereoisomeric *iso*butylamides were examined in a similar way but no crystalline products were obtained.

Iodine-catalysed Irradiation.—The three methyl deca-2 : 4-dienoates containing *cis*-linkages were dissolved in light petroleum (b. p. 40—60°), and a trace of iodine was added. The *cis*-2 : *cis*-4-compound retained a slight pink-purple colour; the *cis*-2 : *trans*-4- and the *trans*-2 : *cis*-4-compound became pale brown, the former also becoming turbid. The solutions in thin glass test-tubes, were irradiated overnight with a " Hanovia " ultra-violet lamp, then washed with dilute aqueous sodium thiosulphate and water, dried, and evaporated. Their infra-red spectra (liquid films) were then examined and no appreciable change had occurred in any case. The experiments were repeated in quartz tubes with the same results.

Thermal Treatment.—Specimens of the four methyl deca-2 : 4-dienoates were sealed in tubes from which the air was not displaced and heated at 160—180° for 45 min. As judged by development of colour the *cis*-2 : *cis*-4- and the *cis*-2 : *trans*-4-stereoisomer had deteriorated most (orange-brown). The *trans*-2 : *cis*-4-form was pale yellow but the colour of the *trans*-2 : *trans*-4-form was unaltered. Their infra-red spectra showed that no appreciable stereomutation had occurred.

Infra-red Spectra.—These (cf. Figs. 2 and 3) were measured on a Grubb-Parsons single-beam instrument with rock-salt optics (see Part I for further details). The author is much indebted to Dr. W. C. Price for these facilities.

The spectra of the stereoisomeric *N*-*iso*butyldeca-2 : 4-dienamides are tabulated below. For abbreviations, see Part III. All samples are liquid films except the *trans*-2 : *trans*-4-amide (paraffin mull).

trans-2 : *trans*-4. 3295 ms, 3075 mw, 2898 s, 2709 w, 1654 s, 1625 s, 1614 s, 1550 s, 1457 s, 1374 s, 1338 m, 1311 mw, 1260 m (i), 1254 m, 1207 mw, 1187 w, 1159 m, 1126 w, 1066 w, 1038 w, 994 s, 943 mw, 920 w, 890 w, 875 m, 856 w, 843 w, 818 mw, 737 mw, 722 mw, 681 mw cm.$^{-1}$.

trans-2 : *cis*-4. 3285 ms, 3076 mw, 2957 s, 2937 s, 2867 s, 1653 s, 1623 s, 1609 ms, 1549 s, 1466 s, 1389 mw, 1368 mw, 1328 m, 1272 m, 1210 mw, 1157 mw, 1101 w, 993 ms, 963 m, 923 w, 870 m, 819 w, 775 m, 729 w cm.$^{-1}$.

cis-2 : *trans*-4. 3285 ms, 3090 w, 2960 s, 2930 s, 2865 ms, 1650 s, 1632 s, 1605 ms, 1546 s, 1464 ms, 1436 ms, 1395 mw, 1369 mw, 1341 w, 1302 w, 1262 ms, 1231 ms, 1270 w, 1156 mw, 1126 w, 1086 w, 998 m, 961 m, 932 w, 922 w, 876 w, 858 w, 823 m, 811 m (i), 729 w cm.$^{-1}$.

cis-2 : *cis*-4. 3285 ms, 3075 mw, 2945 s, 2924 s, 2860 ms, 1720 w, 1649 s, 1628 s, 1595 ms (i), 1546 s, 1466 ms, 1436 m, 1387 mw, 1370 mw, 1340 mw, 1327 mw (i), 1270 m, 1252 m, 1215 mw, 1169 mw, 1157 m, 1126 w, 1101 mw, 994 m, 962 m, 920 w, 911 mw, 824 m, 726 w cm.$^{-1}$.

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