534. *Amides of Vegetable Origin. Part IX.* Total Synthesis of Anacyclin and Related Trienediynamides.*

By L. Crombie and M. Manzoor-i-Khuda.

The structure proposed in Part IV for the natural amide anacyclin, *N-iso*butyltetradeca-*trans*-2 : *trans*-4-diene-8 : 10-diynamide, is confirmed by total synthesis. *N-iso*Butylnona-*trans*-2 : *trans*-4-dien-8-ynamide is first synthesised and then oxidatively cross-coupled with pent-1-yne. By partially hydrogenating synthetic anacyclin, *N-iso*butyltetradeca-*trans*-2 : *trans*-4 : *cis*-8 : *cis*-10-tetraenamide is isolated crystalline, with insecticidal activity. When *N-iso*butylnona-*trans*-2 : *trans*-4-dien-8-ynamide is cross-coupled with *cis*- and with *trans*-pent-2-en-4-yne, *N-iso*butyltetradeca-*trans*-2 : *trans*-4 : *cis*-12- and -*trans*-2 : *trans*-4 : *trans*-12-triene-8 : 10-diynamide are formed. These may be related to the contaminant of natural anacyclin which shows enediyne absorption in the ultraviolet region.

Infrared data reveal that maleic anhydride adducts of the above *N-iso*butyl-*trans*-2 : *trans*-4-dienamides are not anhydrides having a carboxyamide grouping but *N-iso*butylimides having a carboxylic acid group. This is established chemically by preparing the dihydro-adduct of *N-iso*butylsorbamide and maleic anhydride, identical with the dihydro-*N-iso*butylmaleimide adduct of 3-methylpenta-2 : 4-dienoic acid.

Anacyclin was recently isolated from the roots of *Anacyclus pyrethrum* DC. (pellitory) where it occurs with other insecticidal, unsaturated, lipid-*iso*butylamides.[1] The amide itself had little toxicity towards the grain insect *Tenebrio molitor*, but became potent after catalytic semihydrogenation of its two acetylenic linkages. Earlier work [1] indicated that it had structure (IX). This is now confirmed by a synthesis which has been summarised elsewhere.[2]

A necessary intermediate, hept-*trans*-2-en-6-yn-1-al (VI), has been described by Shaw and Whiting,[3] but we improved the reported yield (18%) of its precursor, hepta-2 : 6-diynoic acid, by employing " reversed addition " ; the Grignard reagent from hexa-1 : 5-diyne, prepared by adding 1 mol. of ethylmagnesium bromide to the hydrocarbon, gave, after carboxylation, 34% of hepta-2 : 6-diynoic acid (on a small scale yields of up to 53% were obtained). When the diyne hydrocarbon was added to the Grignard reagent as described by Shaw and Whiting, and the product carboxylated, the yield of unwanted octa-2 : 6-diyndioic acid (II) increased considerably at the expense of hepta-2 : 6-diynoic acid (III). The latter could be converted satisfactorily into its methyl ester by diazomethane, though if the mixture was set aside with an excess of the reagent a crystalline pyrazole, arising from attack at the α-acetylenic linkage, could be isolated. Methyl or ethyl hepta-2 : 6-diynoate was reduced by lithium aluminium hydride to hept-*trans*-2-en-6-yn-1-ol. Shaw and Whiting,[3] who were actually in need of the acid (V), report that oxidation of the enyne alcohol with chromic acid (4 equiv. per mol. of alcohol) gives 69% of hept-*trans*-2-en-6-yn-1-al and 11% of hept-*trans*-2-en-6-ynoic acid. In our work a preponderance of acid (70%) over aldehyde (23%) was obtained when 5·6 equiv. of chromic acid were used, but by reducing the amount to 2·7 equiv. the yield of aldehyde was raised to 62%.

Doebner reaction between hept-*trans*-2-en-6-ynal and malonic acid gave nona-*trans*-2 : *trans*-4-dien-8-ynoic acid (VII) which was converted, *via* the acid chloride, into *N-iso*butylnona-*trans*-2 : *trans*-4-dien-8-ynamide (VIII) in excellent yield. Glaser oxidative coupling with pent-1-yne (3 mol.) gave the cross-coupled material (IX) and only small

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* Part VIII, preceding paper.

[1] Crombie, *J.*, 1955, 999.

[2] Crombie and Manzoor-i-Khuda, *Chem. and Ind.*, 1956, 409.

[3] Shaw and Whiting, *J.*, 1954, 3217.

amounts of the symmetrical by-product (XI) were formed. Synthetic *N-iso*butyltetradeca-*trans*-2 : *trans*-4-diene-8 : 10-diynamide (IX) was a colourless solid which became pink in light and eventually deteriorated to an orange-red substance. It did not depress the m. p. of natural anacyclin, and spectral data support the identity (Table 1 and p. 2774). When hydrogenated (2 mol.) over Lindlar catalyst, synthetic anacyclin gave a crystalline tetrahydro-derivative which, on the basis that such reductions give largely stereospecific *cis*-addition of hydrogen to an acetylenic linkage, is formulated as *N-iso*butyltetradeca-*trans*-2 : *trans*-4 : *cis*-8 : *cis*-10-tetraenamide. Spectroscopic and other data are consistent with this formulation, and the tetraenamide is insecticidally active.

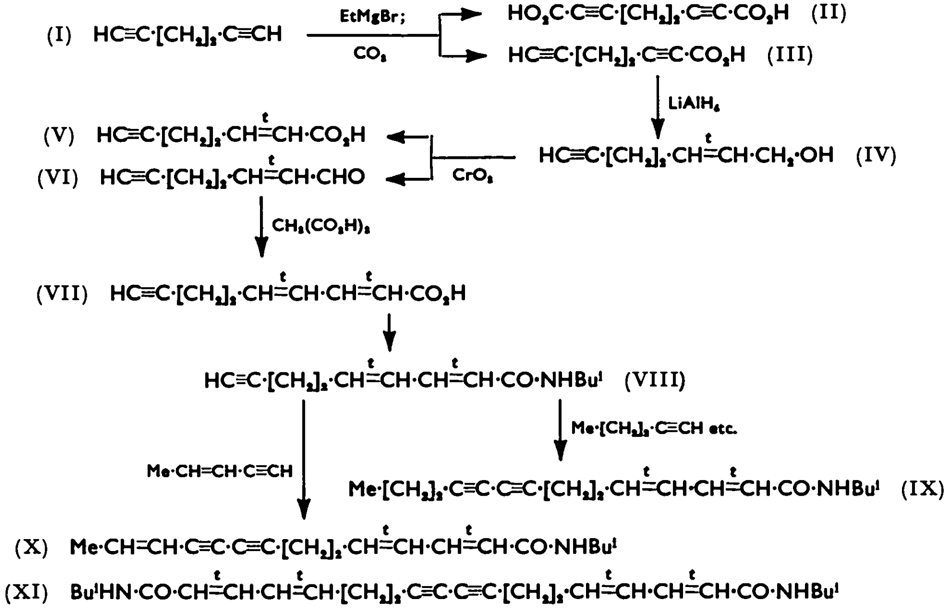

TABLE 1. *Natural and synthetic anacyclin.*

	M. p.	H_2 [b]	$\lambda_{max.}$ (mμ)	ε	Adduct,[c] m. p.
Natural anacyclin [a]	121°	5·8	259	33,500	193°
Synthetic anacyclin	121	6·1	258	34,000	193

[a] Crombie, Part IV. [b] Mols. of hydrogen absorbed over a platinum catalyst. [c] Adduct with maleic anhydride.

$$\text{(XII)}\ Me\cdot[CH_2]_2\cdot C{\equiv}C\cdot C{\equiv}C\cdot[CH_2]_2\cdot CH{=}PPh_3 + OHC\cdot CH{=}CH\cdot CO_2Me\ \text{(XIII)}$$
$$\downarrow$$
$$\text{(XIV)}\ Me\cdot[CH_2]_2\cdot C{\equiv}C\cdot C{\equiv}C\cdot[CH_2]_2\cdot CH{=}CH\cdot CH{=}CH\cdot CO_2Me \longrightarrow \text{(XV)}$$

Almost simultaneously with the publication of our note,[2] Bohlmann and Inhoffen described a different synthesis.[4] This involved cross-coupling pent-1-yne with pent-4-ynol, conversion into the bromide, and then synthesis by the Wittig–Schöllkopf reaction [5] using the aldehyde (XIII) prepared by oxidation of crotonic ester with selenium dioxide. The final stages (XIV) ⟶ (XV) involved successive hydrolysis by alkali and reaction with thionyl chloride and then *iso*butylamine. It is not clear if *trans*-2 : *cis*-4 material was also formed in the Wittig–Schöllkopf reaction, and yields of purified product were not reported.

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[4] Bohlmann and Inhoffen, *Chem. Ber.*, 1956, **89**, 1276.
[5] Wittig and Schöllkopf, *Chem. Ber.*, 1954, **87**, 1318.

TABLE 2. *Ultraviolet data for unsaturated amides and related substances.**

$Me\cdot[CH_2]_4\cdot CH\overset{t}{=}CH\cdot CH\overset{t}{=}CH\cdot CO_2H$ [a]	257 (28,500)
$HC{\equiv}C\cdot[CH_2]_2\cdot CH\overset{t}{=}CH\cdot CH\overset{t}{=}CH\cdot CO_2H$	257 (25,000)
$Me\cdot[CH_2]_4\cdot CH\overset{t}{=}CH\cdot CH\overset{t}{=}CH\cdot CO\cdot NHBu^i$ [a]	258 (29,500)
$HC{\equiv}C\cdot[CH_2]_2\cdot CH\overset{t}{=}CH\cdot CH\overset{t}{=}CH\cdot CO\cdot NHBu^i$	258 (34,000)
$(\cdot C{\equiv}C\cdot[CH_2]_2\cdot CH\overset{t}{=}CH\cdot CH\overset{t}{=}CH\cdot CO\cdot NHBu^i)_2$	257 (71,500)
$Me\cdot[CH_2]_2\cdot C{\equiv}C\cdot C{\equiv}C\cdot[CH_2]_2\cdot CH\overset{t}{=}CH\cdot CH\overset{t}{=}CH\cdot CO_2H$	257 (26,500)
$Me\cdot[CH_2]_2\cdot C{\equiv}C\cdot C{\equiv}C\cdot[CH_2]_2\cdot CH\overset{t}{=}CH\cdot CH\overset{t}{=}CH\cdot CO\cdot NHBu^i$	258 (34,000)
$Me\cdot[CH_2]_4\cdot C{\equiv}C\cdot C{\equiv}C\cdot[CH_2]_8\cdot CO_2H$	226 (440); 240 (440); 252 (250)
$Me\cdot[CH_2]_3\cdot C{\equiv}C\cdot C{\equiv}C\cdot[CH_2]_3\cdot Me$ [b]	228 (440); 239·5 (390); 254 (240)
$Me\cdot CH\overset{t}{=}CH\cdot C{\equiv}C\cdot C{\equiv}C\cdot[CH_2]_2\cdot CH\overset{t}{=}CH\cdot CH\overset{t}{=}CH\cdot CO\cdot NHBu^i$	255 (44,500); 267 (52,000); 283 (28,000)
$Me\cdot CH\overset{c}{=}CH\cdot C{\equiv}C\cdot C{\equiv}C\cdot[CH_2]_2\cdot CH\overset{t}{=}CH\cdot CH\overset{t}{=}CH\cdot CO\cdot NHBu^i$	256 (35,000); 267 (43,000); 283 (19,000)
$Me\cdot[CH_2]_3\cdot CH\overset{t}{=}CH\cdot C{\equiv}C\cdot C{\equiv}C\cdot[CH_2]_7\cdot CO_2Me$ [c]	229 (3000); 240 (6000); 253 (12,500); 267 (20,000); 283 (15,500)
$Me\cdot[CH_2]_2\cdot C{\equiv}C\cdot C{\equiv}C\cdot CH{=}CH\cdot CH_2\cdot OH$ [d]	239·5 (7300); 252 (14,600); 266·5 (21,850); 282·5 (19,440)

* Wavelength in mμ; ε in parentheses.

[a] Part V. [b] Armitage *et al.*, *J.*, 1952, 1998. [c] Crombie and Jacklin, *J.*, 1957, 1632. [d] Bruun *et al.*, *Acta Chem. Scand.*, 1950, **4**, 850.

TABLE 3. *Ultraviolet data for maleic adducts.** †

(XVII); $R = Me\cdot[CH_2]_2\cdot C{\equiv}C\cdot C{\equiv}C\cdot[CH_2]_2\cdot$	240 (650); 254 (410)
(XVII); $R = Me\cdot CH\overset{t}{=}CH\cdot C{\equiv}C\cdot C{\equiv}C\cdot[CH_2]_2\cdot$	239 (5500); 252 (13,200); 266 (19,400); 282 (15,000)
(XVII); $R = Me\cdot CH\overset{c}{=}CH\cdot C{\equiv}C\cdot C{\equiv}C\cdot[CH_2]_2\cdot$	240 (4250); 253 (8500); 267 (12,950); 282 (10,700)

* Wavelength in mμ; ε in parentheses.

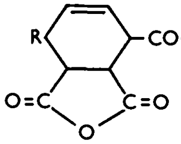
† (XVII), where $R = Me$ or $Me\cdot[CH_2]_4\cdot$, show no high-intensity maxima in the usual range, but rising end-absorption $\varepsilon \sim 2000$ at 210 mμ. See Table 2 for comparative chromophores.

TABLE 4. *Infrared assignments* (*cm.*$^{-1}$) *for unsaturated* iso*butylamides.*‡

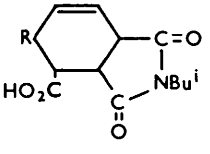
	NH		C≡C	C=O	$CH\overset{t}{=}CH_{I}$	$CH\overset{t}{=}CH_{II}$	Amide B	$\delta'\ (CH\overset{t}{=}CH)_2$
$Me\cdot[CH_2]_4\cdot[CH\overset{t}{=}CH]_2\cdot CO\cdot NHBu^i$ [e]	3295	3075	—	1625	1654	1614	1550	994
$HC{\equiv}C\cdot[CH_2]_2\cdot[CH\overset{t}{=}CH]_2\cdot CO\cdot NHBu^i$	3247	3021	2119	1626	1653	1608	1538	996
$[\cdot C{\equiv}C\cdot[CH_2]_2\cdot[CH\overset{t}{=}CH]_2\cdot CO\cdot NHBu^i]_2$	3263	3030	— [f]	1625	1655	1609	1540	997
$Pr^n\cdot[C{\equiv}C]_2\cdot[CH_2]_2\cdot[CH\overset{t}{=}CH]_2CO\cdot NHBu^i$	3248	3049	— [f]	1622	1653	1609	1540	1000
$Me\cdot CH\overset{t}{=}CH\cdot[C{\equiv}C]_2\cdot[CH_2]_2\cdot[CH\overset{t}{=}CH]_2\cdot CO\cdot NHBu^i$	3236	3040	2232	1621	1650	1612	1546	997
$Me\cdot CH\overset{c}{=}CH\cdot[C{\equiv}C]_2\cdot[CH_2]_2\cdot[CH\overset{t}{=}CH]_2\cdot CO\cdot NHBu^i$	3236	3040	2232	1623	1652	1608	1538	996
$Pr^n\cdot[CH\overset{c}{=}CH]_2\cdot[CH_2]_2\cdot[CH\overset{t}{=}CH]_2\cdot CO\cdot NHBu^i$	3273	3049	—	1623	1659	1611	1538	1005
$Bu^n\cdot[CH{=}CH]_3\cdot[CH_2]_7\cdot CO\cdot NHBu^i$	3252	3049	—	1639	—	—	1554	1006

‡ Paraffin mull spectra. [e] Part V. [f] Acetylenic vibrations very weak or undetectable.

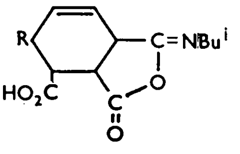
The best samples of anacyclin isolated from natural sources contain about 4% of a conjugated enediyne impurity, as judged by their ultraviolet spectra.[1] This second substance is likely to be closely related to anacyclin and a fair assumption is that the contaminant might be *N-iso*butyltetradeca-*trans*-2 : *trans*-4 : *trans*-12- or -*trans*-2 : *trans*-4 : *cis*-12-triene-8 : 10-diynamide (X). We have prepared both these compounds though it is not yet possible to say if either is the natural conjugated enediyne. For synthesis of compounds of this type, our approach is particularly useful as the flexibility of the final stage enables the standard unit (VIII) to be coupled with a variety of acetylenic hydrocarbons. Both pure *cis*- and pure *trans*-pent-2-en-4-yne [6] were oxidatively coupled with the amide (VIII) to give the two crystalline stereoisomers (X) mentioned above. Each absorbed 7 mols. of hydrogen over a catalyst to give *N-iso*butyltetradecanamide. Infrared spectra (see p. 2775) are in agreement with the allotted configurations; for, besides the usual strong absorption near 996 cm.$^{-1}$ due to the *trans-trans*-conjugated diene system, the *trans*-12-compound has a strong band at 948 cm.$^{-1}$ whilst the *cis*-12-compound has a strong band at 718 cm.$^{-1}$. These are characteristic of *trans*- and *cis*-enynes or -enediynes respectively. There is absorption near 948 cm.$^{-1}$ in the *cis*-12-amide and near 718 cm.$^{-1}$ in the *trans*-12-amide but this does not necessarily mean that partial stereomutation has occurred, for similar coincidences have been found in related pairs of geometrical isomers.[6]



(XVI)



(XVII)



(XVIII)

The ultraviolet spectra are the combined results of the absorption due to a *trans-trans*-dienamide and an enediyne chromophore. Table 2 makes it clear that the intensity contribution of a *cis*-enediyne is less than of the *trans*-isomer, and this is borne out by data for the maleic anhydride adducts (Table 3) in which the dienamide absorption is eliminated. In the infrared region, only the *trans*-enediyne adduct has, as expected, a band at 951 cm.$^{-1}$ and the *cis*-adduct has strong absorption at 722 cm.$^{-1}$.

The structure of maleic anhydride adducts of *N-iso*butyl-*trans*-2 : *trans*-4-dienamides is of interest. Although we have mentioned them earlier and used them in structural work, we have not assigned a structure to them. Bohlmann and Inhoffen [4] have recently given the maleic anhydride adduct from anacyclin the obvious structure (XVI; R = $\mathrm{Pr{\cdot}[C{\equiv}C]_2{\cdot}[CH_2]_2{\cdot}}$). Infrared data lead us to the view that this is incorrect; for, in a series of such adducts, no characteristic vibrations for NH, amide A (carbonyl), amide B, or the anhydride ring can be found. The usual positions for these can be found in Table 5 by reference to the maleic anhydride adducts of *N-iso*butyloctadeca-*trans*-9 : *trans*-11 : *trans*-13-trienamide and α- or β-sanshoöl (such adducts are "normal" as the triene system is remote from the carboxyamide function). Analysis shows that the maleic anhydride adducts of *N-iso*butyl-*trans*-2 : *trans*-4-dienamides must be isomeric with structure (XVI) and on catalytic hydrogenation they absorb 1 mol. of gas. Observations of the infrared spectrum near 2500 cm.$^{-1}$ (broad band) suggest that a free carboxylic acid group is present in the "abnormal" adducts.

Alternative formulations (XVII) and (XVIII) are possible, the former being more consistent with the infrared data. Like *N-iso*butylsuccinimide, prepared as a model substance, all the abnormal maleic anhydride adducts have a strong band near 1200 cm.$^{-1}$ and two others near 1760 and 1705 cm.$^{-1}$. Dr. Elvidge has told us that he and his co-workers have found a wide range of *N*-unsubstituted imides to have a strong band near 1190 and two near 1770 and 1695 cm.$^{-1}$. On this basis the bands near 1760 and 1705 cm.$^{-1}$

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[6] Allan and Whiting, *J.*, 1953, 3314; Allan, Meakins, and Whiting, *J.*, 1955, 1874.

are associated with the imide structure and a third strong band near 1675 cm.$^{-1}$ is assigned to the carboxylic acid function in (XVII). For a normal saturated carboxylic acid group, the carbonyl stretching frequency is low (Bellamy [7] gives 1700—1725 cm.$^{-1}$). The maleic adduct from *N-iso*butylsorbamide was therefore esterified with diazomethane. In the ester, the band at 1672 cm.$^{-1}$ had disappeared and a new strong band at 1731 cm.$^{-1}$ appeared. This is near the normal position for an α-saturated ester (Bellamy [7] gives 1735—1750 cm.$^{-1}$). The bands associated with the imide group were at 1770, 1704, and 1202 cm.$^{-1}$. The assignments in Table 5 therefore seem reasonable.

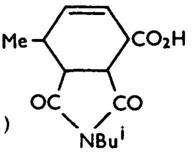
TABLE 5. *Infrared spectra (cm.$^{-1}$) of Diels–Alder adducts.** †

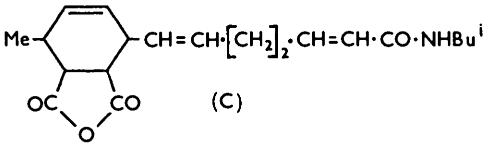
Imides :	Imide Carbonyl Region			Carboxylic	Imide
Hexahydrophthalimide [a]	1786	—	1695	—	1189
Succinimide [a]	1770	—	1704	—	1190
*N-iso*Butylsuccinimide	1765	1739i	1706	—	1203
*N-iso*Butylmaleimide [b]	1757	1727i	1709	—	1196
(XVII); R = $Me{\cdot}[CH_2]_4{\cdot}$	1757	1724i	1709	1675	1198
(XVII); R = $Pr^n{\cdot}[C{\equiv}C]_2{\cdot}[CH_2]_2{\cdot}$	1754	—	1707	1677	1198
(XVII); R = $Me{\cdot}CH\overset{t}{=}CH{\cdot}[C{\equiv}C]_2{\cdot}[CH_2]_2{\cdot}$	1754	1721i	1706	1678	1204
(XVII); R = $Me{\cdot}CH\overset{c}{=}CH{\cdot}[C{\equiv}C]_2{\cdot}[CH_2]_2{\cdot}$	1757	1724i	1709	1678	1200
(XIX)	1752	—	1709	1672	1198
(XX)	1757	1721i	1704	1667	1206
(A)	1767	1736		1692	1208
(XXI)	1751	—	1704 1709i	1669	1205
(B)	1767	1736	1709 1701	1681	1211

Anhydrides :	NH	Anhydride	α-C=C	Amide	
trans-2 : *cis*-6-(C) [c]	3295, 3125	1838, 1765	1669	1618	1543
trans-2 : *trans*-6-(C) [cd]	3280, 3040	1842, 1768	1664	1618	1547
trans-9-(D) [d]	3260, 3050	1843, 1770	—	1645	1547

* Paraffin mull spectra. † The band near 1760 cm.$^{-1}$ in the imides is normally considerably weaker than the other tabulated bands.

[a] Elvidge and Bull, personal communication. [b] There are also bands at 1684, 1604, and 1588 cm.$^{-1}$. [c] Crombie and Tayler, Part VIII. [d] These may be mixtures of the two isomers derived from the two possible modes of addition to an all-*trans*-triene.


(A)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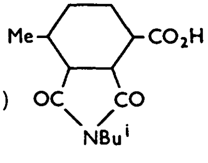
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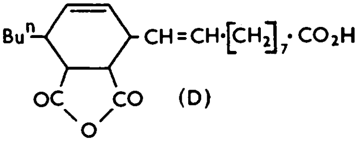
(D)

An attempt was then made to establish the structure of the " abnormal " adducts by synthesis in the following way. 3-Methylpenta-2 : 4-dienoic acid was prepared by modification of a method described by Heilbron *et al.*[8] which involves Reformatski reaction between methyl vinyl ketone and ethyl bromoacetate. A Diels–Alder reaction between 3-methylpenta-2 : 4-dienoic acid and *N-iso*butylmaleimide gave an adduct having spectroscopic data (Table 5) consistent with structure (XX). On catalytic hydrogenation in acidic

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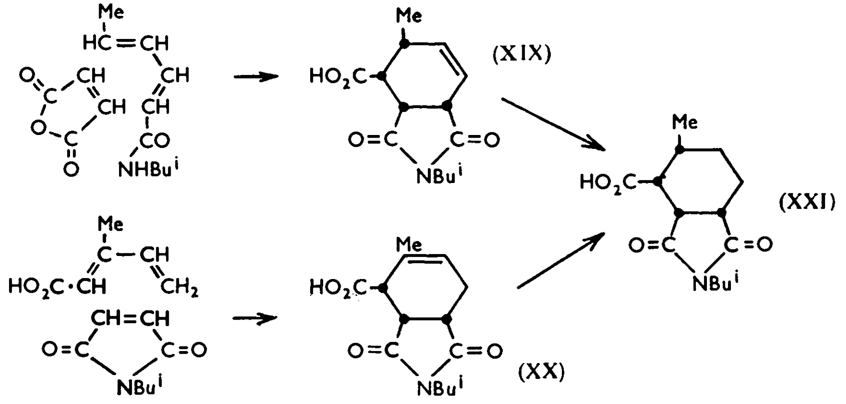
[7] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1954.
[8] Heilbron, Jones, Julia, and Weedon, *J.*, 1949, 1823.

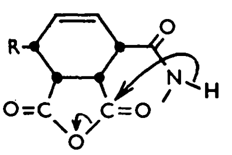
or neutral solution a saturated imide was formed which, on the basis of hindrance to the formation of a *trans*-methyl at the catalyst surface,[9] should be the all-*cis*-compound (XXI). This substance was equated by mixed m. p. with the product obtained when the maleic adduct of *N*-*iso*butylsorbamide was hydrogenated. The all-*cis*-formulation is based on Alder's generalisations: related systems have been examined from this point of view.[10]

Formation of the *N*-*iso*butylimide (XVII) is considered to occur through nucleophilic attack by the amide grouping at the carbon atom of the adjacent anhydride carbonyl grouping, either during the Diels–Alder reaction, or subsequently, as shown diagrammatically in (XXII). Two other unexpected reactions of a diene with maleic anhydride in benzene bear comparison. First, penta-2 : 4-dienol (and related alcohols), when treated with this reagent at 20°, gives directly the lactol (XXIII).[11] In agreement with this structure we find bands at 1754s (γ-lactone), 1698s (carboxylic acid), and 1653w cm.$^{-1}$ (double bond) in the infrared spectrum. Secondly, under reflux, the anil of 2-ethylhexenal (believed to react as Et·CH=CH·CEt=CH·NHPh) is said [12] to form 2 : 4-diethyl-7-oxo-6-phenyl-6-aza*bicyclo*[3 : 2 : 1]oct-3-ene-8-carboxylic acid (XXIV). Such intramolecular reactions, involving a substituent adjacent to the anhydride ring, may occur more commonly than has been appreciated during Diels–Alder reactions with maleic anhydride.


(XIX)

(XXI)

(XX)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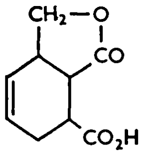
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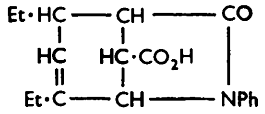
(XXIV)

EXPERIMENTAL

Analyses and light-absorption measurements were carried out in the microanalytical (Miss J. Cuckney) and spectrographic (Mrs. I. Boston and Mr. R. L. Erskine) laboratories of this Department. The ultraviolet absorptions were determined in pure ethanol with a Unicam S.P. 500 instrument (I.B.), and the infrared absorptions with a Grubb-Parsons double-beam

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[9] Linstead, Doering, Davis, Levine, and Whetstone, *J. Amer. Chem. Soc.*, 1942, **64**, 1985.

[10] Alder and Schumacher, *Annalen*, 1950, **571**, 87, 108, 122; Alder and Vogt, *ibid.*, p. 137; Alder and Vagt, *ibid.*, p. 153; Craig, *J. Amer. Chem. Soc.*, 1950, **72**, 1678.

[11] Heilbron, Jones, McCombie, and Weedon, *J.*, 1945, 84.

[12] Snyder, Hasbrouck, and Richardson, *J. Amer. Chem. Soc.*, 1939, **61**, 3558.

instrument (R.L.E.). Unless otherwise indicated, infrared data relate to pure films for liquids and paraffin mulls for solids. For further data see Tables.

Hepta-2 : 6-*diynoic Acid* (III).—A Grignard reagent was prepared from magnesium (15·65 g.) and ethyl bromide (72 g.) in dry tetrahydrofuran (150 ml.) and added dropwise with vigorous stirring to hexa-1 : 5-diyne (50 g.; prepared [13] in 64—67% yield) in tetrahydrofuran (200 ml.). The mixture was set aside (16 hr.) and washed into an autoclave with tetrahydrofuran (70 ml.). Solid carbon dioxide (2½ lb.) was added and the autoclave sealed and set aside (3 days). The product was then decomposed with water and 2N-sulphuric acid and thoroughly extracted with ether. After drying (Na_2SO_4), the extracts were evaporated and the solid product was triturated with cold benzene. Octa-2 : 6-diyndioic acid (15·5 g., 15%) was filtered off and had m. p. 190° after crystallisation. The filtrate was extracted with 2N-sodium hydroxide, and the alkaline extract acidified. Collection with ether, drying, and evaporation gave a solid which was distilled at 0·001 mm. (bath 110—135°). The distillate (26·5 g., 34%) was used directly for esterification; a specimen crystallised once from light petroleum (b. p. 40—60°) gave hepta-2 : 6-diynoic acid, m. p. 53—54°. On a smaller scale, with ethylmagnesium bromide [from magnesium (3·11 g.) and ethyl bromide (14 g.)] in tetrahydrofuran (50 ml.), and hexa-1 : 5-diyne (10 g.) in tetrahydrofuran (25 ml.), and procedure as above, octa-2 : 6-diynedioic acid (approx. 5%) and hepta-2 : 6-diynoic acid (53%; 47% after crystallisation to m. p. 52—53°) were isolated.

Hexa-1 : 5-diyne (40 g.) in tetrahydrofuran (75 ml.) was added slowly, with stirring, to a Grignard reagent prepared from magnesium (12·5 g.), ethyl bromide (56 g.), and tetrahydrofuran (250 ml.), and the mixture stirred (16 hr.) and then heated in nitrogen under reflux for 1 hr. Carboxylation and working up as above gave octa-2 : 6-diynedioic acid (24 g., 28%) and hepta-2 : 6-diynoic acid (7 g., 11%; 6 g. after crystallisation to m. p. 53°). Using this direction of addition, Shaw and Whiting [3] obtained octa-2 : 6-diynedioic acid, m. p. 189—190° (22%), and hepta-2 : 6-diynoic acid, m. p. 52·5—53·5° (18%).

Ethyl Hepta-2 : 6-*diynoate*.—Hepta-2 : 6-diynoic acid (26·5 g.) was added to benzene (31 ml.) containing ethanol (17 ml.) and concentrated sulphuric acid (1·8 ml.), and heated under reflux for 17 hr. in nitrogen. Water was added and the organic layer isolated with ether. Drying, evaporation, and distillation gave ethyl hepta-2 : 6-diynoate (30·5 g., 94%), b. p. 78°/0·6 mm., n_D^{21} 1·4693 [lit.,[3] b. p. 90° (bath-temp.)/1·5 mm., $n_D^{17·5}$ 1·4718].

Methyl Hepta-2 : 6-*diynoate*.—Hepta-2 : 6-diynoic acid (4·0 g.) in dry ether (25 ml.) was treated at 0—5° with diazomethane in ether (added dropwise) until reaction appeared complete. Evaporation *in vacuo* and distillation gave the *methyl ester* (4·22 g., 96%), b. p. 82°/10 mm., n_D^{21} 1·4721 (Found: C, 70·75; H, 6·05. $C_8H_8O_2$ requires C, 70·55; H, 5·9%). Infrared bands at 3245s, 2153w, 2135w ($C\equiv CH$), 2244s ($C\equiv C$ conj. with CO_2Me) and 1711s cm.$^{-1}$ (CO_2Me).

In another experiment the acid (17·5 g.) in ether was left in contact with excess of diazomethane for 2 days at 0°. Distillation gave the above methyl ester (14·8 g.), b. p. 84°/10 mm. The residue in the flask (6·5 g.) crystallised. Recrystallisations from ethanol and from toluene gave a *pyrazole*, m. p. 129° [Found: C, 60·55; H, 5·9; N, 15·55%; *M* (Rast), 203. $C_9H_{10}O_2N_2$ requires C, 60·65; H, 5·65; N, 15·7%; *M*, 178·2]. Ultraviolet max. at 224 mμ (ε 5800), and infrared bands at 3236m, 2118w ($C\equiv CH$), 1724s (CO_2Me), 1709s. The presence of a terminal ethynyl grouping shows that pyrazole formation must have occurred at the α-acetylenic linkage.

Hept-trans-2-*en*-6-*yn*-1-*ol* (IV).—Lithium aluminium hydride (25 g.) was suspended in dry ether (1 l.), and ethyl hepta-2 : 6-diynoate (19·2 g.) in dry ether (150 ml.) was slowly added to it and the mixture refluxed under nitrogen (3 hr.). Iced 8N-sulphuric acid was added and the product worked up to give *hept*-trans-2-*en*-6-*yn*-1-*ol* (12·7 g., 91%), b. p. 56°/0·5 mm., n_D^{21} 1·4745 (Found: C, 76·3; H, 9·25. $C_7H_{10}O$ requires C, 76·3; H, 9·15%). Infrared bands at 3333s (OH), 3246s, 2123m ($C\equiv CH$), 1675m, 969s (*trans*-CH=CH). Similar reduction of the methyl ester gave an 85% yield. Shaw and Whiting [3] give b. p. 106° (bath-temp.)/14 mm., n_D^{20} 1·4739, but could not obtain satisfactory analyses.

Hept-trans-2-*en*-6-*yn*-1-*al* (VI).—Hept-*trans*-2-en-6-yn-1-ol (6 g.) was dissolved in acetone (40 ml.), and a solution (20 ml.) of chromic acid (8N) [2·9 equiv. per mol. of alcohol] in 12N-sulphuric acid added slowly, and with stirring, the temperature being kept below 35°. The mixture was stirred for 2 hr. at 25° and set aside for 18 hr. at 0°. Brine was added, and the solution extracted thoroughly with ether. The ethereal extracts were themselves extracted with N-potassium hydroxide, and the acidic material (1%) was isolated. The neutral ethereal

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[13] Raphael and Sondheimer, *J.*, 1950, 120.

solution was dried, evaporated, and distilled, to give hept-*trans*-2-en-6-yn-1-al (3·65 g., 62%), b. p. 76°/10 mm., $n_D^{22·5}$ 1·4828.

Hept-2-en-6-yn-1-ol (19 g.) was dissolved in acetone (120 ml.), and a solution (120 ml.) of chromic acid (8N) [5·6 equiv. per mol. of alcohol] in 12N-sulphuric acid added slowly and with stirring, at 20—30°. After being stirred at 20° for 2 hr. and set aside for 18 hr., the product was worked up as above to give hept-2-en-6-yn-1-al (4·3 g., 23%) and hept-2-en-6-ynoic acid (15 g., 70%). Using 4 equivs. of chromic acid per mol. of alcohol, Shaw and Whiting obtained 69% of aldehyde and 11% of acid. Hept-*trans*-2-en-6-yn-1-al had infrared bands at 3240, 2262, 2210, 2126 (C≡CH), 2809, 2732, 1686 (C–H and C=O vibrations of α-unsaturated aldehyde), 1634 and 971 cm.$^{-1}$ (conj. *trans*-CH=CH).

Nona-trans-2 : trans-4-*dien*-8-*ynoic Acid* (VII).—Hept-*trans*-2-en-6-ynal (2·35 g.) was dissolved in pyridine (5·5 ml.), and malonic acid (3·7 g.) added. The mixture was set aside for 3 days (the malonic acid dissolved in a few hours) and then heated on the steam-bath for 1 hr. and poured into 2N-hydrochloric acid. The product was extracted with ether, and the ethereal solution extracted with 2N-sodium hydroxide. Acidification and isolation with ether gave *nona*-trans-2 : trans-4-*dien*-8-*ynoic acid* which, when distilled at 118°/0·35 mm., solidified (2·3 g., 72%). Crystallisation from light petroleum (b. p. 40—60°) gave the acid as plates (1·3 g., 41%), m. p. 100—101° (Found : C, 71·8; H, 6·9. $C_9H_{10}O_2$ requires C, 72·0; H, 6·7%). Ultraviolet max. 257 mμ (ε 25,500); infrared max. at 3236m, 2117mw (C≡CH), 1685s (conj. CO_2H), 1631m, 1613m, 998m (conj. *trans-trans*-diene). For comparative data see Part VII.

Nona-trans-2 : trans-4-*dien*-8-*ynoyl Chloride*.—The acid (1·00 g.) was treated with thionyl chloride (1·5 g.), set aside (3 hr.), and then heated at 100° (10 min.). The *acid chloride* (0·98 g., 88%) distilled at 68—76°/1·5 mm. (Found : C, 63·8; H, 5·45. C_9H_9OCl requires C, 64·1; H, 5·4%).

N-iso*Butylnona*-trans-2 : trans-4-*dien*-8-*ynamide* (VIII).—The acid chloride (0·92 g.) was added, dropwise and with shaking, to *iso*butylamine (1·2 g.) in dry ether (50 ml.), and the product was set aside for 2 hr. and then washed with water, 2N-hydrochloric acid, sodium hydrogen carbonate solution, and water. After drying and evaporation, the residue was crystallised from light petroleum (b. p. 60—80°). The N-iso*butylamide* (0·78 g., 69%) had m. p. 91° (Found : C, 75·85; H, 9·4; N, 6·8. $C_{13}H_{19}ON$ requires C, 76·05; H, 9·35; N, 6·8%). Ultraviolet max. 258 mμ (ε 34,000).

N-iso*Butyltetradeca*-trans-2 : trans-4-*diene*-8 : 10-*diynamide* (*Anacyclin*) (IX).—*N-iso*Butyl-nona-*trans*-2 : *trans*-4-dien-8-ynamide (500 mg.) and pent-1-yne (550 mg.) were dissolved in methanol (10 ml.), and a solution of cuprous chloride (1·2 g.) and ammonium chloride (2·5 g.) in 0·08N-hydrochloric acid (10 ml.) added. The mixture was shaken in oxygen for 4½ hr. (no further gas absorption after 2½ hr.). 2N-Hydrochloric acid was added and the solution extracted with ether containing a little chloroform. The extracts were dried and evaporated and the residue boiled with light petroleum (b. p. 60—80°) containing a little chloroform and filtered hot. N-iso*Butyltetradeca*-trans-2 : trans-4-*diene*-8 : 10-*diynamide* (344 mg., 52%) crystallised from the filtrate and, recrystallised from light petroleum (b. p. 60—80°), had m. p. 121° (Found : C, 79·15; H, 9·25. $C_{18}H_{25}ON$ requires C, 79·65; H, 9·3%). When admixed, it did not depress the m. p. of natural anacyclin, m. p. 119—120°. The amide became bright pink on exposure to light. On microhydrogenation (6·1H_2 absorbed), *N-iso*butyltetradecanamide, m. p. and mixed m. p. 65°, was obtained. *all*-trans-*Di*-(N-iso*butyl*)*octadeca*-2 : 4 : 14 : 16-*tetraene*-8 : 10-*diyne*-1 : 18-*diamide*, insoluble in light petroleum containing a little chloroform (see above; 71 mg., 4%), crystallised from chloroform containing a little light petroleum and had m. p. 245—246° (decomp.), becoming rose-pink at about 100° [Found : C, 76·15; H, 8·7%; *M* (Rast), 429. $C_{26}H_{36}O_2N_2$ requires C, 76·45; H, 8·9%; *M*, 409]. See Tables for spectral data. Natural and synthetic anacyclin had infrared max. at 3248, 3031, 2717, 2156, 1986, 1747, 1653, 1622, 1608, 1537, 1453, 1373, 1350, 1336, 1302, 1294, 1258, 1207, 1167, 1158, 1139, 1129, 1088, 1075, 1062, 1035, 1000, 944, 925, 898, 872, 817, 734, 723 cm.$^{-1}$.

Anacyclin–Maleic Anhydride Adduct.—Synthetic anacyclin (80 mg.) was heated in a sealed tube with maleic anhydride (30 mg.) in benzene (0·5 ml.) for 16 hr. at 100°. The solid which crystallised (80 mg.) was decolorised with charcoal and recrystallised from benzene, to give the *adduct* (35 mg.), m. p. 193° decomp. (Found : C, 71·25; H, 7·5. $C_{22}H_{27}O_4N$ requires C, 71·5; H, 7·35%).

Tetradeca-trans-2 : trans-4-*diene*-8 : 10-*diynoic Acid*.—Nona-*trans*-2 : *trans*-4-dien-8-ynoic acid (140 mg.) and pent-1-yne (210 mg.), dissolved in methanol (4 ml.), were added to a solution of cuprous chloride (0·4 g.) and ammonium chloride (1 g.) in 0·08N-hydrochloric acid (4 ml.). Oxidative coupling (3½ hr.), as above, gave *tetradeca*-trans-2 : trans-4-*diene*-8 : 10-*diynoic acid* (160 mg., 80%), m. p. 148—152°, raised by crystallisation from a mixture of light petroleum (b. p. 60—80°) and ether to 154—155° (Found : C, 77·6; H, 7·45. $C_{14}H_{16}O_2$ requires C, 77·75; H, 7·45%). Infrared max. (paraffin mull) : 2150vw (diyne), 1688s, 1677s (CO_2H), 1635m, 1614m, 1003m (conj. *trans-trans*-diene α to carboxyl). The acid was converted into the acid chloride with thionyl chloride and treated with *iso*butylamine, to give *N-iso*butyltetradeca-*trans*-2 : *trans*-4-diene-8 : 10-diynamide, m. p. 121°, equated with natural anacyclin by the infrared spectrum. Bohlmann and Inhoffen [4] report the acid to have m. p. 58°.

Pent-trans-3- *and Pent*-cis-3-*enyne*.—The *cis–trans*-hydrocarbon mixture was prepared and separated by fractional distillation through a Stedman column according to Allan and Whiting's directions.[6] Pent-*cis*-3-enyne had b. p. 45·0—45·1°, n_D^{27} 1·4278, and the *trans*-stereoisomer, b. p. 52·1—52·2°, $n_D^{21·5}$ 1·4352 [lit. :[6] *cis*, b. p. 44·5—44·6°, n_D^{20} 1·4330 (n_D^{27} 1·4285 using temp. coeff. 0·00064); *trans*, b. p. 52·0—52·2°, n_D^{20} 1·4368 ($n_D^{21·5}$ 1·4358 using temp. coeff. 0·00067)]. The infrared spectra corresponded with the recorded data.[6]

N-iso*Butyltetradeca*-trans-2 : trans-4 : trans-12-*triene*-8 : 10-*diynamide* (X).—*N-iso*Butylnona-*trans*-2 : *trans*-4-dien-8-ynamide (600 mg.) and pent-*trans*-3-enyne (700 mg.) in methanol (11 ml.) were added to a solution of cuprous chloride (1·1 g.) and ammonium chloride (2·75 g.) in 0·08N-hydrochloric acid (11 ml.) and oxidatively coupled (4 hr.). Working up as usual gave N-iso-*butyltetradeca*-trans-2 : trans-4 : trans-12-*triene*-8 : 10-*diynamide* (450 mg., 61%) which when crystallised from light petroleum (b. p. 60—80°)–chloroform had m. p. 150·5° (Found : C, 80·3; H, 8·6. $C_{18}H_{23}ON$ requires C, 80·25; H, 8·6%). The product was not very photosensitive though it became faintly rose-pink on prolonged exposure to sunlight. It had infrared max. at 3236, 3040, 2874, 2703, 2398, 2232, 1859, 1725, 1650, 1621, 1612, 1546, 1452, 1374, 1364, 1351, 1342, 1300, 1264, 1209, 1164, 1155, 1147, 1126, 1108, 1082, 1062, 1030, 997, 948, 909, 866, 818, 736, 724, 676 cm.$^{-1}$. On microhydrogenation (6·75 H_2 absorbed), a tetradecahydro derivative, m. p. 65°, was obtained, undepressed on admixture with *N-iso*butyltetradecanamide. Symmetrically coupled material (XI) (50 mg.), m. p. 244—246°, was also isolated. A *maleic anhydride adduct* was prepared by heating the trienediynamide (100 mg.) with maleic anhydride (40 mg.) in benzene (0·8 ml.) in a sealed tube for 18 hr. and, recrystallised from benzene (charcoal), had m. p. 186—187° (Found : N, 3·9. $C_{22}H_{25}O_4N$ requires N, 3·8%).

N-iso*Butyltetradeca*-trans-2 : trans-4 : cis-12-*triene*-8 : 10-*diynamide* (X).—*N-iso*Butylnona-*trans*-2 : *trans*-4-dien-8-ynamide (550 mg.) and pent-*cis*-3-enyne (700 mg.) in methanol (11 ml.) were added to a solution of cuprous chloride (1·1 g.) and ammonium chloride (2·75 g.) in 0·08N-hydrochloric acid (11 ml.), and oxidatively coupled in the usual way, to give N-iso*butyltetradeca*-trans-2 : trans-4 : cis-12-*triene*-8 : 10-*diynamide* (354 mg., 52%) which, after crystallisation from light petroleum (b. p. 60—80°), had m. p. 100—101° (Found : C, 80·05; H, 8·65%). This had infrared max. at 3236, 3040, 2833, 2703, 2232, 1873, 1745, 1720, 1652, 1623, 1608, 1538, 1460, 1399, 1376, 1364, 1349, 1330, 1304, 1259, 1206, 1166, 1158, 1136, 1128, 1077, 1062, 1032, 996, 944, 924, 907, 871, 816, 769, 718 cm.$^{-1}$. The white product rapidly became dull pink in light. On microhydrogenation (6·7 H_2 absorbed), *N-iso*butyltetradecanamide, m. p. and mixed m. p. 65°, was isolated. Symmetrically coupled material (XI) (50 mg.), m. p. 244—246°, was also isolated. The *maleic anhydride adduct*, prepared as above, had m. p. 186—187° (Found : C, 71·5; H, 6·95. $C_{22}H_{25}O_4N$ requires C, 71·9; H, 6·85%). The infrared spectrum was different from that of the isomer containing a *trans*-12-linkage. For spectroscopic data see Tables.

N-iso*Butyltetradeca*-trans-2 : trans-4 : cis-8 : cis-10-*tetraenamide*.—Synthetic anacyclin (150 mg.) was hydrogenated in ethyl acetate (7 ml.), Lindlar catalyst deactivated with a drop of quinoline being used. When 1·95 mol. of hydrogen had been absorbed, the hydrogenation was discontinued and the catalyst filtered off. The filtrate was evaporated *in vacuo* at 20°, dissolved in ether, and washed with 2N-sulphuric acid and then water. The ethereal solution was dried (Na_2SO_4) and concentrated *in vacuo*. Light petroleum (b. p. 40—60°) was added, precipitating an oil. The supernatant layer was decanted and, on being set aside at 0°, deposited crystals : after recrystallisation in a similar manner the *tetraene-amide* (30 mg.) had m. p. 100—101° (Found : C, 78·75; H, 10·3. $C_{18}H_{29}ON$ requires C, 78·5; H, 10·6%). Microhydrogenation 3·9 H_2. Ultraviolet max. at 256 mμ (ε 34,000). The usual amide and diene bands were present in the infrared spectrum. The *tetraene-amide* was a sialogogue and was found [by Dr. M. Elliott and Mr. P. Needham (Rothamsted Experimental Station)] to be insecticidally active against mustard beetles.

Maleic Anhydride Adduct of N-iso*Butylsorbamide*.—*N-iso*Butylsorbamide (5 g.) and maleic anhydride (2·7 g.) in benzene (40 ml.) were heated under reflux for 16 hr. After cooling, the *adduct* (XIX) (6 g.), m. p. 183—184° (unchanged by four crystallisations from benzene), was filtered off (Found: C, 63·35; H, 7·35. $C_{14}H_{19}O_4N$ requires C, 63·35; H, 7·2%). Microhydrogenation 1·04 H_2. Ultraviolet absorption: no high-intensity max. $>$210 mμ; ε at 210 and 280 mμ, 2100 and 75 respectively. The *dihydro-adduct* (XXI), crystallised from anhydrous benzene, had m. p. 168—169°, somewhat dependent on rate of heating (Found: C, 62·55; H, 7·5. $C_{14}H_{21}O_4N$ requires C, 62·9; H, 7·9%). It was prepared by hydrogenation in ethyl propionate at palladium–carbon.

The adduct, m. p. 183—184°, was converted into the *methyl ester*, a viscous liquid, b. p. 160°/0·5 mm., by treatment with ethereal diazomethane (Found: C, 64·35; H, 7·5. $C_{15}H_{21}O_4N$ requires C, 64·5; H, 7·6%).

3-*Methylpenta*-2 : 4-*dienoic Acid*.—A Reformatski reaction was carried out in the usual way between zinc wool (25 g.) activated with mercuric chloride (0·2 g.) and covered with benzene (300 ml.), methyl vinyl ketone (27 g.), and ethyl bromoacetate (60 g.) in benzene (150 ml.). When reaction was complete, the mixture was heated under reflux for 2 hr., cooled, and treated with acetic acid (90 g.) in water (1·8 l.). The benzene layer was separated, washed until free from acid, dried, evaporated, and distilled, to give crude hydroxy-ester, b. p. 57—66°/4·5 mm. (16·2 g.), n_D^{20} 1·4366—1·4372. There was no ultraviolet absorption ($E^{1\%}_{1\,\text{cm.}} < 20$ at wavelengths $>$225 mμ). Infrared bands were at 3485 (OH), 1644, 995, 924 cm.$^{-1}$ (vinyl).

The hydroxy-ester (5·0 g.) was heated in nitrogen under reflux with phosphorus oxychloride (6·0 g.) in benzene (30 ml.) for 30 min. After being cooled and washed with water (3 × 50 ml.) the benzene solution was dried (Na_2SO_4), evaporated, and distilled, to give crude ester (3·2 g.), b. p. 46—75°/2 mm., n_D^{27} 1·4698—1·4715. Light absorption max. 250 mμ (ε 15,500). Infrared bands at 1710 (α-unsatd. ester), 1626 and 1600 (conj. diene), 991 and 928 cm.$^{-1}$ (conj. vinyl).

Crude diene ester (9·8 g.) was hydrolysed in nitrogen with potassium hydroxide (8·5 g.) in refluxing methanol (160 ml.) and worked up in the usual way, to give 3-methylpenta-2 : 4-dienoic acid (2·7 g.), b. p. 88—100°/3—5 mm., n_D^{22} 1·5156 (Found: C, 64·35; H, 7·5. Calc. for $C_6H_8O_2$: C, 64·25; H, 7·2%). Light absorption max. 250 mμ (ε 18,500). Infrared bands at 1689 (α-unsatd. acid), 1639, 1627, and 1605, 1592 (conj. diene: the usual doublet seems to be split into four bands), 991, and 926 cm.$^{-1}$ (conj. vinyl). The *S*-benzylthiuronium salt had m. p. 161° (Found: C, 60·45; H, 6·55. Calc. for: $C_{14}H_{18}O_2N_2S$: C, 60·4; H, 6·5%). Heilbron and his collaborators[8] give b. p. 60°/0·05 mm., n_D^{22} 1·5186, light absorption max. 249 mμ (ε 20,500), *S*-benzylthiuronium salt of m. p. 162°.

N-iso*Butylmaleimide*.—Maleic anhydride (12·5 g.) was dissolved in dry benzene (20 ml.), and *N-iso*butylamine (15 g.) added. The mixture was heated under reflux for 30 min. with exclusion of moisture. After distillation of the solvent, water was added and the mixture filtered and washed with water. The solid product was purified by dissolution in sodium carbonate solution and, after extraction with ether, reprecipitated with acid and filtered off. The *half* iso*butylamide* (12·8 g.) was washed with water and dried *in vacuo*. It crystallised from benzene–light petroleum (b. p. 40—60°) in plates, m. p. 99—100° (Found: C, 56·1; H, 7·6%; equiv., 164. $C_8H_{13}O_3N$ requires C, 56·1; H, 7·65%; equiv., 171). There were infrared bands at 3185, 3040, 1706, 1637, 1589, and 1517 cm.$^{-1}$.

This amide (7·5 g.) was heated from 180° to 220° (bath temp.) at 760 mm. in a stream of nitrogen and then distilled under reduced pressure. N-iso*Butylmaleimide* (1·5 g.), m. p. 47—48°, was obtained in transparent crystals (Found: C, 62·45; H, 7·15. $C_8H_{11}O_2N$ requires C, 62·7; H, 7·25%). Microhydrogenation 1·0 H_2.

*N-iso*Butylsuccinimide, prepared by refluxing together *N-iso*butylamine and succinic anhydride, had m. p. 28° when crystallised from light petroleum (b. p. 40—80°).

N-iso*Butylmaleimide Adduct of* 3-*Methylpenta*-2 : 4-*dienoic Acid*.—*N-iso*Butylmaleimide (0·35 g.) and 3-methylpenta-2 : 4-dienoic acid (0·26 g.) were heated together in a sealed tube in benzene (1·7 ml.) at 100° for 16 hr. The *adduct* (XX) (0·3 g.) was recrystallised from benzene to m. p. 189—190° (Found: C, 63·2; H, 7·2. $C_{14}H_{19}O_4N$ requires C, 63·4; H, 7·2%). Microhydrogenation 0·97 H_2.

The *dihydro-adduct* (XXI) was prepared by hydrogenating the adduct (XX) in ethyl acetate over Adams platinum catalyst. Even when crystallised five times from benzene, the substance separated in poorer crystalline form (m. p. 168—170°: somewhat dependent on rate of heating) than the hydrogenated adduct prepared from maleic anhydride and *N-iso*butylsorbamide, though its m. p. was not depressed by the latter (Found: C, 63·05; H, 7·95. $C_{14}H_{21}O_4N$ requires C, 62·9; H, 7·9%). The infrared spectra of the two substances were closely similar though there were small variations at longer wavelengths, suggesting impurity in one or both samples. A second specimen of the dihydro-adduct was prepared by hydrogenation over Adams catalyst in glacial acetic acid. Filtration and evaporation left a chalky solid; this was extracted with ether, and light petroleum (b. p. 40—60°) added, and the solution allowed to crystallise at 0°, giving a small yield of the dihydro-adduct. This crystallised in needles, m. p. 168° undepressed by, and similar in form to, the material derived from *N-iso*butylsorbamide.

Maleic Anhydride Adduct of N-iso*Butyl-β-elæostearamide.*—*N-iso*Butyl-β-elæostearamide, prepared in the usual way, had m. p. 79—80° (Found: C, 79·0; H, 11·8. Calc. for $C_{22}H_{39}ON$: C, 79·2; H, 11·8%). Ultraviolet max. 258 (41,900), 268 (58,400), and 278 mμ (43,400). Jacobson [14] gives m. p. 78—79°. The maleic anhydride adduct, prepared from amide (200 mg.) and anhydride (57 mg.) in dry benzene (0·8 ml.) by heating at 100° for 16 hr., was an oil which eventually crystallised from ether–light petroleum (b. p. 30—40°) when cooled in solid carbon dioxide–ethanol. It had m. p. 46—49° (unsharp) and was difficult to purify completely. It may contain the products of addition to both the 9 : 11- and the 11 : 13-diene linkage.

N-iso*Butylmaleimide Adduct of Sorbic Acid.*—Prepared in the usual way from imide (0·34 g.) and acid (0·26 g.) in benzene (2·5 ml.), the *adduct* (0·27 g.) formed needles, m. p. 156·5—157° from benzene–light petroleum (b. p. 60—80°) (Found: C, 63·3; H, 7·35. $C_{14}H_{19}O_4N$ requires C, 63·4; H, 7·2%). When hydrogenated in ethyl acetate at Adams catalyst, a *dihydro-derivative* was isolated which, crystallised from benzene–ether–light petroleum (b. p. 40—60°), had m. p. 135—136° (Found: C, 62·7; H, 8·05. $C_{14}H_{21}O_4N$ requires C, 62·9; H, 7·95%).

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[14] Jacobson, *J. Amer. Chem. Soc.*, 1952, **74**, 3423.