*Amides of Vegetable Origin. Part VII.** *Synthesis of* N-iso*Butyldodeca-*trans-2 : trans-4 : trans-8- *and* trans-2 : trans-4 : cis-8-*trienamide and Their Relation to Sanshoöl I.*

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Consideration of the light absorption of sanshoöl I, the accepted gross structure of which is *N-iso*butyldodeca-2 : 4 : 8-trienamide (I), suggests that if the structure is correct, it must have a *trans*-2 : *trans*-4-configuration. The two possible stereoisomers, *trans*-2 : *trans*-4 : *trans*-8- and *trans*-2 : *trans*-4 : *cis*-8- are stereospecifically synthesised. Neither is identical with sanshoöl I. There are other discrepancies in the published spectroscopic data for sanshoöl I and it is concluded that either structure (I) is incorrect or else the amide has never been obtained in a state approaching purity. Synthesis of other stereoisomers has therefore been suspended.

The fruits of the Japanese tree *Zanthoxylum piperitum* D.C. are used as an anthelmintic and contain an insecticidal sialogogue sanshoöl I. This, on hydrogenation, yields *N-iso*butyldodecanamide (Murayama and Shinozaki, *J. Pharm. Soc. Japan*, 1931, **51**, 379; Asano and Kanematsu, *ibid.*, p. 384; Asano and Aihara, *ibid.*, 1949, **69**, 79). Fresh bark is a better source of sanshoöl I and in addition is a good source of the less pungent component sanshoöl II (Aihara, *ibid.*, 1950, **70**, 43). Sanshoöl I is very unstable to air, absorbs hydrogen equivalent to 3·24 double bonds over a palladium catalyst, and on oxidation with permanganate yields *N-iso*butyloxamic, succinic, oxalic, and butyric acid. Its ultraviolet-light absorption ($\lambda_{max.}$ 267·5 mμ, ε 33,000) indicates, according to Aihara (*loc. cit.*), the presence of a conjugated dienamide chromophore, and on this basis he considers sanshoöl I to be *N-iso*butyldodeca-2 : 4 : 8-trienamide (I).

$$CH_3{\cdot}[CH_2]_2{\cdot}CH{:}CH{\cdot}[CH_2]_2{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CO{\cdot}NHBu^i \quad (I)$$

This paper reports limited syntheses in this field. There are eight possible stereoisomers of the triene (I) but if the gross structure proposed by Aihara is correct, and his preparation is uncontaminated by impurity having strong light absorption in the 267·5 mμ region, only those isomers with a *trans*-2 : *trans*-4-diene system can be entertained. This follows from the extinction coefficient since absorption data for the four stereoisomeric *N-iso*butyldeca-2 : 4-dienamides (Part V, Crombie, *J.*, 1955, 1007) suggest that any *cis*-containing combination of linkages in the 2 : 4-diene system of sanshoöl I would give rise to a value of less than ~26,000. Confirmatory information might come from infrared absorption measurements or ease of reaction with maleic anhydride but these have not been reported for the natural product. Accepting this simplifying evidence, we have now prepared the two stereoisomers with *trans*-2 : *trans*-4-linkages.

Table 1. *Dodeca*-2 : 4 : 8-*trienoic acids.*

	M. p.	*p*-Bromophenacyl ester, m. p.	*N-iso*Butylamide, m. p.	Unsatn.
all-*trans*	80—81°	128°	97—98°	2·8
trans-2 : *trans*-4-*cis*-8	23—23·5	87—87·5	62—63	3·1

* No. of double bonds determined by microhydrogenation of the *iso*butylamide.

All-*trans*-(I) was synthesised by application of the coupling reaction reported in Part II (Crombie, *J.*, 1952, 4388) which gives the crude enyne hydrocarbon (II). By a series of steps, applied previously in a similar case (Crombie, *Chem. and Ind.*, 1952, 1034; Part V, *loc. cit.*), this was converted into the crystalline *trans*-2 : *trans*-4 : *trans*-8-acid (IV) and its *iso*butylamide. Properties of these compounds are summarised in Table 1.

The *trans*-2 : *trans*-4 : *cis*-8-amide (I) was built up from nona-1 : 5-diyne, prepared by

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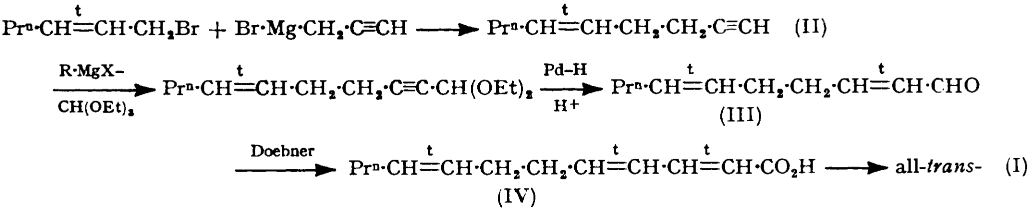
* Part VI, *J.*, 1955, 1025.

Raphael and Sondheimer's method (*J.*, 1950, 120). This was converted into 1 : 1-diethoxydeca-2 : 6-diyne and thence, by semi-hydrogenation, into the *cis-cis*-diene acetal whence acidic hydrolysis produced the *trans*-2 : *cis*-6-diene aldehyde (III), inversion of configuration occurring only at the 2 : 3-position (for references see Part V); Raphael and Sondheimer (*J.*, 1951, 2693) used this reaction in a similar case. Properties of the two stereoisomeric deca-2 : 6-dienals prepared in this investigation are summarised in Table 2. The aldehydes have extremely persistent odours, detectable at high dilution, in line with their being higher homologues of the perfume, violet leaf aldehyde, nona-2 : 6-dienal (Sondheimer, *J. Amer. Chem. Soc.*, 1952, **74**, 4040). The 2 : 4-dinitrophenylhydrazone of the *cis-trans*-aldehyde was obtained in two forms, which had identical melting points, ultraviolet light absorptions, and infrared spectra (paraffin mulls), and there is no doubt that they are polymorphs and not geometrical isomers about the C=N linkage as has sometimes been found (cf. Ramirez and Kirby, *ibid.*, 1954, **76**, 1037).



$$\mathrm{Pr^n{\cdot}CH\overset{t}{=}CH{\cdot}CH_2Br + Br{\cdot}Mg{\cdot}CH_2{\cdot}C{\equiv}CH \longrightarrow Pr^n{\cdot}CH\overset{t}{=}CH{\cdot}CH_2{\cdot}CH_2{\cdot}C{\equiv}CH} \quad \text{(II)}$$

$$\xrightarrow[\mathrm{CH(OEt)_3}]{\mathrm{R{\cdot}MgX-}} \mathrm{Pr^n{\cdot}CH\overset{t}{=}CH{\cdot}CH_2{\cdot}CH_2{\cdot}C{\equiv}C{\cdot}CH(OEt)_2} \xrightarrow[\mathrm{H^+}]{\mathrm{Pd-H}} \underset{\text{(III)}}{\mathrm{Pr^n{\cdot}CH\overset{t}{=}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH\overset{t}{=}CH{\cdot}CHO}}$$

$$\xrightarrow{\text{Doebner}} \underset{\text{(IV)}}{\mathrm{Pr^n{\cdot}CH\overset{t}{=}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH\overset{t}{=}CH{\cdot}CH\overset{t}{=}CH{\cdot}CO_2H}} \longrightarrow \text{all-}trans\text{-} \quad \text{(I)}$$

TABLE 2. *Deca-2 : 6-dienals.*

2 : 3	6 : 7	$\lambda_{max.}$ (mμ)	ε	2 : 4-Dinitrophenylhydrazone			
					M. p.	$\lambda_{max.}$[b]	ε
trans	*trans*	217	12,500	Flat, orange needles	125·5°	375	30,000
cis	*trans*	217	13,500	Red-orange needles	115—116	375	27,000
				Yellow plates	115—116	374	26,500

[a] In hexane. [b] In chloroform.

In an alternative approach to the *trans-cis*-series, coupling of hex-*cis*-2-enyl chloride and propargylmagnesium bromide gave the crude hydrocarbon (II), and among other contaminants allenic material was present. Conversion into the decadienal was carried out as in the *trans-trans*-series. The product was shown to have the *trans*-2 : *cis*-6-configuration by conversion into the 2 : 4-dinitrophenylhydrazone and comparison with the specimens obtained as above. Configuration of the *cis*-halide involved in the coupling must therefore be largely retained. This, and related reactions of geometrically isomeric allylic compounds, will be discussed elsewhere.

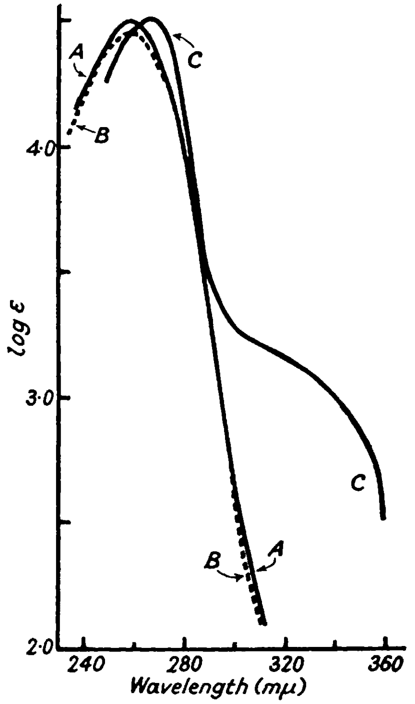
Infrared spectra of the two stereoisomeric deca-2 : 4 : 8-trienoic acids and amides have been examined and relevant data are in Table 3. The *trans*-2 : *trans*-4 : *trans*-8-trienamide is particularly interesting. From our previous data (Part V) we would expect one strong band in the out-of-plane deformation region to be present at 994 cm.$^{-1}$ because of the *trans*-2 : *trans*-4-diene system, and one at *ca.* 968 cm.$^{-1}$ because of the internal *trans*-linkage. Both are present. However, had the stereochemistry of this compound not been known from stereospecific synthesis, the two vibrations might alternatively have been ascribed

TABLE 3. *Infrared assignments* (*cm.*$^{-1}$) *for dodecatrienoic acids and amides.*[a]

2 : 3	4 : 5	8 : 9	NH		C=O	C=C$_{I}$	C=C$_{II}$	ΔC=C	δ′(CH=CH)$_2$	
					iso*Butylamides*[b]					
trans	*trans*	*trans*	3265	3060	1623	1655	1613	42	993	967
trans	*trans*	*cis*	3295	3060	1626	1657	1618	39	998	—
					Acid					
trans	*trans*	*trans*	—	—	1684	1634	1610	24	1005	968
trans	*trans*	*cis*	—	—	1684	1636	1613	23	1000	—

[a] Paraffin mulls. [b] See Part V, Table 9, for comparative data.

to a *cis*-2 : *trans*-4- or *trans*-2 : *cis*-4-diene*iso*butylamide system since two vibrations, at approximately 995 and 962 cm.$^{-1}$, are characeristic of this (Part V). The example emphasises the need for care in application of infrared correlations in complex molecules. As expected, only one strong band at 998 cm.$^{-1}$ is found for a *trans*-2 : *trans*-4 : *cis*-8-compound in the region under consideration. Both stereoisomeric amides have C=C stretching vibrations in the position expected for a *trans*-2 : *trans*-4-diene.



Absorption spectra of (*A*) N-iso*butyldeca*-trans-2 : trans-4 : trans-8-*trienamide*, (*B*) *its* trans-2 : trans-4 : cis-8-*isomer*, *and* (*C*) *sanshoöl* I (*Aihara's curve*).

N-*iso*Butyldodeca-*trans*-2 : *trans*-4 : *cis*-8-trienamide is physiologically more active than the all-*trans*-isomer. It is a more potent sialogogue and has knock-down and low toxicity towards *Tenebrio molitor* (the first completely synthetic *iso*butylamide to show significant toxicity towards this insect) : the all-*trans*-compound is almost inactive in these respects. When tested against houseflies the *trans*-2 : *trans*-4 : *cis*-8- was markedly more effective than the all *trans*-isomer but only about half as effective as *N*-*iso*butyldeca-*trans*-2 : *trans*-4-dienamide. [Testing of the four stereoisomers of the latter structure (Part V) has now been completed against houseflies. Like the *trans*-2 : *cis*-4-, the *cis*-2 : *trans*-4- and the *cis*-2 : *cis*-4-diene*iso*butylamides are only about one-tenth as toxic as the *trans*-2 : *trans*-4-compound, stressing the dependence of physiological activity on stereochemistry in these compounds.]

The melting points of both *N*-*iso*butyldeca-2 : 4 : 8-trienamides and the lack of physiological effects from the all-*trans*-isomer make it impossible to equate either of them with natural sanshoöl I which, according to Aihara, is an oil, difficult to crystallise from any solvent, though solidifying at room temperature. Either sanshoöl I is not (I) or else the natural stereoisomer of gross structure (I) has not yet been isolated pure. The position of its maximal absorption is at appreciably longer wavelengths than is usual for a conjugated dienamide (see Figure and Table 4) and Aihara's curve has a strong inflexion at long wavelength which is inexplicable for a compound of gross structure (I).

In the light of these results we have postponed further synthetic work on stereoisomers of the amide (I) until natural sanshoöl I has been re-examined.

TABLE 4. *Ultraviolet-light absorption data for decadienoic and dodecatrienoic acid derivatives* (*in absolute ethanol*).

2 : 3	4 : 5	8 : 9		Acid	*N*-*iso*Butylamide	*p*-Bromophenacyl ester
trans	*trans*	*trans*	$\lambda_{max.}$	259	259	264
			ε	27,000	32,000	48,500
trans	*trans*	*cis*	$\lambda_{max.}$	259	259	264
			ε	25,500	29,000	49,000
trans	*trans* [a]	—	$\lambda_{max.}$	257	258	263
			ε	28,500	29,500	52,000

[a] See Part V for data on the remaining three stereoisomers.

EXPERIMENTAL

Analyses and light-absorption measurements were carried out in the microanalytical (Mr. F. H. Oliver) and spectrographic (Mrs. I. Boston and Mr. R. L. Erskine, B.Sc.) laboratories of this Department. The ultraviolet absorptions were determined with a Unicam instrument unless otherwise stated (I.B.) and the infrared absorptions with a Grubb-Parsons double beam instrument (R.L.E.). For further data see Tables.

1 : 1-*Diethoxydeca*-trans-6-*en*-2-*yne*.—Crude nona-*trans*-5-en-1-yne was prepared by treating propargylmagnesium bromide (from propargyl bromide, 46·0 g., and magnesium, 9·2 g.) in anhydrous ether (120 ml.) with *trans*-hex-2-enyl bromide (57·0 g.) [Bouis, *Ann. Chim.* (*France*), 1928, **9**, 403] in ether (60 ml.). For details see Crombie (Part II). The crude product had b. p. 144—155° (22·5 g.), n_D^{21} 1·4520—1·4525, and was contaminated with halogen-containing impurity.

Crude nona-5-en-1-yne (22·5 g.) in dry ether (50 ml.) was added to a Grignard reagent prepared from magnesium (4·88 g.) and ethyl bromide (26 g.) in ether (100 ml.). The product was heated under reflux (2 hr.), then cooled, and ethyl orthoformate (35 g.) was added dropwise. After further heating under reflux (6 hr.) the ether was evaporated and the residue maintained at 100° (1 hr.), cooled, and treated with ether and saturated ammonium chloride solution. The organic layer was isolated with ether, washed with saturated ammonium chloride solution, then water, and dried ($MgSO_4$). Solvent and excess of ethyl orthoformate were evaporated and the residue, when distilled, gave 1 : 1-*diethoxydeca*-trans-6-*en*-2-*yne* (10·7 g.), b. p. 86°/0·5 mm., n_D^{20} 1·4520 (Found : C, 74·35; H, 10·95. $C_{14}H_{24}O_2$ requires C, 74·9; H, 10·8%).

1 : 1-*Diethoxydeca*-cis-2 : trans-6-*diene*.—The above enyne (10·24 g.) was mixed with ethyl acetate (50 ml.) and added to pre-hydrogenated Lindlar catalyst (2·0 g.) in ethyl acetate (50 ml.). This mixture was shaken in hydrogen until 965 ml./N.T.P. had been absorbed (calc. for absorption of 1 mol., 1025 ml./N.T.P.). As the hydrogenation became slow, fresh catalyst (6·0 g.) was added after 780 ml. of gas had been absorbed. Filtration, evaporation, and distillation gave 1 : 1-*diethoxydeca*-cis-2 : trans-6-*diene* (8·6 g.), b. p. 78—80°/0·8 mm., n_D^{19} 1·4509 (Found : C, 74·7; H, 11·45. $C_{14}H_{26}O_2$ requires C, 74·35; H, 11·6%).

Deca-trans-2 : trans-6-*dienal*.—1 : 1-Diethoxydeca-*cis*-2 : *trans*-6-diene (9·2 g.) was rapidly steam-distilled from 2N-sulphuric acid (150 ml.). The distillate (350 ml.) was saturated with salt and throughly extracted with ether. The extracts were dried and evaporated and the trans-2 : trans-6-*diene aldehyde* (5·2 g.) distilled; it had b. p. 72—74°/0·1 mm., n_D^{20} 1·4678 (Found : C, 79·1; H, 10·8. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). The 2 : 4-*dinitrophenylhydrazone* crystallised from 95% ethanol in flat orange needles. It melted completely at 125·5° after sudden shrinkage to a turbid liquid at 124° (Found : C, 57·7; H, 6·0; N, 16·9. $C_{16}H_{20}O_4N_4$ requires C, 57·8; H, 6·0; N, 16·8%).

Dodeca-trans-2 : trans-4 : trans-8-*trienoic Acid*.—Deca-*trans*-2 : *trans*-6-dienal (5·2 g.) was added to an ice-cold mixture of malonic acid (4·27 g.) and anhydrous pyridine (4 ml.) and set aside at 25° (48 hr.). Two phases which were formed initially disappeared by the end of this time. The product was heated at 110° (1 hr.), cooled, and acidified with ice-cold 50% sulphuric acid, and the acidic and neutral materials were extracted with light petroleum (b. p. 40—60°). The *acid* was extracted from this with 10% sodium hydroxide solution and purified in the usual way. On distillation it had b. p. 140—150°/0·05 mm. (2·34 g.) and crystallised. After one crystallisation from light petroleum (b. p. 40—60) it had m. p. 70—73° raised after three crystallisations to m. p. 80—81° (shining plates) (Found : C, 73·95; H, 9·5. $C_{12}H_{18}O_2$ requires C, 74·2; H, 9·35%). The p-*bromophenacyl ester* formed flat needles from ethanol (Found : Br, 20·5. $C_{20}H_{23}O_3Br$ requires Br, 20·45%).

N-iso*Butyldodeca*-trans-2 : trans-4 : trans-8-*trienamide*.—The foregoing acid (0·21 g.) was treated with a slight excess of thionyl chloride and set aside overnight. After being heated under reflux for 20 min. the product was distilled and the acid chloride collected (b. p. 110—120°/0·25 mm.), treated in anhydrous ether with excess of ethereal *iso*butylamine, and poured into water. The mixture was extracted with ether, and the extract washed with N-sodium hydroxide, N-hydrochloric acid, and water. After drying and evaporation the *product* crystallised from light petroleum (b. p. 40—60°) as needles (150 mg.) (Found : C, 76·7; H, 10·65. $C_{16}H_{27}ON$ requires C, 77·05; H, 10·9%).

1-*Chlorohex*-cis-2-*ene*.—Pent-1-ynylmagnesium bromide was prepared from pent-1-yne (40·8 g.) in ether in the usual way and converted into hex-2-yn-1-ol (38 g., 65%; b. p. 100°/53 mm., n_D^{17} 1·4540) by treatment with gaseous formaldehyde according to the method of Newman and Wotiz (*J. Amer. Chem. Soc.*, 1949, **71**, 1292). The 3 : 5-dinitrobenzoate had m. p. 67° (Newman and Wotiz give b. p. 87—89°/58 mm.; 3 : 5-dinitrobenzoate, m. p. 64—65°).

Hex-2-yn-1-ol (40·0 g.) was hydrogenated in ethyl acetate (50 ml.) with a pre-reduced palladium–calcium carbonate catalyst (5%; 3 g.) until 9·14 l. of hydrogen had been absorbed at N.T.P. The catalyst was removed, solvent evaporated, and the residue distilled, giving *cis*-hex-2-en-1-ol (28·8 g.), b. p. 90—91°/56 mm., n_D^{22} 1·4363. This alcohol (280 g.) in pyridine

(8·0 g.) was treated at −10° to −15° with phosphorus trichloride (18 g.) with vigorous stirring, then stirred for 1 hr. at −10° and 1 hr. at 25°. The crude chloride (33 g.) was isolated by distillation at 0·05 mm. When washed with sodium hydrogen carbonate solution and then with water and distilled, the *chloride* (17·3 g.) had $n_{\mathrm{D}}^{19\cdot5}$ 1·4430 (Found : C, 61·5; H, 9·65. $C_6H_{11}Cl$ requires C, 60·75; H, 9·3%). It showed only weak absorption at ~966 cm.$^{-1}$.

Preparation of 1 : 1-*Diethoxydeca*-cis-6-*en*-2-*yne by the Coupling Method.*—The coupling was carried out with propargyl bromide (18·5 g.), magnesium (3·74 g.), and 1-chlorohex-*cis*-2-ene (17·3 g.) under conditions similar to those described in Part II. Crude hydrocarbon (21·9 g.), b. p. 130—140°, n_{D}^{21} 1·4650—1·4700, was collected by distillation. Halogen was present and the infrared spectrum showed the presence of allene (1963 cm.$^{-1}$) as well as monosubstituted acetylene (3250, 2135 cm.$^{-1}$).

Crude hydrocarbon (21·9 g.) in ether (30 ml.) was added to ethylmagnesium bromide (from magnesium, 4·5 g.) in ether (150 ml.), stirred for 1 hr. at 25°, and then refluxed for 1 hr. Ethyl orthoformate (25 g.) was added after cooling and the mixture refluxed for 6 hr. in nitrogen. The ether was removed by distillation, the residue heated for 1 hr. on the steam-bath, and cold saturated ammonium chloride added. Extraction with ether, washing, drying, and distillation gave 1 : 1-*diethoxydec*-cis-6-*en*-2-*yne* (2·0 g.), b. p. 104°/0·5 mm., $n_{\mathrm{D}}^{20\cdot5}$ 1·4581 (Found : C, 74·7; H, 10·8. $C_{14}H_{24}O_2$ requires C, 74·95; H, 10·8%).

Deca-trans-2 : cis-6-*dienal.*—The enyne acetal (1·91 g.) was hydrogenated in purified light petroleum (20 ml.; b. p. 80—100°) with pre-hydrogenated Lindlar catalyst (1·2 g.). Gas absorption ceased when 180 ml. of hydrogen at N.T.P. had been absorbed (calc. for semi-reduction of the acetylenic linkage, 198 ml. at N.T.P.). Filtration, evaporation, and distillation gave 1 : 1-diethoxy-*cis*-2 : *cis*-6-diene, b. p. 80°/0·5 mm., $n_{\mathrm{D}}^{22\cdot5}$ 1·4470.

The acetal (0·5 g.) was steam-distilled from 2N-sulphuric acid, and the distillate (25 ml.) saturated with salt, and thoroughly extracted with ether. Drying, evaporation, and distillation gave the trans-2 : cis-6-*diene aldehyde*, b. p. 59—60°/0·1 mm., $n_{\mathrm{D}}^{21\cdot5}$ 1·4730 (Found : C, 78·95; H, 10·6. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). Its 2 : 4-dinitrophenylhydrazone had m. p. 114—115°, undepressed (114—116°) when admixed with the 2 : 4-dinitrophenylhydrazone of deca-*trans*-2 : *cis*-6-dienal prepared by the stereospecific method described below.

Nona-1 : 5-*diyne.*—Hexa-1 : 5-diene, prepared by Turk and Channan's method (*Org. Synth.*, 1949, **27**, 7), was converted into the tetrabromide in 92% yield. The latter (620 g.) was dehydrobrominated according to Raphael and Sondheimer's directions (*J.*, 1950, 120) with sodamide from sodium (310 g.) and ferric nitrate (3 g.) in liquid ammonia (5 l.), to give hexa-1 : 5-diyne (54 g.; 47%), b. p. 89—90°, $n_{\mathrm{D}}^{27\cdot5}$ 1·4342. Monoalkylation according to the same authors' directions gave nona-1 : 5-diyne (54·3 g., 45%), b. p. 80°/10—12 mm., $n_{\mathrm{D}}^{19\cdot5}$ 1·4560, from hexa-1 : 5-diyne (78 g.) and propyl iodide (180 g.). Raphael and Sondheimer (*loc. cit.*) give b. p. 87·5—88·5°/758 mm., n_{D}^{23} 1·4380—1·4382, for hexa-1 : 5-diyne and b. p. 62°/19 mm., n_{D}^{21} 1·4562—1·4565, for nona-1 : 5-diyne.

1 : 1-*Diethoxydeca*-2 : 6-*diyne.*—Nona-1 : 5-diyne (54·3 g.) in ether (100 ml.) was added to ethylmagnesium bromide, prepared from magnesium (11·95 g.) and ethyl bromide (60 g.) in ether (160 ml.), and heated under reflux for 2 hr. Ethyl orthoformate (80 g.) was added and refluxing continued for 6 hr. The ether was then distilled, the residue heated on a steam-bath for 1 hr., then cooled, and saturated ammonium chloride solution and ether were added. Washing, drying, and distillation of the organic layer gave 1 : 1-*diethoxydeca*-2 : 6-*diyne* (68 g.), b. p. 96—98°/0·15 mm., 108°/0·35 mm., n_{D}^{19} 1·4599 (Found : C, 75·7; H, 10·1. $C_{14}H_{22}O_2$ requires C, 75·65; H, 9·95%).

Deca-trans-2 : cis-6-*dienal.*—The diyne acetal (14·9 g.) was hydrogenated in ethyl acetate (40 ml.) and quinoline (1 ml.) containing Lindlar catalyst (8 g.). When 3·01 l. (N.T.P.) of hydrogen had been absorbed, reaction was stopped (gas absorption had almost ceased) and the mixture filtered. The filtrate was washed with 2N-hydrochloric acid to remove quinoline, then with water, and dried. On evaporation of the solvent the strong aldehyde odour suggested that some hydrolysis had taken place. 1 : 1-Diethoxydec-*cis*-2 : *cis*-6-diene was therefore not purified but the crude acetal was steam-distilled from 2N-sulphuric acid (110 ml.). In a second experiment in which neither quinoline nor acid treatment was employed, 1 : 1-*diethoxydeca*-cis-2 : cis-6-*diene* (70%), b. p. 86°/0·35 mm., n_{D}^{23} 1·4485, was isolated (Found : C, 74·45; H, 11·5%). The steam-distillate was saturated with salt and extracted with ether. These extracts were dried, evaporated, and distilled, to give deca-*trans*-2 : *cis*-6-dienal (7·5 g.), b. p. 58—60°/0·2 mm. (Found : C, 78·9; H, 10·7%). The 2 : 4-*dinitrophenylhydrazone* (Found : C, 57·7; H, 6·0%) was obtained as red-orange needles by slow crystallisation from ethanol. Yellow plates with marked electrostatic properties separated from the filtrate and also when the needle form was dissolved and crystallised from hot ethanol. Both forms had m. p. 115—116° and this was not depressed on admixture. When admixed with the 2 : 4-dinitrophenylhydrazone of the ***trans-trans***-aldehyde there was a marked depression of m. p.

Dodeca-trans-2 : trans-4 : cis-8-*trienoic Acid*.—The *trans*-2 : *cis*-4-aldehyde (7·3 g.) was added with shaking to finely powdered malonic acid (5·9 g.) in anhydrous pyridine (4·5 ml.) at 0° and set aside for 48 hr. at 25°. The mixture was then worked up as described for the all-*trans*-acid and distilled, to give crude *acid* (3·6 g.), b. p. 135—148°/0·07 mm., n_D^{20} 1·5110—1·5210. It was purified by crystallisation at −5° from light petroleum (b. p. 40—60°) and then had m. p. 23—23·5° (needles) (Found : C, 74·3; H, 9·5%). Its p-*bromophenacyl ester* formed plates from a small volume of 95% ethanol (Found : C, 61·3; H, 6·2. $C_{20}H_{23}O_3Br$ requires C, 61·3; H, 6·0%).

N-iso*Butyldodeca*-trans-2 : trans-4 : cis-8-*trienamide*.—This *amide* was prepared in a similar manner to the all-*trans*-amide and crystallised at low temperature from light petroleum (b. p. 60—80°) (Found : C, 76·85; H, 10·85%).

Hydrogenation of the Triene Acids.—The all-*trans*- and the *trans*-2 : *trans*-4 : *cis*-8-acid were completely hydrogenated in acetic acid. After filtration, the solvent was evaporated. Without further purification the residues melted at 44·5° and 45° respectively and were not depressed on admixture with genuine lauric acid.

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