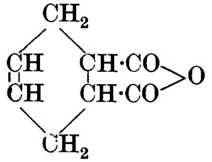
CXVII.—*Properties of Conjugated Compounds. Part VII. The Additive Formation of* cyclo*Hexenes.*

By ERNEST HAROLD FARMER and FRANK LOUIS WARREN.

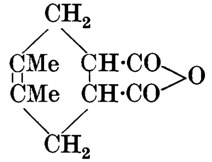
SEVERAL open-chain butadienes yield dimerides which are substituted *cyclo*hexenes; *cyclo*pentadiene and *cyclo*hexadiene yield polycyclic dimerides in which the additively formed rings are reputed (but not yet conclusively demonstrated) to be four-carbon and six-carbon structures respectively. If the opinions of Staudinger, Wieland, and their collaborators (*Helv. Chim. Acta*, 1924, **7**, 23; *Annalen*, 1925, **446**, 19) respecting the constitution of di*cyclo*pentadiene be accepted, the *cyclo*hexene-forming tendency cannot be regarded as an intrinsic property of the butadienes (compare Lebedev's " butadiene type " of dimerisation, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1249). The circumstances which determine the constitution of these and similar additive products are of the greatest interest in relation to butadienoid polarisation. The formation of both a *cyclo*butane and a *cyclo*hexene (corresponding to the formation of 1 : 2- and 1 : 4-dibromides) from the same hydrocarbon has never been reported and it remains to be discovered to what extent cyclic addition of the polymeric type is modifiable by varying the polar character, the spatial configuration or the length of the conjugated system of the hydrocarbon.

Recently Diels and Alder have published (*Annalen*, 1928, **460**, 98) an interpretation of the well-known reaction between *p*-benzoquinone and *cyclo*pentadiene and have extended the application of this addition to the combination of maleic anhydride, acraldehyde and similar reagents with butadienoid hydrocarbons in general. In so doing they have not only furnished an elegant method for the characterisation of conjugated hydrocarbons but have brought to notice a type of addition which is *outwardly* analogous to the polymeric process already mentioned. Since in these additions the difficulties which attend the control of purely polymeric processes and the recognition of the reaction products thereof are largely absent, the reagents of Diels and Alder are admirably suited to the study of additive behaviour. Employing, therefore, maleic anhydride as an addendum, we have made observations on the possibility of modifying the *cyclo*hexene-forming tendency.

Addition to Open-chain Butadienes.—Diels and Alder record that the simple open-chain and cyclic butadienes unite with maleic anhydride to give anhydro*cyclo*hexenes in quantitative yield. *All* the reaction products are assumed to be analogous to the compound (I) derived from butadiene itself, in which the presence of a six-carbon ring has been definitely established. We have confirmed the homogeneity of the products and the quantitative nature of the yields obtainable from the hydrocarbons examined by Diels and Alder and have found the same to hold with other hydrocarbons. Further, we have demonstrated that Diels and Alder's formula (I)



(I.)



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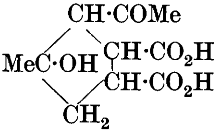


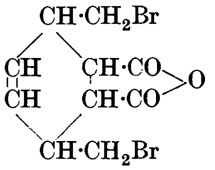
(III.)

(the position of the double bond had been assumed) is correct: the anhydride changes smoothly on oxidation into ββ′-dicarboxyadipic acid.

βγ-Dimethylbutadiene yields the *compound* (II), which is converted by ozonolysis into the ketonic acid

$$COMe{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}CH(CO_2H){\cdot}CH_2{\cdot}COMe,$$

or its cyclised equivalent (III). αζ-Dibromo-$\Delta^{\beta\delta}$-hexadiene yields (on heating with maleic anhydride) a crystalline derivative to which the formula (IV) is assigned. This very stable *anhydride* containing only one double bond (as determined by hydrogenation) yields almost quantitatively a *dilactone* (V), reducible catalytically to the saturated *lactone* (VI). The latter substance, however, could not be successfully oxidised to hexahydroprehnitic acid (VIII) for direct comparison with specimens obtained in the ways described below.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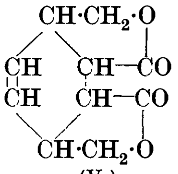
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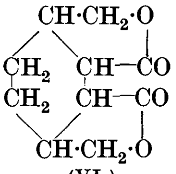
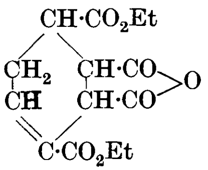

(VI.)

From these experiments and others carried out as a routine check on the purity of hydrocarbon samples, there is every reason to believe that *cyclo*hexene formation from open-chain butadienes is complete and remains unaffected (except as regards velocity of reaction) by variation of the position of the alkyl substituents.

Addition to Heterogeneous Conjugated Substances.—Ethyl muconate and sorbic acid react with maleic anhydride on prolonged heating. The additive product from the former gives oxalic acid so readily and extensively on treatment with permanganate or on ozonolysis that, in the absence of the observations of Baeyer (*Annalen*, 1890, **258**, 163) and Perkin and Pickles (J., 1905, **87**, 299) on the intense destructive action of permanganate on the hydrophthalic acids, its representation by a *cyclo*hexene structure such as (VII) would seem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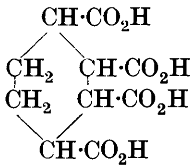
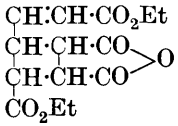
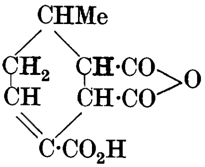

(VIII.)


(IX.)

to be out of the question. It is converted, however, on reduction and hydrolysis into a stable tetrabasic *acid* which not only yields a distillable *dianhydride* on treatment with acetyl chloride but shows no tendency, in the form of its *ester*, to undergo the Dieckmann reaction with sodium. These properties, although not absolutely identifying the reduced acid as hexahydroprehnitic acid (VIII), are inconsistent with the alternative formulation of the additive compound as the *cyclo*butane derivative (IX) or a Δ^{β}(etc.)-isomeride thereof. Complete proof has been sought by attempting to convert the *anhydro-ester* (VII) into the corresponding aromatic acid, prehnitic acid. Dehydrogenation, however, is not successful beyond the diolefinic stage, the final product being apparently a dihydroprehnitic acid. Ethyl *cis-cis*-muconate does not react appreciably with maleic anhydride even on prolonged heating.

The structure of the sorbic acid derivative is not easily demonstrable. The oxidation products are liquids, difficult to isolate in a pure state but of a character indicating their formation from the *cyclo*hexene compound (X) rather than from a corresponding *cyclo*butane compound. Since both additive products yield strongly enolic acids at an early stage during oxidation, αβ-positions are assigned to the double bonds in (VII) and (X).

Addition to Cyclic Butadienes.—The union of open-chain and cyclic butadienes with maleic anhydride is attended by the liberation of much heat; this is particularly striking with the cyclic hydrocarbons and reaches a maximum vigour with *cyclo*pentadiene. With *cyclo*hexadiene, the reaction appears to be a two-stage process in which the second stage, that of ring closure, is marked by the liberation of heat and is capable of acceleration or retardation, within limits, at will. The product is correctly represented by the *bridged cyclo*hexene formula (XI), since it yields on oxidation the identical geometrical form of hexahydroprehnitic acid (VIII) previously derived from the muconic derivative (VII).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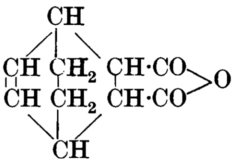
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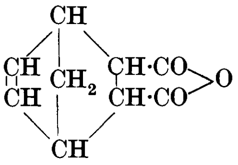
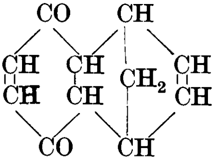

(XII.)

The correctness of Diels and Alder's formula (XII) for the *cyclo*pentadiene derivative is less certain, since it has not been possible to show that the tetracarboxylic acid derived by oxidation is unquestionably a *cyclo*pentane and not a *cyclo*butane derivative. On the contrary, although the anhydro-derivatives from *cyclo*pentadiene and *cyclo*hexadiene do not show any such difference in stability as that which characterises the hydrocarbon dimerides (one of these is oxidised with ease and the other with great difficulty), the tetrabasic oxidation product of the former is definitely inferior in stability to all the *cyclo*hexane acids which have been examined and therefore may not safely be assumed to contain a *cyclo*pentane ring. Subsequent to the completion of this portion of our work, Diels and Alder's formula (XII) was attacked by Bergel and Widmann (*Annalen*, 1928, **467**, 76) on grounds of the correspondence in instability of the *cyclo*pentadiene-quinone compound (XIII) and di*cyclo*pentadiene. Since Bergel and Widmann have obtained by oxidation of the latter a liquid tetrabasic acid considered to be (XIV), it is suggested that the constitution of the maleic anhydride and quinone derivatives may well be analogous to that of di*cyclo*pentadiene, *i.e.*, contain an additively formed *cyclo*butane ring. The liquid tetrabasic acid now described by Bergel and Widmann was examined by one of us a year ago : its stability appears inferior to that to be expected of a *cyclo*pentane ring. Thus, although there are grounds for suspecting that *cyclo*pentadiene differs from other hydrocarbons in its mode of adding a non-dividing addendum, the definite production of *cyclo*butane forms is hardly to be considered as established beyond all doubt.



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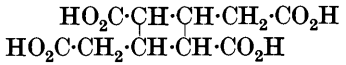
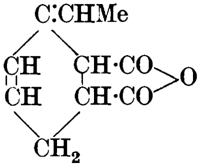


(XIV.)



(XV.)

Addition to the $\Delta^{\alpha\gamma\epsilon}$-Hexatrienes.—Maleic anhydride may be added with ease to van Romburgh's hexatriene (*trans*), the reaction yielding almost quantitatively a crystalline anhydride : to this the constitution (XV) is assigned on the following grounds. Degradation by ozonolysis yields acetaldehyde and a very strongly enolic aldehyde : the latter breaks down progressively on treatment with permanganate, apparently owing to the successive formation and decomposition of ketosuccinic (hydroxymaleic) acids, to yield oxalic acid as the main product [$CHO{\cdot}CO{\cdot}CH(CO_2H){\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CHO \longrightarrow (CO_2H)_2 + HO_2C{\cdot}CO{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$, etc.]. A similar decomposition takes place when the acid corresponding to (XV) is directly oxidised with permanganate.

cis-Hexatriene also combines additively with maleic anhydride. The addition product appeared at first to be isomeric, rather than identical, with that from the *trans*-hydrocarbon. It was a slightly impure liquid which solidified only after numerous distillations and the lapse of many weeks : this behaviour was in strong contrast with the remarkable crystallising capacity of the other anhydride. However, since from the first both anhydrides gave identical anilic acids and hydration products (as well as similar oxidation products), it is probable that the crystallisation of the newly obtained anhydride had merely been inhibited by impurity. This is the more likely in that any initial configurational difference between the products, due to the geometrical forms of the hydrocarbons, might be expected to disappear during the double-bond migration (presumably post-additive) which results in the appearance of ethylidene- instead of vinyl-*cyclo*hexenes.

trans-Hexatriene adds bromine both at the 1 : 2- and at the 1 : 6-positions (hitherto quinoline perbromide has been employed in preparing the 1 : 2-dibromide) : attachment at the 1 : 4-positions appears to be unfavoured. With maleic anhydride, there is exclusive attachment at the 1 : 4-carbon atoms, and the selection of the second point of attachment (at one or other of the even carbon atoms of the chain) seems not unconnected with the universal strong tendency towards the formation of six-carbon rings. Indeed it seems probable that, in all ring-forming additions of the type here considered, the intermolecular attachments are established consecutively and that the mode of completion of addition is determined—so far as choice between rival polarised centres of the butadiene chain is concerned—by configurational opportunism.

EXPERIMENTAL.

General Method.—The reactants in molecular proportion were kept in dry benzene solution. In some instances heating at 100° was necessary to effect addition (compare Diels and Alder, *loc. cit.*).

4 : 5-*Dimethyl*-cis-Δ^4-*tetrahydrophthalic anhydride* (II) was obtained quantitatively by keeping the solution of $\beta\gamma$-dimethylbutadiene and maleic anhydride for 24 hours at room temperature. It crystallised from petroleum (b. p. 60—80°) in long colourless needles, m. p. 78° (Found : C, 66·55; H, 6·65. $C_{10}H_{12}O_3$ requires C, 66·6; H, 6·7%). When heated for a few minutes with ten times its weight of water, the anhydride yielded 4 : 5-*dimethyl*-cis-Δ^4-*tetrahydrophthalic acid*, which readily separated from the aqueous liquor and crystallised from aqueous alcohol in colourless prisms, m. p. 180—192° (Found : C, 60·6; H, 7·1; *M*, dibasic, 199. $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·1%; *M*, 198). The acid reverted partly to the anhydride at its melting point.

When a chloroform solution of the anhydride was ozonised for several hours, a solid, somewhat sticky ozonide separated. This, after removal of chloroform at room temperature, was kept with water for several weeks. The crystalline acid produced, much of which could be filtered off directly and the remainder obtained by evaporating the aqueous liquor to dryness, was washed with ether and recrystallised from a small amount of water; m. p. 186°, with anhydride formation (Found: C, 51·9; H, 6·0; *M*, dibasic, 232. $C_{10}H_{14}O_6$ requires C, 52·15; H, 6·1%; *M*, 230). Of the two possible structures for this acid, octane-βη-dione-δε-dicarboxylic acid and the corresponding cyclol, 3-*acetyl*-4-*methyl*-cyclo*pentan*-4-*ol*-1 : 2-*dicarboxylic acid* (III), the latter is regarded as correct; although the acid yielded crystalline derivatives with the usual reagents for ketones, it did not yield ββ′-dicarboxyadipic acid on further oxidation with permanganate or hypobromite.

An acid, which appears to be a lactonised form of the open-chain octanedionedicarboxylic acid, was precipitated when the original anhydride was heated for a few minutes with dilute nitric acid (1 : 1) and the solution cooled; it formed colourless flakes, m. p. 219°, softening at 210° [Found: *M* (monobasic), 232; *M* (dibasic towards hot baryta), 232].

cis-Δ^4-Tetrahydrophthalic anhydride was obtained quantitatively from butadiene and maleic anhydride by keeping the solution of the reactants for 24 hours. The melting points of the anhydride and of the corresponding *cis*-Δ^4-tetrahydrophthalic acid were identical with those recorded by Diels and Alder.

The anhydride (3 g.) was hydrolysed by warming with a slight excess of sodium bicarbonate solution, and the product oxidised at 0° with 3% permanganate solution in the usual way. The equivalent of 2 atoms of oxygen per molecule of anhydride was readily absorbed and a second 2 atoms more slowly. From the product, worked up in the usual way, ether extracted a slightly gummy crystalline acid, and a further quantity of the same acid was obtained by evaporating the aqueous mother-liquor to dryness and extracting the residue. This acid was the lower-melting stereo-form of βγ-dicarboxyadipic acid, a colourless crystalline powder, m. p. 188—189° (Found: C, 40·8; H, 4·3; *M*, tetrabasic, 236. Calc.: C, 41·0; H, 4·3%; *M*, 234). This form, in view of the spatial distribution in the parent isomeride, should represent the *meso*-isomeride: steric formulæ have not been allotted to the two dicarboxyadipic acids, but by analogy with αα′-dimethylsuccinic acid the lower-melting acid should have the *meso*-configuration.

3 : 6-*Dibromomethyl*-cis-Δ^4-*tetrahydrophthalic Anhydride* (IV).—Addition of maleic anhydride to αζ-dibromo-$\Delta^{\beta\delta}$-hexadiene in benzene was effected at 100° during 5½ hours. The solvent was then removed from the almost black product, the residue mixed with dry ether, and the coarsely crystalline precipitate obtained recrystallised from light petroleum; it formed colourless slender needles

or (from benzene) short prisms, m. p. 98° (Found: Br, 47·4. $C_{10}H_{10}O_3Br_2$ requires Br, 47·3%). The ethereal liquor contained unchanged dibromide, maleic acid, and a further small quantity of the condensation product. Yield, 67%.

Careful oxidation of the *anhydride* with permanganate in neutral aqueous acetone, during which 4 atoms of oxygen per molecule were absorbed, yielded only gummy acids. The anhydride could not be hydrolysed by boiling water; when, however, it was boiled with aqueous sodium carbonate (2 mols. per mol. of anhydride), dissolution was slowly effected. The alkaline solution, after being boiled with charcoal and acidified, yielded white flakes, which recrystallised from water in fern-like leaves, m. p. 159—163° after softening at 147°. This substance, stable towards sodium bicarbonate, behaved as a *dilactone* (V) of 3 : 6-dihydroxymethyl-*cis*-Δ^4-tetrahydrophthalic acid (Found: C, 62·0; H, 5·1; *M*, dibasic, 196. $C_{10}H_{10}O_4$ requires C, 61·85; H, 5·15%; *M*, 194). Yield, 63%. Attempts to oxidise the sodium salt of the dihydroxy-acid to ββ′-dicarboxyadipic acid proved futile. Permanganate in particular caused extensive degradation to oxalic acid.

Lactone of 3 : 6-*Dihydroxymethylhexahydrophthalic Acid* (VI).—Catalytic reduction of the preceding lactone was readily effected, one molecule of hydrogen being absorbed. The saturated *lactone* crystallised from aqueous alcohol in colourless prisms, m. p. 119—120° (Found: C, 61·5; H, 6·1. $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·1%). Attempts were made to oxidise this substance to hexahydroprehnitic acid by Fournier's method (*Bull. Soc. chim.*, 1909, **5**, 920): the product was a mixture of oxalic acid and an acid (colourless prisms from water; m. p. 135°) which, although greatly resembling the acid sought, had approximately the composition $C_{10}H_{12}O_5$.

Addition to trans-αβ-*Dibromo*-$\Delta^{\gamma\epsilon}$-*hexadiene*.—A benzene solution of maleic anhydride and the dibromide (the latter prepared by the method of Farmer, Laroia, Switz, and Thorpe, J., 1927, 2953) in equimolecular proportion was kept for 12 hours and then heated for 5 hours at 100°. On removal of the solvent, a dark viscous mass remained from which no portion of the reactants could be recovered. Although addition had occurred, a pure addition product could not be isolated. Isomerisation of the αβ-dibromide had occurred to some extent during the heating, since a quantity of the dilactone, m. p. 159—163°, derivable from αζ-dibromo-$\Delta^{\beta\delta}$-hexadiene was obtained by boiling the crude condensation product with aqueous sodium carbonate for 20 minutes.

3 : 6-*Dicarbethoxy*-Δ^3-*tetrahydrophthalic anhydride* (VII) was prepared from maleic anhydride and ethyl *trans-trans*-muconate at

100° (yield : 29% after 5 hours; 50% after 18 hours). It separated from the cooled reaction mixture in spherical crystal aggregates which, after twice crystallising from chloroform, formed white flakes, m. p. 185—188° (Found: C, 56·5; H, 5·4. $C_{14}H_{16}O_7$ requires C, 56·8; H, 5·4%).

The anhydro-ester was boiled with water for 20 minutes, and the cooled solution neutralised with sodium carbonate. The product was oxidised : 3% permanganate solution equivalent to 4 atoms of oxygen was supplied, the bulk of which was reduced in 3½ hours at 0° and the remainder on standing over-night at room temperature. The product, freed from manganese, was boiled for 20 minutes to complete the hydrolysis of ester groups; it was then concentrated to small bulk, acidified, and extracted with ether. The extract yielded oxalic acid mixed with a relatively small proportion of acidic gum. The yield of oxalic acid was much too large to be correlated with the amount of oxygen supplied. Reduction of the proportion of permanganate employed led to the production of an enolic syrupy acid and oxalic acid. Since the enolic material was invariably produced at an early stage in the reaction, the double bond is assigned to the Δ^3-position.

In order to discover whether double-bond movement occurred during opening of the anhydride ring the anhydro-ester was ozonised. The ozonide on warming with water lost carbon dioxide and yielded a deep yellow solution; the latter, however, on further oxidation with alkaline hydrogen peroxide, yielded oxalic acid as the only recognisable product.

From the anhydro-ester the corresponding tetraethyl ester (colourless prisms, m. p. 75°) was obtained by the action of alcoholic hydrogen chloride. By alternate addition of bromine, and removal of hydrogen bromide with diethylamine or pyridine, it was sought to convert the ester successively into ethyl dihydroprehnitate and ethyl prehnitate. The final product, however, after two such series of operations (in the second series, bromine was absorbed only under strong illumination) yielded on hydrolysis an *acid* corresponding in composition to dihydroprehnitic acid (colourless prisms from water; m. p. 241° with decomp.) (Found: C, 47·2; H, 3·1. $C_{10}H_8O_8$ requires C, 47·0; H, 3·1%).

3 : 6-*Dicarboxyhexahydrophthalic Acid* (*Hexahydroprehnitic Acid*) (VIII).—Dicarbethoxy-Δ^3-tetrahydrophthalic acid was hydrogenated catalytically in the presence of colloidal palladium. For this purpose the above-described anhydro-ester was boiled for 30 minutes with water, and the product diluted with alcohol. Addition of 1 mol. of hydrogen was complete in a few hours; prolonged treatment with hydrogen caused no further absorption. The

reduction product was isolated in the usual way and immediately hydrolysed with boiling dilute hydrochloric acid. On concentration of the acid solution to small bulk, the saturated *acid* separated slowly in large rectangular prisms containing $1H_2O$. These were twice recrystallised from very small quantities of water, and then had m. p. about 168° (variable with the rate of heating owing to anhydride formation) (Found : C, 43·0; H, 5·1; *M*, tetrabasic, 281. $C_{10}H_{12}O_8,H_2O$ requires C, 43·2; H, 5·05%; *M*, 278).

The *tetraethyl* ester, formed by saturating an alcoholic solution of the acid with hydrogen chloride, was a colourless oil, b. p. 238°/15 mm. (Found : C, 58·1; H, 7·5. $C_{18}H_{28}O_8$ requires C, 58·1; H, 7·5%). It was recovered unchanged after treatment in toluene with pulverised sodium.

The *dianhydride* separated in well-formed prisms, m. p. 223—225°, when the acid was refluxed for several hours with pure acetyl chloride (Found : C, 53·5; H, 3·5. $C_{10}H_8O_6$ requires C, 53·5; H, 3·5%). It distilled unchanged, save for slight resinification, at greatly reduced pressure.

6-*Carboxy*-3-*methyl*-cis-Δ^5-*tetrahydrophthalic anhydride* (X) was obtained by heating a benzene solution of maleic anhydride and sorbic acid for 18—38 hours at 100° and immediately pouring off the hot liquor from the hard prismatic mass which had separated. The latter very sparingly soluble substance (m. p. 174°) was purified by treating it several times with boiling benzene and with ether. Yield : 57% in 18 hours; 80% in 36 hours. The anhydride could be dissolved in boiling water without appreciable hydrolysis; boiling for 1 hour with water yielded 6-*carboxy*-3-*methyl*-cis-Δ^5-*tetrahydrophthalic acid*, which formed colourless prisms, m. p. 194° with anhydride formation (Found : C, 52·5; H, 5·2; *M*, tribasic, 231. $C_{10}H_{12}O_6$ requires C, 52·6; H, 5·3%; *M*, 228).

The anhydride yielded a semi-solid ozonide, insoluble in chloroform. Decomposition of the ozonide with water yielded no volatile aldehyde; the syrupy aldehydic material obtained was extensively broken down to oxalic acid by further gentle oxidation with permanganate. When the anhydride was carefully oxidised with alkaline permanganate (3 atoms of oxygen per molecule of anhydride), no oxalic acid was produced, but an enolic acid which lost carbon dioxide on heating and was further oxidisable by alkaline hydrogen peroxide or sodium hypochlorite to a viscous polybasic acid. Although oxidation followed a course generally consistent with the formula assigned, the acidic products could not be obtained sufficiently pure for identification.

The acid, when catalytically hydrogenated in the presence of palladium, absorbed 1 mol. of hydrogen and gave 6-*carboxy*-3-*methyl*-

cis-*hexahydrophthalic acid*, which crystallised from water in glistening prisms containing $1H_2O$, m. p. 194—196° (Found : C, 48·5 ; H, 6·5. *M*, tribasic, 247. $C_{10}H_{16}O_7$ requires C, 48·4 ; H, 6·45% ; *M*, 248).

Addition to Cyclic Butadienes.—The addition of maleic anhydride to *cyclo*hexadiene (compare Diels and Alder, *loc. cit.*) was effected in various solvents. When the reactants were mixed, the solution (especially in benzene) assumed a deep yellow colour ; after a few minutes, the temperature began to rise rapidly and the colour gradually faded; if the solution was kept cool, the yellow colour could be preserved for many hours. In the absence of a solvent reaction was very vigorous, the temperature rising to 150° and above, but in certain solvents, such as ether, the reaction was greatly retarded. The addition to *cyclo*pentadiene took place very vigorously in all solvents and explosively in the absence of a solvent.

Oxidation of Dicyclo*octenedicarboxylic Acid* (*Ethane*-$^{1:2}\Pi^{1:4}$-Δ^5-cyclo*hexene*-2 : 3-*dicarboxylic Acid*).—Oxidation of the *cyclo*hexadiene addition product with alkaline permanganate (4 atoms of oxygen per molecule) at 0° yielded a solid tetrabasic *acid*, m. p. 168° (decomp.), which formed colourless prisms containing $1H_2O$ (Found : C, 43·15 ; H, 5·0 ; *M*, tetrabasic, 281·6. $C_{10}H_{14}O_9$ requires C, 43·2 ; H, 5·0% ; *M*, 278), mixed with a syrupy acid which appeared to be an impure form of the solid acid. The latter gave the same dianhydride and was in all observed respects identical with the acid obtained by hydrogenating the ethyl muconate addition product described above.

Oxidation of the cyclo*Pentadiene–Maleic Anhydride Condensation Product.*—Permanganate oxidation in this instance differed from all similar oxidations of hydrocarbon–maleic anhydride products in the indefiniteness of the end point and in the resinification which occurred (with blackening of the solution) during concentration of the oxidation liquor. These points are characteristic of the corresponding oxidation of *dicyclo*pentadiene. The dark brown viscous acid obtained deposited colourless prisms of a tetrabasic *acid*, m. p. 181—182° with anhydride formation (Found : C, 42·9; H, 4·2; *M*, tetrabasic, 250. $C_9H_{10}O_8$ requires C, 42·9; H, 4·1%; *M*, 246). Esterification of the non-solidifiable portion (*tetraethyl* ester, colourless mobile liquid, b. p. 226°/14 mm. Found: C, 57·0; H, 7·2. $C_{10}H_{18}O_8$ requires C, 57·0; H, 7·3%), followed by hydrolysis with hydrochloric acid, permitted separation of the resinous matter and the accumulation of considerable quantities of the solid acid. The attempts which have been made to determine whether this acid is to be regarded as *cyclo*pentane-1 : 2 : 3 : 4-tetracarboxylic acid or as *cyclo*butane-1 : 2 : 3-tricarboxy-4-acetic acid have so far been without success. Unlike the analogous *cyclo*hexane acids, it gradually reduced alkaline permanganate.

Addition to trans-*Hexatriene.*—The benzene solution of maleic anhydride and hexatriene was kept at room temperature for 14 hours and then heated at 100° for 5 hours. After removal of the solvent at reduced pressure an oil remained which soon solidified (m. p. 46°). This substance, *3-ethylidene*-cis-Δ^4-*tetrahydrophthalic anhydride*, separated from petroleum (b. p. 40—60°) in very long, colourless needles, m. p. 51·5°, b. p. 148°/6 mm. (Found : C, 67·6; H, 5·6. $C_{10}H_{10}O_3$ requires C, 67·4; H, 5·6%). With aniline it yielded an *anilic acid* (colourless flakes, m. p. 174°. Found : C, 71·1; H, 6·2. $C_{16}H_{17}O_3N$ requires C, 70·85; H, 6·3%). Yield, quantitative.

On boiling with water for 10 minutes the anhydride passed into solution. Extraction of the cooled product with ether yielded the corresponding *3-ethylidene*-cis-Δ^4-*tetrahydrophthalic acid*, which crystallised from water in colourless prisms, m. p. 164—166° with evolution of steam (Found : C, 61·4; H, 6·3; *M*, dibasic, 197·6. $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·1%; *M*, 196).

Ozonisation of a chloroform solution of the anhydride at 0° for 9 hours caused the separation of a sticky ozonide which, after removal of the solvent, was gently heated with water. The vapours evolved during heating, smelling strongly of acetaldehyde, were swept by a stream of carbon dioxide into an acetic acid solution of β-naphthol containing some hydrochloric acid (compare Mulliken, "Identification of Pure Organic Compounds," I, 23). A considerable quantity of ethylidene-β-dinaphthyl oxide, m. p. 172·5° (mixed m. p. with authentic specimen, 172·5°), was obtained. The colourless aqueous liquor, which gave a very intense purple colour with ferric chloride, assumed a dark brown colour on boiling; on extraction with ether it yielded syrupy products from which only oxalic acid could be obtained on further oxidation with permanganate; on neutralisation with alkali and addition of ammonia it yielded a small amount (too small for investigation) of an insoluble calcium salt which had the characteristic properties of precipitated calcium tricarballylate.

The oxidation of the anhydride with ice-cold permanganate solution was studied in some detail. Invariably 7 atoms of oxygen per molecule of anhydride were readily taken up, after which reduction of permanganate became very slow. Isolation of the oxidation product at this stage—a stage corresponding to the production of α-oxalyltricarballylic acid—yielded a strongly enolic acid (intense purple colour with ferric chloride). Further oxidation of the latter with permanganate could be slowly accomplished at room temperature : interruption of the oxidation process and isolation of the product from portions of the material yielded always oxalic acid and syrupy enolic acids until finally practically the whole of the original anhydride had been converted into oxalic acid.

Addition to cis-*Hexatriene.*—A benzene solution of the hydrocarbon (which contained a little of the *trans*-isomeride) and maleic anhydride was kept for 12 hours and then heated at 100° for 5 hours. From the cooled product, some insoluble matter (highly polymerised material) was filtered off, and the solvent removed at reduced pressure. The crude liquid anhydride obtained (yield, 83%; b. p. 120—150° after a very small proportion of maleic anhydride had distilled) was rigorously fractionated and specimens were analysed. All fractions were very slightly impure, although all gave nearly quantitative yields of an anilic acid and of an ethylidene-*cis*-tetrahydrophthalic acid identical with the corresponding compounds from the *trans*-hydrocarbon. Ultimately, after many distillations and the lapse of several weeks, practically the whole of the material solidified; the solid after two recrystallisations was found to be identical with the ethylidene-*cis*-tetrahydrophthalic anhydride derived from the *trans*-hydrocarbon. On ozonisation the once-distilled crude liquid anhydride gave results identical with those recorded for the pure solid anhydride.

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