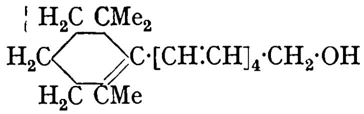
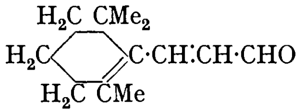
151. *Studies in the Synthesis of Vitamin-A. Part III.*

By J. W. Batty, A. Burawoy, I. M. Heilbron, W. E. Jones, and A. Lowe.

In Parts I and II (J., 1935, 585; 1936, 561) the preparation of a number of intermediates in the attempted synthesis of vitamin-A has been described, but since one of the main difficulties is the introduction of the side-chain methyl groups in the requisite positions, work has simultaneously been carried out with the object of synthesising ι-(2 : 2 : 6-trimethyl-Δ^6-*cyclo*hexenyl)-$\Delta^{\beta\delta\zeta\theta}$-nonatetraen-α-ol (I), which might be expected to resemble the vitamin in physiological properties. The key compound in this proposed synthesis, β-(2 : 2 : 6-trimethyl-Δ^6-*cyclo*hexenyl)acraldehyde (II) (β-*cyclo*citrylideneacetaldehyde), could theoretically be obtained by direct condensation of acetaldehyde either with β-*cyclo*citral or alternatively with citral and subsequent ring closure of the resultant α-aldehydo-δθ-dimethyl-$\Delta^{\alpha\gamma\eta}$-nonatriene (III) as in the conversion of ψ- into β-ionone. The extension of the side chain would then be effected by further condensation with acetaldehyde or crotonaldehyde Since preliminary experiments on condensations involving β-*cyclo*citral proved unpromising for reasons to be described in a subsequent publication, attention was concentrated on the alternative route.

(I.)





(II.)

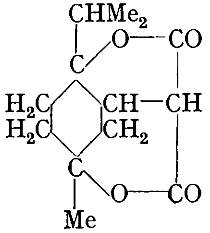
At the commencement of this work, the only method of preparation of α-aldehydo-δθ-dimethyl-$\Delta^{\alpha\gamma\eta}$-nonatriene (III) described in the literature, apart from a very brief statement concerning its formation by the condensation of citral with acetaldehyde in the presence of sodium hydroxide (Anon., *Chem. Zentr.*, 1932, I, 2104), was the reduction of the phenylimido-chloride of the corresponding acid with chromous chloride (v. Braun and Rudolph, *Ber.*, 1934, **67**, 1735). Since this method did not appear suited to the preparation of relatively large quantities of the aldehyde, an alternative route was investigated.

$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}CHO$

(III.)

$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH{:}C(CO_2H)_2$

(IV.)



(V.)

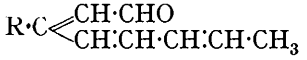
By the condensation of citral with malonic acid in the presence of pyridine, Verley (*Bull. Soc. chim.*, 1899, **21**, 415) obtained a mixture of δθ-dimethyl-$\Delta^{\alpha\gamma\eta}$-nonatriene-α-carboxylic acid and a solid which he assumed to be citrylidenemalonic acid. A detailed investigation of the latter compound, however, by Kuhn and Hoffer (*Ber.*, 1931, **64**, 1243) led these authors to the conclusion that it did not possess the structure (IV) but was more probably a cyclic dilactone (V).

In support of the view that (IV) cannot represent the true structure, we have found that, whereas such a substance would be expected to exhibit selective absorption in the region of 3000 A., the compound in question shows only general absorption and moreover fails to give acetone on treatment with ozonised oxygen. This anomalous behaviour appears to be limited to the compound under discussion, since the citrylidenecyanoacetic acid, m. p. 122°, of Tiemann (*Ber.*, 1898, **31**, 3329) exhibits a well-defined band at 3005 A. (Table II) and, in contrast to "citrylidenemalonic acid," is readily soluble in cold dilute sodium hydroxide solution. We have further ascertained that "citrylidenemalonic acid" is decarboxylated quantitatively on distillation under reduced pressure in presence of a trace of copper-bronze, giving δθ-dimethyl-$\Delta^{\alpha\gamma\eta}$-nonatriene-α-carboxylic acid, b. p. 125—130°/1 mm. (*methyl* ester, b. p. 137—140°/15 mm.), the facile formation of which is difficult to reconcile with formula (V).

Distillation of the barium salt of the monocarboxylic acid with barium formate under reduced pressure gives α-aldehydo-δθ-dimethyl-$\Delta^{\alpha\gamma\eta}$-nonatriene (III) in 30% yield, which shows a well-defined absorption band at 2900 A. (Table II), a position in good agreement with theoretical deductions. Contrary, however, to the observation of v. Braun and Rudolph (*loc. cit.*), who record two semicarbazones, m. p. 150° and 93—102°, we could only obtain one semicarbazone, m. p. 167°, in agreement with the findings of Kuhn, Badstübner, and Grundmann (*Ber.*, 1936, **69**, 104), who, while this work was in progress, published details of the preparation of (III) by condensation of citral with acetaldehyde in the presence of a piperidine–acetic acid catalyst. We have repeated the preparation of (III) according to the latter authors' method and find that both the aldehyde and its semicarbazone ($\lambda_{max.}$ 3045 A.; Table II) are spectroscopically identical with those obtained by the alternative method; further, no depression in m. p. was observed on admixture of the two semicarbazones.

α-Aldehydo-δθ-dimethyl-$\Delta^{\alpha\gamma\eta}$-nonatriene condenses readily with cyanoacetic acid in the presence of aqueous alkali, giving *α-cyano-ζχ-dimethyl-$\Delta^{\alpha\gamma\epsilon\iota}$-undecatetraene-α-carboxylic acid* (VI) as a viscous oil which, like citrylidenecyanoacetic acid (cf. Tiemann, *loc. cit.*), presumably consists of a mixture of isomers. Repeated extraction of the oil with light petroleum gave a crystalline solid, m. p. 150° ($\lambda_{max.}$ 3480 A.; Table II), which appeared to be a single modification of (VI); the remainder of the oil could not be obtained solid.

(VI.) $R{\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}CH{:}C(CN){\cdot}CO_2H$



$$R{\cdot}C\begin{cases}CH{\cdot}CHO\\ CH{:}CH{\cdot}CH{:}CH{\cdot}CH_3\end{cases}$$

(VII.)

(VIII.) $R{\cdot}CMe{:}CH{\cdot}[CH{:}CH]_2{\cdot}CHO$

$$R{\cdot}C\begin{cases}CH{\cdot}CH{:}CH{\cdot}CHO\\ CH{:}CH{\cdot}CH_3\end{cases}$$

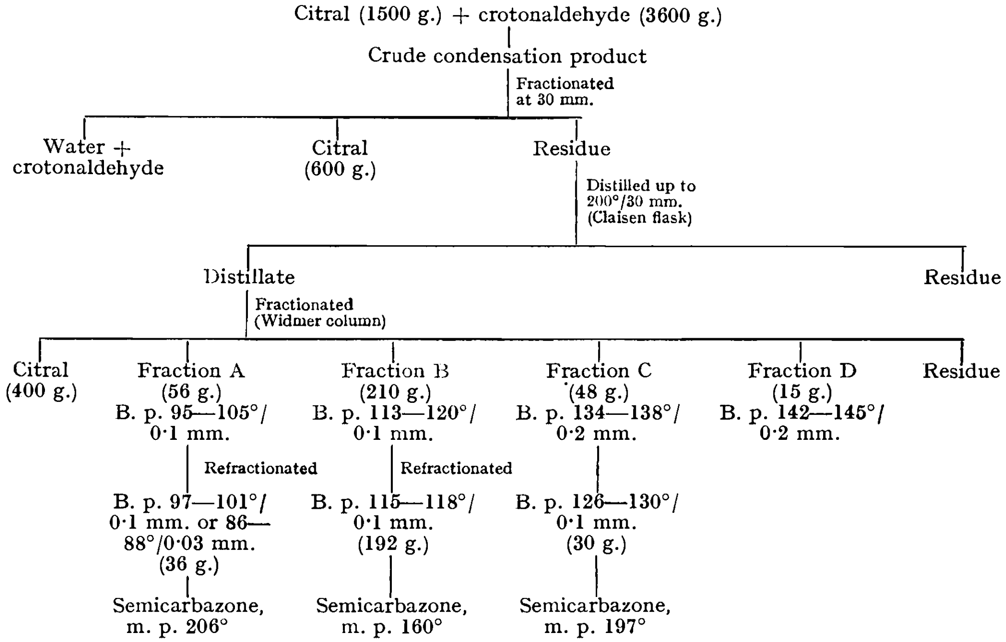
(IX.)

($R = CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2$.)

An examination of the mother-liquors from which the semicarbazone of (III), prepared by the method of Kuhn, Badstübner, and Grundmann (*loc. cit.*), had been isolated revealed the presence of a small quantity of a second *semicarbazone*, m. p. 158°. Analysis of this proved it to be derived from a condensation product of citral with two molecules of acetaldehyde and, on the assumption that it is an alicyclic compound, the fact that it shows a well-defined absorption band at 3255 A. (Table II) indicates the presence of a conjugated system of the type $>C{=}C{-}C{=}C{-}C{=}C{-}C{=}O$. On this evidence the parent aldehyde might be either (VII), (VIII), or (IX). In order to gain further information regarding this product, and also to explore the possibility of obtaining (VIII) directly, we have made a detailed study of the condensation of citral with crotonaldehyde, employing the piperidine–acetic acid catalyst. The general method of working up the complex reaction mixture is summarised in Table I, but so far only fractions A, B, and C have been examined in detail.

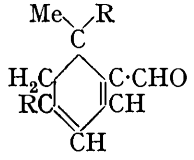
Fraction A.—Refractionation of this gave a main portion, b. p. 86—88°/0·03 mm. (36 g.), yielding a *semicarbazone*, m. p. 206°. This showed an absorption band at 3255 A. (Table II), from which it follows that it contains the same conjugated system as the semicarbazone, m. p. 158°, referred to above, with which, as shown by analysis, it is isomeric.

TABLE I.

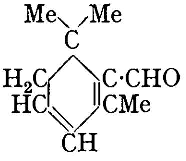


Fraction B.—Redistillation gave as main fraction (192 g.) a pale yellow oil, b. p. 115—118°/0·1 mm., from which a crude semicarbazone was obtained which on fractional crystallisation yielded a further small quantity of the compound, m. p. 206°. The main product consisted of a *semicarbazone*, m. p. 160°, spectroscopically identical with (Table II), and showing no depression in m. p. on admixture with, the semicarbazone, m. p. 158°, already referred to. The identity of these two compounds eliminates (IX) from further consideration.

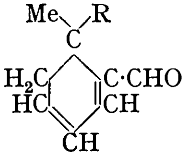
In any discussion of the structures of the aldehydes produced in this condensation, it is necessary to consider, in addition to the various open-chain types, the possibility of the formation of cyclic products. Bernhauer and Irrgang (*Annalen*, 1936, **525**, 43), from preliminary work on the condensation of citral with crotonaldehyde in the presence of baryta, and by analogy with their work on the intermolecular condensation of crotonaldehyde, concluded that their product probably possessed a cyclic structure. Further, Fischer and Löwenberg (*Annalen*, 1932, **494**, 278) have demonstrated that the action of sodamide on citral gives a good yield of a cyclic aldehyde for which structure (X) was tentatively advanced.



(X.)



(XI.)



(XII.)

That, however, the semicarbazone, m. p. 160°, is actually derived from an open-chain aldehyde was evidenced by quantitative microhydrogenation, which revealed the presence of five double bonds, including the semicarbazido-linkage. The further fact that the free *aldehyde*, $C_{14}H_{20}O$ (2 : 4-*dinitrophenylhydrazone*, m. p. 104—105°), regenerated from the semicarbazone by distillation with steam in presence of oxalic acid, has an absorption band at 3140 A. confirms the presence of the conjugated system observed in the case of the semicarbazone (cf. α-aldehydo-$\Delta^{\alpha\gamma\epsilon}$-heptatriene; Hausser, Kuhn, Smakula, and

Hoffer, *Z. physikal. Chem.*, 1935, **29**, 372). In order to differentiate between (VII) and (VIII) the aldehyde was treated with ozone : acetone and lævulaldehyde (isolated as its 2 : 4-dinitrophenylhydrazone) were obtained, a result proving that it is α-aldehydo-ζχ-dimethyl-$\Delta^{\alpha\gamma\epsilon\iota}$-undecatetraene (VIII).

The nature of the difference between the semicarbazones of m. p. 160° and 206° has yet to be determined, but that they are closely related is indicated by their absorption spectra, which, except for a slight difference in the extinction coefficients (Table II), are practically identical. This close similarity is also observed in the *phenylsemicarbazones*, m. p. 173° and 134°, which were obtained by heating the respective semicarbazones, m. p. 206° and 160°, with aniline.

Fraction C.—Redistillation gave a main fraction, b. p. 126—130°/0·1 mm. (30 g.), from which a *semicarbazone*, m. p. 197°, was obtained, which, although isomeric with those from fractions A and B, differs in possessing an absorption band at 2855 A. (Table II), indicating possibly a cyclic structure. That it does not possess structure (XII), however, would appear probable, since such a compound might be expected to show a close spectroscopic similarity to safranal (XI), the semicarbazone of which possesses a band at 3230 A. (Kuhn and Wendt, *Ber.*, 1936, **69**, 1550). Further work is at present in hand with the object of determining the structure of this aldehyde.

As mentioned elsewhere (Heilbron and Jones, *J. Soc. Chem. Ind.*, 1936, **55**, 813), a satisfactory method of converting α-aldehydo-ζχ-dimethyl-$\Delta^{\alpha\gamma\epsilon\iota}$-undecatetraene (VIII) into α-aldehydo-δ-(2 : 2 : 6-trimethyl-Δ^6-*cyclo*hexenyl)butadiene has been worked out and will be reported upon in the near future. The analogous condensation of citral with β-methylcrotonaldehyde is at present being investigated.

TABLE II.

	Compound.	B. p. or M. p.	$\lambda_{max.}$, A.	$\epsilon_{max.}$	Remarks.
(i)	$\mathrm{R{\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}CO_2H}$	B. p. 132—134°/ 1 mm.	2720	12,800	From "citrylidenemalonic acid"
(ii)	$\mathrm{R{\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}CHO}$	B. p. 105—108°/ 0·1 mm.	2900	15,960	From citral + acetaldehyde
(iii)	Semicarbazone of (ii)	M. p. 166—168°	3045	47,200	From citral + acetaldehyde
(iv)	,, ,, (ii)	M. p. 167°	3045	47,500	From distillation of barium salt of (i)
(v)	$\mathrm{R{\cdot}CMe{:}CH{\cdot}[CH{:}CH]_2{\cdot}CHO}$	B. p. 114—118°/ 0·05 mm.	3140	12,490	Regenerated from semicarbazone,m.p. 160°
(vi)	Semicarbazone of (v)	M. p. 158°	3255	28,000	Isolated from mother-liquors of (iii)
(vii)	,, ,, (v)	M. p. 160°	3255	27,100	From citral + crotonaldehyde
(viii)	Phenylsemicarbazone of (v)	M. p. 134°	3320	28,700	From (vii) + aniline
(ix)	Semicarbazone of fraction A	M. p. 206°	3255	24,400	—
(x)	Phenylsemicarbazone of fraction A	M. p. 173°	3320	26,600	From (ix) + aniline
(xi)	Semicarbazone of fraction C	M. p. 197°	2855	21,100	—
(xii)	Anil of (v)	B. p. 178—182°/ 15 mm.	2680	10,000	—
(xiii)	$\mathrm{R{\cdot}CMe{:}CH{\cdot}CH{:}C(CN){\cdot}CO_2H}$	M. p. 122°	3005	23,100	From citral + cyanoacetic acid
xiv)	$\mathrm{R{\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}CH{:}C(CN){\cdot}CO_2H}$	M. p. 150°	3480	34,100	From (ii) + cyanoacetic acid

Solvent, alcohol. $\mathrm{R = CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2}$.

EXPERIMENTAL.

δθ-*Dimethyl*-$\Delta^{\alpha\gamma\eta}$-*nonatriene*-α-*carboxylic Acid*.—" Citrylidenemalonic acid " (35 g., m. p. 186°), prepared as described by Verley (*loc. cit.*) and freed completely from ether-soluble products, was heated with copper-bronze (0·1 g.) at 130—140° (oil-bath temperature) for 1½ hours at 10—15 mm. The liquid residue was then distilled with a free flame, yielding a colourless oil, b. p. 130—135°/1 mm., which on redistillation gave the pure monocarboxylic acid (25 g.), b. p. 132—134°/1 mm.

Methyl δθ-*Dimethyl*-$\Delta^{\alpha\gamma\eta}$-*nonatriene*-α-*carboxylate*.—A solution of the above acid (50 g.) in aqueous sodium bicarbonate (23 g. in 500 c.c. of water) was shaken with methyl sulphate

(17 g.) for 24 hours at room temperature. The suspension was then ether-extracted, and the ethereal solution, after repeated washing with sodium carbonate solution, dried over sodium sulphate. The oil obtained after removal of solvent gave on distillation a main fraction (32 g.), b. p. 137—160°/12 mm., which on redistillation yielded the pure *methyl* ester as a pale yellow oil, b. p. 137—140°/15 mm. (Found : C, 75·2; H, 9·7. $C_{13}H_{20}O_2$ requires C, 75·0; H, 9·6%).

α-Aldehydo-δθ-dimethyl-$\Delta^{\alpha\gamma\eta}$-nonatriene (III).—Redistilled δθ-dimethyl-$\Delta^{\alpha\gamma\eta}$-nonatriene-α-carboxylic acid (24 g.) was dissolved in aqueous potassium hydroxide (7 g. in 60 c.c. of water) and a solution of barium chloride (15 g. in 70 c.c. of water) was slowly added with stirring. The precipitated barium salt, after being dried by suspension in benzene and distillation of the latter under reduced pressure, was thoroughly mixed with anhydrous barium formate (20 g.), and the whole diluted with an equal bulk of silver sand. After being maintained at 150—160°/1 mm. for 1 hour, the mixture was heated directly with a luminous flame until no more liquid distilled. The crude aldehyde (5·5 g.) on redistillation gave pure α-aldehydo-δθ-dimethyl-$\Delta^{\alpha\gamma\eta}$-nonatriene, b. p. 105—110°/0·1 mm. Its semicarbazone crystallised from methyl alcohol in short colourless needles, m. p. 167°, alone or mixed with a specimen, m. p. 166—168°, prepared by the method of Kuhn, Badstübner, and Grundmann (*loc. cit.*).

Condensation of Citral with Acetaldehyde.—Citral (76 g.) was condensed with acetaldehyde exactly as described by Kuhn, Badstübner, and Grundmann (*loc. cit.*), giving α-aldehydo-δθ-dimethyl-$\Delta^{\alpha\gamma\eta}$-nonatriene (14 g.) as a pale yellow oil, b. p. 125—135°/2 mm. The aldehyde (5 g.) was converted into its semicarbazone in the normal manner with alcoholic semicarbazide acetate, and the product fractionally crystallised. In confirmation of the results of Kuhn, Badstübner, and Grundmann, only one semicarbazone, m. p. 166—168°, of α-aldehydo-δθ-dimethyl-$\Delta^{\alpha\gamma\eta}$-nonatriene could be isolated. From the mother-liquors of the above semicarbazone, however, a small quantity of a *semicarbazone* of α-aldehydo-ζχ-dimethyl-$\Delta^{\alpha\gamma\epsilon\iota}$-undecatetraene was isolated by concentration. It crystallised from aqueous methyl alcohol in short colourless needles, m. p. 158° (Found : C, 69·1; H, 8·6; N, 16·0. $C_{15}H_{23}ON_3$ requires C, 69·0; H, 8·8; N, 16·1%).

For spectroscopic examination α-aldehydo-δθ-dimethyl-$\Delta^{\alpha\gamma\eta}$-nonatriene was regenerated from its semicarbazone by distillation in steam with 10% aqueous oxalic acid. It formed a pale yellow oil with an ester-like odour, b. p. 105—108°/0·1 mm.

Condensation of Citral with Crotonaldehyde.—A mixture of citral (250 g.) and crotonaldehyde (100 g.) containing a piperidine–acetic acid catalyst (10 g. of an equimolecular mixture of piperidine and glacial acetic acid in the minimum volume of absolute alcohol) was maintained at 110—120° (oil-bath temperature) in an atmosphere of carbon dioxide. When the internal temperature had reached 100—105°, a further quantity of crotonaldehyde (100 g.) was added : the procedure was repeated until a total of 600 g. of crotonaldehyde had been introduced; the reaction mixture was then maintained at 120° for 1 hour after the last addition of crotonaldehyde. The combined crude condensation product from six runs (1500 g. of citral), after removal of the aqueous layer, was fractionated at 30 mm., a Lapworth column being used to remove water, crotonaldehyde and citral. The residue was distilled from a Claisen flask, the whole of the material which distilled up to 200°/30 mm.being collected and fractionated through a Widmer column. The distillate was separated into the following fractions : (1) citral; (2) fraction A, b. p. 95—105°/0·1 mm.; (3) fraction B, b. p. 113—120°/0·1 mm. (210 g.); (4) fraction C, b. p. 134—138°/0·2 mm. (48 g.); (5) fraction D, b. p. 142—145°/0·2 mm. (15 g.).

Fraction A. After refractionation (Widmer column) this gave a pale yellow oil (36 g.), b. p. 86—88°/0·03 mm., which was treated with alcoholic semicarbazide acetate in the normal manner. The *semicarbazone* crystallised from methyl alcohol, in which it was sparingly soluble in the cold, in colourless needles, m. p. 206°, which slowly turned pale yellow in light (Found : C, 68·9; H, 8·8; N, 16·2. $C_{15}H_{23}ON_3$ requires C, 69·0; H, 8·8; N, 16·1%). For further characterisation the semicarbazone (1 g.) was heated for 15 minutes at 160—180° with aniline (2 g.). The residue was cooled, dissolved in 10% aqueous acetic acid, and extracted several times with ether, the ethereal solution then being washed successively with 10% acetic acid, sodium carbonate solution, and water. After drying over sodium sulphate and removal of the solvent, the residue was repeatedly crystallised from methyl alcohol, giving the corresponding *phenylsemicarbazone* in fine yellow needles, m. p. 173° (Found : C, 74·8; H, 8·1; N, 12·5. $C_{21}H_{27}ON_3$ requires C, 74·8; H, 8·0; N, 12·5%).

Fraction B. Refractionation (Widmer column) gave a main fraction (192 g.), b. p. 115—118°/0·1 mm., which was treated with semicarbazide acetate. Fractional crystallisation from methyl alcohol gave a small quantity of the above semicarbazone, m. p. 206°, and a more soluble isomeric *semicarbazone* crystallising from methyl alcohol in colourless needles, m. p.

160°, which also turned pale yellow on exposure to light (Found : C, 69·0; H, 8·8; N, 16·2. $C_{15}H_{23}ON_3$ requires C, 69·0; H, 8·8; N, 16·1%).

Quantitative microhydrogenation of the semicarbazone, m. p. 160°, by the method of Jackson and Jones (J., 1936, 895) gave the following results : 3·870 mg. of semicarbazone required 1·450 c.c. of hydrogen at 767·5 mm. and 16° (4·1 |=) in the cold, 1·650 c.c. (4·9 |=) on warming (solvent decalin).

The free *aldehyde* of fraction B, obtained by steam-distillation of the semicarbazone, m. p. 160°, with 10% aqueous oxalic acid, was a pale yellow oil, b. p. 114—118°/0·05 mm. (Found : C, 82·6; H, 9·8. $C_{14}H_{20}O$ requires C, 82·4; H, 9·8%). Its *phenylsemicarbazone*, prepared as described above, crystallised from methyl alcohol in yellow needles, m. p. 134° (Found : C, 74·9; H, 8·0; N, 12·3. $C_{21}H_{27}ON_3$ requires C, 74·8; H, 8·0; N, 12·5%). The aldehyde readily formed a 2 : 4-*dinitrophenylhydrazone* by heating with the reagent for a short time in glacial acetic acid, the product crystallising from dilute acetic acid in red micro-needles, m. p. 104—105° (Found : C, 62·6; H, 6·4; N, 14·8. $C_{20}H_{24}O_4N_4$ requires C, 62·5; H, 6·3; N, 14·6%). The *anil* was obtained by heating the aldehyde (10 g.) with aniline (4·5 g.) at 100° for 2 hours; the mixture was then cooled and ether-extracted, the solution dried over sodium sulphate, and the solvent removed. Distillation of the residue gave a main fraction, b. p. 225—230°/25 mm., which on refractionation gave the pure anil as a yellowish-brown viscous oil, b. p. 178—182°/15 mm. (Found : C, 85·7; H, 8·9; N, 4·8. $C_{20}H_{25}N$ requires C, 86·0; H, 9·0; N, 5·0%).

Ozonisation of α-*Aldehydo*-ζχ-*dimethyl*-$\Delta^{\alpha\gamma\epsilon\iota}$-*undecatetraene*.—Ozonised oxygen was passed through a solution of the aldehyde (2 g., regenerated from the semicarbazone, m. p. 160°) in carbon tetrachloride (30 c.c.) for 12 hours. The dark-coloured semi-solid ozonide obtained on removal of solvent by decantation was decomposed by refluxing with water for 1 hour, and the resultant clear solution steam-distilled. The first runnings contained acetone (2 : 4-dinitrophenylhydrazone, m. p. 128°) and the later distillate contained a product which reduced Fehling's solution and gave a yellow, sparingly soluble 2 : 4-dinitrophenylhydrazone. Crystallisation of the latter from nitrobenzene–alcohol gave yellow needles, m. p. 235—236°, which were identified as lævulaldehyde-2 : 4-dinitrophenylhydrazone (Strain, *J. Amer. Chem. Soc.*, 1935, **57**, 760) by comparison with an authentic specimen prepared by ozonisation of citral.

Fraction C. The *semicarbazone* from this fraction separated from methyl alcohol as a colourless microcrystalline powder, m. p. 197°, which, in contrast to the semicarbazones from fractions A and B, showed no tendency to turn yellow in light (Found : C, 68·8; H, 8·8; N, 16·0. $C_{15}H_{23}ON_3$ requires C, 69·0; H, 8·8; N, 16·1%).

α-*Cyano*-ζχ-*dimethyl*-$\Delta^{\alpha\gamma\epsilon\iota}$-*undecatetraene*-α-*carboxylic Acid* (VI).—α-Aldehydo-δθ-dimethyl-$\Delta^{\alpha\gamma\eta}$-nonatriene (5 g.) was shaken with a solution of cyanoacetic acid (4·5 g.) in aqueous sodium hydroxide (2 g. in 100 c.c.) until all the oil had disappeared (about ½ hour). After two extractions with ether, the aqueous suspension of the sodium salt of (VI) was acidified with dilute hydrochloric acid and ether-extracted. Removal of the solvent from the dried ethereal solution left a brown oil (5·5 g.), from which boiling ligroin (b. p. 80—100°) extracted a yellow solid. Repeated crystallisation of the latter from aqueous alcohol yielded one form of α-*cyano*-ζχ-*dimethyl*-$\Delta^{\alpha\gamma\epsilon\iota}$-*undecatetraene*-α-*carboxylic acid* (VI) as a pale yellow, microcrystalline solid, m. p. 150° (Found : C, 73·5; H, 8·0; N, 5·7. $C_{15}H_{19}O_2N$ requires C, 73·5; H, 7·8; N, 5·7%). All attempts to obtain the ligroin-insoluble portion of the condensation product solid have been unsuccessful.

The authors thank Imperial Chemical Industries Ltd. (Dyestuffs Group) for a scholarship awarded to one of them (A. L.).

THE UNIVERSITY, MANCHESTER. [*Received, March 6th*, 1937.]