127. *Addition of Maleic Anhydride and Ethyl Maleate to Substituted Styrenes.*

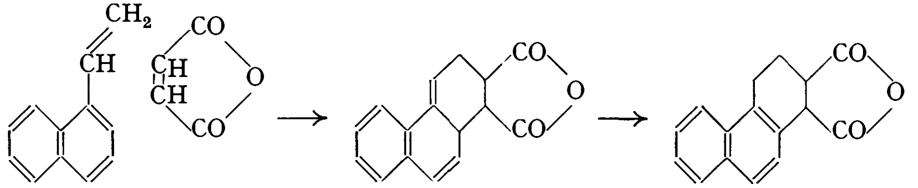
By B. J. F. Hudson and Sir Robert Robinson.

There does not appear to be any recorded instance of a simple Diels–Alder adduct (1 : 1) being formed by *o*-β(1 : 4)-addition to styrene or one of its substituted derivatives. In an attempt to realise such a reaction *iso*safrole, on account of its accessibility, was tried first and found to give 1 : 1 adducts with maleic anhydride and ethyl maleate. These substances are regarded as 1 : 2 : 3 : 4-tetrahydronaphthalene derivatives on account of their stability to permanganate. *iso*Eugenol methyl ether behaved like *iso*safrole and, of the stereoisomeric *iso*eugenol ethyl ethers, the *cis*-compound formed a normal adduct with maleic anhydride.

2 : 3-Dimethoxy-α-propenylbenzene formed a simple adduct with greater difficulty, but no such products were obtained from anethole or *m*-methoxy-α-propenylbenzene, or from any styrene unsubstituted in the β-position. The reaction succeeds with 3 : 4-*methylenedioxy*-β-*propylstyrene*, but not with 3 : 4-methylenedioxy-β-bromostyrene or with ethyl β-piperonylacrylate. It seems, therefore, that the necessary conditions are substantially those obtaining in *iso*safrole and its close analogues.

The opportunity is taken to include an account of a preliminary study of the use of benzylidenepyruvic esters as philodienes. In one case the normal product was isolated, but in others, although the reaction obviously took place, the products could not be purified.

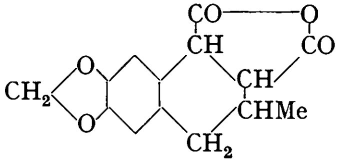
In the course of an investigation of " heteropolymers " Wagner-Jauregg (*Ber.*, 1930, **63**, 3213) obtained a compound, $C_{22}H_{16}O_6$, by addition of *as*.-diphenylethylene (1 mol.) to maleic anhydride (2 mols.). This was degraded to 1-phenyl-1 : 2 : 3 : 4-tetrahydronaphthalene-3 : 4-dicarboxylic acid and to 1-phenylnaphthalene, but the formation of the compound was not considered to be due to 1 : 4-addition of maleic anhydride in the first place (*Annalen*, 1931, **491**, 1). Cohen (J., 1937, 1315) found that 1-vinylnaphthalene adds maleic anhydride normally and probably with the usual shift of the double bonds, because the product is unsaturated and is readily isomerised to an aromatic naphthalene as shown in the scheme :

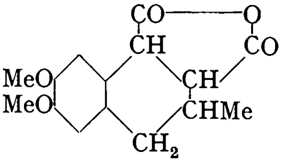


Bergmann and Bergmann (*J. Amer. Chem. Soc.*, 1937, **59**, 443) proposed the similar use of 1-β-naphthyl*cyclo*pentene as a route to *cyclo*pentenophenanthrene derivatives and this was realised by Bachmann and Kloetzel (*ibid.*, 1938, **60**, 2204), who also used 1-α-naphthyl*cyclo*pentene. These authors assume that the products are of the normal type in which one double bond becomes exocyclic to the naphthalene nucleus, but this view is based on analogy only.

We wished to apply a similar reaction in the simple benzene series and in particular to *m*-methoxystyrene with a synthetical objective. The first results have already been indicated in the summary. The *adducts* from *iso*safrole and *iso*eugenol methyl ether are (I) and (II) respectively

(I.)





(II.)

The dehydrogenation of (I) was attempted by heating with sulphur, but the product contained that element and was of complex constitution. The process was accomplished by heating with palladised charcoal (cf. Diels and Gädke, *Ber.*, 1925, **58**, 1231) and the yellow 6 : *7-methylenedioxy-3-methylnaphthalene-1 : 2-dicarboxylic acid anhydride* was obtained. In order to prove the orientation of addition to the benzene nucleus, (II) was oxidised by potassium permanganate to metahemipinic acid.

Piperonylallylene was expected to yield a dihydronaphthalene derivative by union with maleic anhydride, but the only product isolated was the above-mentioned methylenedioxymethylnaphthalenedicarboxylic acid anhydride. On the other hand, *iso*safrole and ethyl acetylenedicarboxylate yield the expected dihydronaphthalene derivative in the form of the anhydride of the dicarboxylic acid. It is to be noted that the dihydronaphthalenes anticipated in these two cases are not the same. The substance from piperonylmethylacetylene and maleic anhydride would be a derivative of succinic acid, that from *iso*safrole and ethyl acetylenedicarboxylate would be a derivative of maleic acid. The facilitation of dehydrogenation by the attached carboxyl groups is exemplified in the well-known biological conversion of succinic acid into fumaric acid.

The various styrenes, anethole and *m*-anethole gave heteropolymers, but methylenedioxystyrene reacted with maleic anhydride to form a relatively simple substance which has not yet been fully investigated.

The following deductions from these experiments may be made : (1) An alkoxy-group in the *p*-position to the unsaturated side-chain of a styrene enhances the tendency to unite with maleic anhydride. An *o*-alkoxyl is probably similarly effective but in a less degree. Only one example bears on this point.

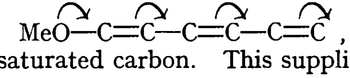
(2) An alkoxy-group in the *m*-position to the side chain has no such effect and appears to exert a stabilising influence.

(3) When both *m*- and *p*-alkoxy-substituents are present, the capacity for addition to maleic anhydride is not completely suppressed but the reaction is not so facile as with the simple *p*-substituted derivatives.

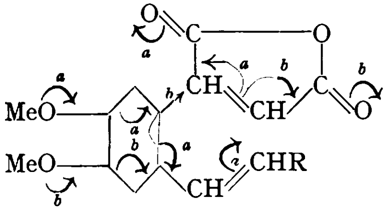
(4) Naphthalene derivatives (1 : 1 adducts) are only obtained (*a*) when there is a *m*-alkoxy-group, which is, of course, *p*- to the carbon atom of the benzene ring involved in the cyclisation, and (*b*) when the styrene derivative is β-alkylated.

It is likely that the cyclisation process is a slow one and the requisite styrene is therefore one of relatively feeble additive power. Otherwise complex heteropolymer formation competes too successfully with that of the naphthalene ring. This is probably the reason for condition 4 (*b*).

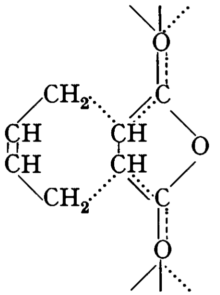
Conclusions (1) and (2) are in harmony with the theory that the Diels–Alder reaction is *initiated* by an anionoid-cationoid reaction in which the diene is anionoid. In other terms the molecules unite by the formation or part formation of a co-ordinate link, or again the philodiene oxidises the diene in the first place.

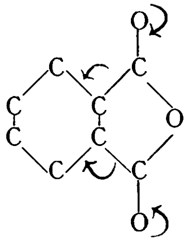
The hetero-enoid system,  $\mathrm{MeO{-}C{=}C{-}C{=}C{-}C{=}C}$, functions to enhance the anionoid character of the β-unsaturated carbon. This supplies an acceptable explanation of (1). In regard to (2), the *m*-methoxyl can have no such effect and its general inductive effect would be in the opposite direction.

Similarly 4(*a*) is strong evidence that the cyclisation is ***also an anionoid reaction*** of the benzene nucleus and again this has reference only to the first phase of the formation of the bond in question. Thus the two first phases may be combined in the annexed expression. Such a process produces strains due to the positive and negative charges on the oxygen atoms and to the disturbance of the aromatic nucleus. It assumes that the diene component is the electron donor and the maleic anhydride the electron acceptor; it is a homogeneous reduction of the maleic anhydride. But in the end the contributions of electrons of the two components to the new bonds are equal and therefore at a certain stage electrons must pass in the reverse direction as the result of a strain-relief phase or phases.



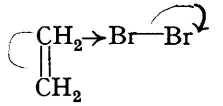
If for simplicity of representation we take the case of butadiene, the end of a process such as the above would be the following, in which the dotted lines each represent one electron.



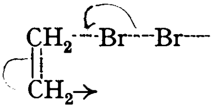


The necessary strain-relief is shown on the right.

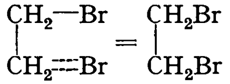
There is one important difference between this model and our actual examples. In the butadiene case an electron deficit develops on the α- and δ-carbon atoms, but in *iso*safrole and similar substances this electron deficit is remedied by the electrons supplied by the alkoxy-groups and all that need be postulated is the development of a positive charge on the oxygen atoms of these groups. The above must not be taken to imply that we think the first phases will proceed to the end before the strain-relief operates; there will probably be an alternation of phases of the two types. Nor do we consider that such a scheme must apply to all Diels–Alder reactions, particularly with such components as acraldehyde or acrylic esters in which only the β-carbon atom is essentially cationoid in character. There is little evidence that can shed light on the mechanism in these cases, but there is a theoretical possibility of a completed cycle in which one position of the diene and philodiene is anionoid and the other position of each is cationoid. On the other hand, the possibility exists that many reactions at present regarded as proceeding in a complete cycle with passage of a small current round the closed circuit are actually effectively homopolar as the result of reversals following an original displacement. Such a view often combines the advantages of the simple polar mechanisms (especially the explanation of orientation and points of attack) with those of homopolar mechanisms (analogies with radical and atom reactions) (cf. Presidential Address, this vol., p. 220). The formation of ethylene bromide may be used in illustration of this hypothesis, which is generally applicable unless ions are among the products (*e.g.*, ethylene, chlorine and water to chlorohydrin and hydrogen chloride).



1st *Phase*



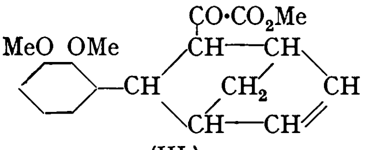
2nd *Phase*



3rd *Phase*

The bromine *atom* produced in the second phase may also attack some other ethylene molecule, before or after the latter has engaged a bromine molecule. Or one ethylene molecule may attack two bromine molecules, producing ethylene bromide and two bromine atoms. In considering such mechanisms in relation to kinetics it must be recognised that the reactions of bromine atoms will be very rapid and that there will be some loss due to recombination to bromine molecules.

A different line of investigation was instituted with a view to the synthesis of 10-hydroxy-3 : 4-dimethoxyphenanthrene. This is required in order to determine whether the hydroxycodeine of Ach and Knorr (*Ber.*, 1903, **36**, 3067) is 9- or 10-hydroxycodeine. It was proposed to add butadiene to *methyl* o-*veratrylidenepyruvate*, reduce the double bond and keto-group of the product, and cyclise to a hydro-derivative of the required phenanthrene or alternatively to dehydrogenate at an appropriate stage before cyclisation. The unsaturated keto-ester reacts normally with *cyclo*pentadiene to yield (III), but its adduct with butadiene could not be isolated.



(III.)

EXPERIMENTAL.

6 : 7-*Methylenedioxy*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-1 : 2-*dicarboxylic Acid and Derivatives.*—*Anhydride* (I). A mixture of *iso*safrole (13 g.), maleic anhydride (10 g.), and xylene (40 c.c.) was refluxed for 3 hours (the reaction was sometimes effected at 100°). The solid (10 g., m. p. 110—120°) that separated on cooling was collected, washed with alcohol, and extracted with hot chloroform. On cooling, pale yellow crystals, m. p. 138—139° separated; the insoluble portion dissolved in hot pyridine, but separated on cooling as a white amorphous solid, m. p. above 260° (decomp.) (Found : C, 59·9; H, 4·2%). This polymer was very sparingly soluble in most organic solvents; it dissolved in hot aqueous sodium hydroxide with part regeneration of its generators. The xylene mother-liquor was concentrated by distillation to one-fifth of its original volume, and alcohol (50 c.c.) added. This gave a pale yellow solid (5 g., m. p. 139—140°) identical with the chloroform-soluble material (above). The *adduct* (total yield, 40—50%) crystallised from ethylene chloride–light petroleum or from much light petroleum (b. p. 60—80°) in faintly yellow, slender needles, m. p. 142—143° (Found : C, 64·3; H, 4·9. $C_{14}H_{12}O_5$ requires C, 64·6; H, 4·6%). The fluorescein, obtained by heating with resorcinol and a trace of sulphuric acid, exhibited a very intense ivy-green fluorescence in alkaline solution. The *phenylimide* separated when a mixture of the anhydride (1·0 g.), aniline (0·35 g.), and toluene (10 c.c.) was refluxed for 1 hour. It crystallised from much alcohol in clusters of slender colourless needles, m. p. 243° (Found : N, 4·2. $C_{20}H_{17}O_4N$ requires N, 4·2%).

The anhydride dissolved in aqueous sodium hydroxide on gentle heating and the dibasic *acid* obtained on acidification of the solution crystallised from acetic acid in fine, colourless needles, m. p. 143° (decomp.), being obviously converted into the anhydride (Found : C, 60·3; H, 5·3. $C_{14}H_{14}O_6$ requires C, 60·4; H, 5·1%). The substance is readily soluble in aqueous sodium carbonate and is stable to permanganate in cold solution. An attempted oxidation to hydrastic acid was unsuccessful, but this fact is not significant in view of the low yields of hydrastic acid always experienced in oxidations with hot alkaline permanganate.

Ethyl ester. A mixture of *iso*safrole (18 g.) and ethyl maleate (20 g.) was refluxed for 2 hours, and the orange-red liquid then distilled. After unchanged material the *adduct* was obtained as a viscous, pale yellow liquid, b. p. 205—210°/1·3 mm. (yield, 20%). The substance crystallised in contact with alcohol and separated from this solvent in prisms, m. p. 92—93° (Found : C, 64·7; H, 6·6. $C_{18}H_{22}O_6$ requires C, 64·6; H, 6·6%). Hydrolysis with alcoholic potassium hydroxide, followed by acidification and heating, gave the anhydride, m. p. 142—143°, which did not depress the m. p. of an authentic specimen.

Dehydrogenation. The anhydride (6 g.) and flowers of sulphur (1·4 g.) were heated together at 185—190° for 1½ hours. The cooled mass was broken up and extracted with alcohol (Soxhlet). The dark red solution deposited crystals on cooling and the substance was recrystallised from dioxan, being obtained in pale yellow, slender needles, m. p. 237° (Found : C, 60·9; H, 3·4; S, 6·4%). The substance is not affected by boiling aqueous sodium sulphite. It dissolves slowly in boiling aqueous sodium hydroxide and the solution on cooling and acidification gives a colourless precipitate. On heating, this turns yellow (anhydride formation ?) and some sulphur dioxide is evolved. In a similar experiment at a higher temperature a different product was obtained; yellow needles, m. p. 235—236°, from acetic acid (Found: C, 57·5; H, 3·0; S, 13·3%).

The dehydrogenation proceeded rapidly when the anhydride was heated with palladised charcoal. A mixture of the adduct (0·3 g.) and the catalyst (0·1 g., prepared according to Diels and Gädke, *loc. cit.*) was gradually heated to 300° in a stream of carbon dioxide. After ½ hour, the product, which had largely sublimed, was collected and crystallised from acetic acid, being obtained as golden-yellow needles, m. p. 242—243° (Found: C, 65·7; H, 3·5. $C_{14}H_8O_5$ requires C, 65·6; H, 3·1%).

6 : 7-*Methylenedioxy*-3-*methylnaphthalene*-1 : 2-*dicarboxylic acid anhydride* dissolves in hot aqueous sodium hydroxide and a colourless acid is obtained on acidification. This becomes yellow when the solution is heated, due to conversion into the anhydride. The latter substance was also obtained by heating piperonylallylene (5·8 g.) (Foulds and Robinson, J., 1914, **105**, 1964) in xylene (20 c.c.) with maleic anhydride (2·9 g.) at 150° for 2 hours. Unchanged material was removed by distillation, and the dark red residue triturated with ether. The yellow solid so obtained crystallised from acetic acid in yellow needles, m. p. 238° (Found: C, 65·4; H, 3·4%).

6 : 7-*Methylenedioxy*-3-*methyl*-3 : 4-*dihydronaphthalene*-1 : 2-*dicarboxylic Acid Anhydride*.—A mixture of *iso*safrole (4·5 g.) and ethyl acetylenedicarboxylate (5·0 g.) became immediately deep red, but no adduct could be isolated and the liquid was heated on the steam-bath for 1 hour and at 200° for 5 minutes. On cooling, yellow needles (0·5 g.) separated; the substance was recrystallised from methyl alcohol, being obtained in a similar form, m. p. 178° (Found: C, 65·3; H, 4·1. $C_{14}H_{10}O_5$ requires C, 65·0; H, 3·9%). The corresponding colourless dicarboxylic acid, obtained in the usual way, reverted to the yellow anhydride on heating in aqueous acid solution. The original filtrate, which doubtless contained more of this substance, was inadvertently lost.

Ethyl 7-*Benzoyloxy*-6-*methoxy*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-1 : 2-*dicarboxylate*.—A mixture of *iso*eugenol (14 g.) and ethyl maleate (15 g.) was refluxed for 4 hours and distilled. Unchanged substances, b. p. 95—120°/1·5 mm., were first obtained and then the adduct (7 g.), b. p. 236—237°/1·5 mm., came over as a viscous oil that set to a glassy mass and could not be crystallised. The substance is readily soluble in cold aqueous sodium hydroxide and its alcoholic solution develops a dark green coloration on the addition of ferric chloride. The *benzoyl* derivative, prepared by the Schotten–Baumann method, crystallised from alcohol in white prisms, m. p. 117—118° (Found: C, 68·1; H, 6·5. $C_{25}H_{28}O_7$ requires C, 68·2; H, 6·4%).

Derivatives of 6 : 7-*Dimethoxy*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-1 : 2-*dicarboxylic Acid*.—*Anhydride* (II). A mixture of *O*-methyl*iso*eugenol (24 g.), maleic anhydride (18 g.), and xylene (50 c.c.) was refluxed for 5 hours and kept for 2 days; xylene (45 c.c.) was then distilled. The residue, an orange-red, glassy mass, was boiled with alcohol (200 c.c.); a solid then separated (30 g., m. p. 101—103°). This was dissolved in chloroform and a little light petroleum added to precipitate a small quantity of polymeric material. The *adduct* was recovered from the filtrate and crystallised from acetic anhydride, or from a relatively large volume of light petroleum (b. p. 80—100°). It formed short, pale yellow prisms, m. p. 107° (Found: C, 65·3; H, 5·8. $C_{15}H_{16}O_5$ requires C, 65·2; H, 5·8%). The behaviour with hot alkaline solutions and subsequent acidification is like that of the adduct from *iso*safrole. The acid is stable to cold alkaline permanganate. The *phenylimide* crystallised from alcohol–chloroform (9 : 1) in colourless needles, m. p. 163° (Found: N, 3·8. $C_{21}H_{23}O_5N$ requires N, 3·8%).

Oxidation. Aqueous potassium permanganate (160 c.c. of 10%) was gradually added to a boiling solution of the acid (from 10 g. of anhydride) in aqueous sodium carbonate. When all the permanganate was reduced, the solution was filtered, saturated with ammonium sulphate, and exhaustively extracted with ether (20 extractions). The acid in the ether was isolated and mixed with aqueous ethylamine (10%), and the solution distilled, finally at 6 mm. pressure. The solid distillate crystallised from alcohol in white prisms, m. p. 228° alone or mixed with authentic metahemipinethylimide (Found: C, 61·0; H, 5·7. Calc. for $C_{12}H_{13}O_4N$: C, 61·3; H, 5·5%).

Ethyl ester. A mixture of *O*-methyl*iso*eugenol (24 g.) and ethyl maleate (22·5 g.) was refluxed for 6 hours and distilled. Unchanged material (15 g., b. p. 80—110°/1 mm.) was followed by the *adduct* (21 g.), a yellow oil, b. p. 212—214°/1·5 mm. After some weeks the substance crystallised in white needles, m. p. 70° (Found: C, 65·4; H, 7·2. $C_{19}H_{26}O_6$ requires C, 65·2; H, 7·5%). The reaction between *O*-methyl*iso*eugenol and ethyl maleate is reversible. The yield never exceeds 50% and if the adduct is heated it reverts to some extent into its generators.

Dehydrogenation of this ester was effected in the usual manner by heating with palladised charcoal. The product (yield, 50%), 6 : 7-*dimethoxy*-3-*methylnaphthalene*-1 : 2-*dicarboxylic acid* *anhydride*, crystallised from ethylene chloride in small, yellow prisms, m. p. 250—251° (m. p. 251—252° from acetic acid) (Found : C, 65·6; H, 4·6. $C_{15}H_{12}O_5$ requires C, 66·1; H, 4·5%). The corresponding acid is colourless and becomes yellow and insoluble in cold aqueous alkalis on heating in suspension in acid solution.

6-*Methoxy*-7-*ethoxy*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-1 : 2-*dicarboxylic Acid and Derivatives*.—We are indebted to Dr. T. F. West for specimens of *cis*- and *trans*-*O*-ethyl*iso*eugenol, the separation of which he has described (*J. Soc. Chem. Ind.*, 1939, **59**, 275 T). The *trans*-compound, m. p. 64°, gave only heteropolymers with maleic anhydride under varied conditions. With ethyl maleate, substances, b. p. 190—210°/0·3 mm. and b. p. 210—220°/0·5 mm., were obtained. These b. p. ranges are approximately those anticipated for the 1 : 1-adduct (see below), but neither the products themselves nor the acids obtained on hydrolysis could be crystallised. Analysis of these fractions gave results low in carbon content. On the other hand the *cis*-isomer (b. p. 256—257°) behaved like *O*-methyl*iso*eugenol.

The condensation with maleic anhydride (1·25 mols.) was carried out in boiling xylene solution (5 hours), and the product separated by distillation (b. p. 200—240°/0·5 mm.) and purified by successive crystallisation from acetone, benzene, and benzene–light petroleum. It was obtained in pale yellow prisms, m. p. 130—131° (Found : C, 66·1; H, 6·1. $C_{16}H_{18}O_5$ requires C, 66·2; H, 6·2%). The yield was 40—50% and very little polymer was formed. The mother-liquors contained a dark yellow, uncrystallisable oil. This *anhydride* closely resembles the analogous substances described above in its properties.

Ethyl ester. An equimolecular mixture of *cis*-*O*-ethyl*iso*eugenol and ethyl maleate was refluxed for 4 hours and distilled. The fractions were : up to 130°/0·25 mm. (unchanged materials) ; a thick yellow oil, b. p. 186—205°/0·5 mm. ; a thick yellow oil, b. p. 205—220°/0·5 mm. The last fraction could not be crystallised, but the second solidified partly on keeping at 0° and the solid was separated and crystallised from methyl alcohol (yield, 20%), being obtained in white needles, m. p. 105—106° (Found : C, 65·5; H, 7·4. $C_{20}H_{28}O_6$ requires C, 65·9; H, 7·8%). Hydrolysis with alcoholic potassium hydroxide and acidification afforded the *dicarboxylic acid*, which crystallised from aqueous acetic acid in colourless needles, m. p. 208—209° (decomp. to yellow oil) (Found : C, 62·4; H, 6·7. $C_{16}H_{20}O_6$ requires C, 62·3; H, 6·6%). In this as in other cases there is a possibility of the formation of stereoisomerides and perhaps of structural isomerides also, so the total yields of adducts cannot be justly estimated from the amounts of the homogeneous products isolated. In almost all of the reactions there was evidence of the formation of by-products.

5 : 6-*Dimethoxy*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-1 : 2-*dicarboxylic Acid Anhydride*.—A mixture of 2 : 3-dimethoxypropenylbenzene (15 g.) (Douetheau, *Bull. Soc. chim.*, 1912, **11**, 656. Cf. Klages and Epplesheim, *Ber.*, 1903, **36**, 3591), maleic anhydride (9 g.), and xylene (25 c.c.) was refluxed for 5 hours, and xylene (20 c.c.) then removed by distillation. The orange-red oil was triturated with alcohol (100 c.c.), and a pale yellow, amorphous heteropolymer (1 g., m. p. 180—200°) collected. The filtrate was diluted with water, and the precipitated oil separated, dried, and distilled. After unchanged material (up to 260°) had been removed, the residue was a glassy mass that solidified when ground with alcohol. The substance (1 g.) was crystallised from acetic anhydride and then from chloroform–light petroleum and was obtained in slender needles, m. p. 159—160° (Found: C, 64·6; H, 5·8. $C_{15}H_{16}O_5$ requires C, 65·1; H, 5·8%). The properties of the substance closely resembled those of the 6 : 7-dimethoxy-analogue.

1-*Piperonyl*-Δ^1-*pentene*.—The action of *n*-butylmagnesium bromide on piperonal, carried out in the usual way, gave a mixture of products. These included piperonylpentene, piperonylbutylcarbinol, probably piperonyl alcohol (so-called, really piperonylcarbinol), and a substance, b. p. 206—208°/1 mm. (Found : C, 71·9; H, 7·3. $C_{24}H_{30}O_5$ requires C, 72·3; H, 7·6%), which is probably *piperonylbutylcarbinyl ether*. As this substance decomposed at 250—300° to a mobile oil and water and as the carbinol would also decompose under such conditions, the whole product (from piperonal, 40 g., *n*-butyl bromide, 37 g., and magnesium, 8 g.) was isolated, boiled for a short time until decomposition appeared to be complete, and then distilled at the ordinary pressure, the fraction (20·5 g.), b. p. 273—276°, being collected (Found : C, 75·6; H, 7·6. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%). *Piperonylpentene* was obtained as a very pale yellow oil with a safrolaceous odour.

6 : 7-*Methylenedioxy*-3-*propyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-1 : 2-*dicarboxylic Acid Anhydride*.—The adduct from piperonylpentene and maleic anhydride was obtained in the usual manner. The yield was about 10%, but very little heteropolymer was formed. The substance crystallised from ethylene chloride–light petroleum (b. p. 40—60°, 20 : 1) in faintly yellow

prisms, m. p. 138° (Found : C, 66·0; H, 5·8. $C_{16}H_{16}O_5$ requires C, 66·6; H, 5·6%). This *anhydride* exhibits the usual properties of its class.

Negative Results and Notes on Substances Employed.—No adducts were obtained from *iso*safrole and acraldehyde, *iso*safrole and *p*-benzoquinone (colour developed), *iso*safrole and α-naphthaquinone (colour developed), ethyl piperonylacrylate (m. p. 68—69°; lit., m. p. 67—68°) and maleic anhydride, β-bromopiperonylethylene and maleic anhydride, piperonylacetylene and maleic anhydride, *m*-hydroxystyrene and maleic anhydride, *m*-methoxystyrene with maleic anhydride (a very small amount of heteropolymer) and with ethyl maleate, *m*-methoxypropenylbenzene with maleic anhydride and with ethyl maleate, and it may be mentioned, phthalic anhydride and *cyclo*pentadiene.

m-Methoxystyrene was prepared by the method of Klages and Epplesheim (*loc. cit.*). These authors state that it has b. p. 89—90°/14 mm., but we find b. p. 90°/5 mm., which is in better accord with analogies. The decarboxylation of *m*-methoxycinnamic acid does not provide a satisfactory alternative method of preparation. Direct heating (cf. Organic Syntheses, Collected Vol., p. 430) and heating in diphenylmethane gave negligible yields and the best procedure was to heat the acid with copper chromite. Even in this way 10 g. of the acid gave only 2 g. of methoxystyrene.

m-Hydroxystyrene has been obtained by Komppa (*Ber.*, 1893, **26**, 677) from *m*-aminostyrene. We prepared it by the usual application of the Grignard reaction. *m*-Hydroxybenzaldehyde was benzoylated by the Schotten–Baumann process; the benzoyl derivative crystallised from aqueous alcohol in stout needles, m. p. 47°, and formed a *semicarbazone* which crystallised from methyl alcohol in slender, colourless needles, m. p. 209° (Found : N, 15·0. $C_{15}H_{13}O_3N_3$ requires N, 14·8%). In the Grignard reaction *m*-benzoyloxybenzaldehyde (50 g.), methyl iodide (33 g.), and magnesium (5·5 g.) were used. The fraction of the product, b. p. 180—210°/16 mm., nearly all having b. p. 205—208°, was collected (yield, 50%). This was hydrolysed by means of aqueous alcoholic potassium hydroxide, and the phenol liberated from the diluted solution by carbon dioxide. The hydroxystyrene had b. p. 119—120°/16 mm. (Komppa gives b. p. 114—116°/16 mm.) and was a colourless oil that rapidly polymerised when exposed to the air.

m-Methoxypropenylbenzene has been prepared by Moureu (*Bull. Soc. chim.*, 1893, **15**, 1024) by Perkin condensation of *m*-methoxybenzaldehyde and propionic anhydride, but no b. p. was recorded. Applying the method of Klages and Epplesheim (*loc. cit.*) for *m*-methoxystyrene and using ethylmagnesium iodide instead of methylmagnesium iodide, we obtained it in 60% yield as a colourless oil, b. p. 128—129°/20 mm.

Piperonylacetylene was prepared by the method of Feuerstein and Heimann (*Ber.*, 1901, **34**, 1469) in 45% yield. These authors apparently did not isolate the pure compound but characterised it by a silver derivative. It is a colourless liquid, b. p. 90°/3 mm.

o-Veratrylmethylcarbinol was obtained in 50% yield by the action of methylmagnesium iodide on *o*-veratraldehyde. It is a colourless, viscous oil, b. p. 151—152°/15 mm. in agreement with Pauly and Buttlar (*Annalen*, 1911, **383**, 284). It was dehydrated on distillation in steam to 2 : 3-dimethoxystyrene, but this substance was so readily oxidised or polymerised in contact with air that it was not obtained quite pure (Found : C' 72·1; H, 7·5. $C_{10}H_{12}O_2$ requires C, 73·2; H, 7·3%).

Reaction of Maleic Anhydride with p-*Methoxystyrene and* 3 : 4-*Methylenedioxystyrene.*—No simple 1 : 1 adduct was formed in either case. Apparently the same substance is formed when a benzene solution of equimolecular proportions of *p*-methoxystyrene and maleic anhydride is heated on the steam-bath for 15 minutes or kept in the cold for 65 hours. In the latter case 5 g. of methoxystyrene afforded 6·2 g. of a white, amorphous solid (Found : C, 63·2, 64·7, 63·8; H, 4·9, 5·1, 5·3%). This *heteropolymer* is soluble in hot aqueous alkalis (absence of methoxystyrene polymerides) and in ethyl acetate, but all attempts to crystallise it were fruitless. These observations are reported by Dr. L. Golberg. Condensation of 2 mols. of *p*-methoxystyrene with 3 mols. of maleic anhydride gives $C_{30}H_{26}O_{11}$, which requires C, 64·0; H, 4·6%.

A solution of methylenedioxystyrene (10 g.) and maleic anhydride (7 g.) in benzene (100 c.c.) was kept for 24 hours at 0°. The solution was concentrated and a white powder separated; it was collected and washed with benzene, m. p. *ca.* 250° (yield, 80%) (Found : C, 65·5; H, 4·1%; *M*, cryoscopic in camphor, 482). The same substance was obtained when a solution of the above quantities of the components in toluene (500 c.c.) was kept at 0° for 4 days. It is apparently not a very complex polymer; the molecular weight estimation agrees with the formula $C_{26}H_{20}O_{10}$ (*M*, 492), but the carbon estimation is 3% too high for this; the ratio appears to be between 2 : 2 and 2 : 3. The substance is insoluble in most organic solvents but dissolves readily in acetone and is sparingly soluble in *s*-tetrachloroethane. A dilute solution in this solvent does not decolorise bromine. It dissolves readily in aqueous ammonia and slowly in boiling aqueous sodium hydroxide. Acidification of the solution precipitates a white, amorphous solid and, on boiling, some methylenedioxystyrene is regenerated. The polymer is of a similar type to those obtained from stilbene and other arylated ethylenes by Kuhn and Wagner-Jauregg (*Ber.*, 1930, **63**, 2662).

Action of Maleic Anhydride on Anethole.—This experiment was performed under a variety of conditions, of which one example is given. In no case was any simple 1 : 1 adduct obtained. A mixture of anethole (15 g.), maleic anhydride (10 g.), and xylene (30 c.c.) was kept for several weeks at room temperature. The amorphous, white precipitate was collected, washed with benzene and alcohol, and thoroughly freed from solvent. The *substance* had m. p. 153—154° and was readily soluble in ethylene chloride, sparingly so in acetic acid and chloroform (Found : C, 66·4; H, 5·3. $4C_{10}H_{12}O,5C_4H_2O_3$ or $C_{60}H_{58}O_{19}$ requires C, 66·5; H, 5·4%). When the components were heated together with or without a solvent, a more complex polymer, eithe leathery or jelly-like, was obtained. Trituration with alcohol gave a white powder, m. p. *ca.* 250°. All these substances have the properties of acid anhydrides.

Methyl Benzylidenepyruvate.—The esterification of benzylidenepyruvic acid (Erlenmeyer, *Ber.*, 1903, **36**, 2528) and similarly constituted acids is very difficult and in some cases the appropriate conditions have not been found. In this example the acid (19 g.) was refluxed for 4 hours with methyl alcohol (65 g.) containing hydrogen chloride (3 g.). The product (yield, 55%) had b. p. 184—186°/4 mm. and solidified; it separated from benzene–light petroleum in yellow crystals, m. p. 74—75° (Found : C, 69·6; H, 5·4. $C_{11}H_{10}O_3$ requires C, 69·4; H, 5·3%). When the *ester* (5 g.) was shaken with *cyclo*pentadiene (10 g.) and a little methyl alcohol for 2 days, the solution had become colourless. Nevertheless it was not found possible to isolate the adduct. It was hydrogenated (palladised charcoal and 2—3 atms. pressure) in methyl-alcoholic solution, and the product hydrolysed. The oily acid could not be crystallised, but it yielded a *semicarbazone* that crystallised from methyl alcohol in white needles, m. p. 207—208° (decomp.) (Found : N, 12·4. $C_{16}H_{19}O_3N_3,CH_4O$ requires N, 12·7%).

Methyl 2 : 3-*Dimethoxybenzylidenepyruvate.*—Aqueous sodium hydroxide (70 c.c. of 10%) was added to a mixture of *o*-veratraldehyde (20 g.) and pyruvic acid (10 g.), which was kept at 20—30° and stirred for 2 hours. The filtered solution was acidified, and the solid collected and crystallised from aqueous alcohol (3 : 1), being obtained in small, yellow needles, m. p. 136° (yield, 40%). The *methyl* ester, obtained in 50% yield by following the procedure described above, had b. p. 188—189°/0·4 mm. and crystallised from aqueous methyl alcohol in yellow needles, m. p. 63° (Found : C, 62·6; H, 5·8. $C_{13}H_{14}O_5$ requires C, 62·4; H, 5·6%).

Methyl 5-o-*Veratryl*-3 : 6-*methylene*-Δ^1-cyclo*hexene*-4-*oxalate* (III).—A mixture of the foregoing ester (1·0 g.), *cyclo*pentadiene (5 g.), and alcohol (0·5 g.) at room temperature was mechanically agitated for 2 days. The solution was cooled to −14°, and chilled light petroleum (50 c.c. of b. p. 60—80°) added. After keeping in the refrigerator, colourless prisms separated. These were collected and dried, m. p. 74—75° (yield, 50%) (Found : C, 68·4; H, 6·4. $C_{18}H_{20}O_5$ requires C, 68·3; H, 6·4%).

A description of our further experiments in this field is reserved because the interest is not connected with the main topic of this communication.

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