221. *The Coupling Reaction of Cinnamyl Halides.* meso-αβ-*Divinyldibenzyl and the Phenylvinylmethyl Radical.*

By H. P. Koch.

The composition of the isomeric diphenylhexa-1 : 5-diene mixture produced by the coupling of cinnamyl halides over magnesium has been determined spectrographically, and the course of the reaction is discussed with reference to existing work on crotylmagnesium halides. Pure 1 : 6-diphenylhexa-1 : 5-diene free from fluorescent impurities has been obtained, and meso-3 : 4-*diphenylhexa*-1 : 5-*diene* has been isolated and characterised for the first time. The new hydrocarbon undergoes thermal rearrangement to a mixture of 1 : 6- and 1 : 4-diphenylhexa-1 : 5-dienes above 100°, largely or entirely by a mechanism involving the intermediate formation of free phenylvinylmethyl radicals. Phenylvinylmethyl is also produced transitorily when allylbenzene reacts with diacetyl peroxide, or by dissociation of 1 : 4-diphenylhexa-1 : 5-diene above 200°. Alder's conclusions relating to the course of addition of maleic anhydride or azodicarboxylic ester to allylbenzene are re-examined in the light of the present work.

The coupling of cinnamyl halides over metallic magnesium in ether was first studied by Rupe and Bürgin (*Ber.*, 1910, **43**, 172) who thereby prepared crystalline dicinnamyl (1 : 6-diphenylhexa-1 : 5-diene) (I; R = Ph) accompanied by a second incorrectly formulated oily hydrocarbon which was much later identified by Prévost (*Bull. Soc. chim.*, 1931, **49**, 1372) and by Gilman and Harris (*J. Amer. Chem. Soc.*, 1932, **54**, 2072) as the isomeric 1 : 4-diphenylhexa-1 : 5-diene, also designated *iso*dicinnamyl (II; R = Ph). Contrary to statements made by the original authors, it was claimed by von Braun and Köhler (*Ber.*, 1918, **51**, 88) that cinnamyl bromide gave much better yields of the desired crystalline isomer than did the chloride, but this experience was not confirmed either by Kuhn and Winterstein (*Helv. Chim. Acta*, 1928, **11**, 87) or by the work now described. Dicinnamyl free from isomers was, however, prepared from 1 : 6-dihydroxy-1 : 6-diphenylhexane by Borsche and Wollemann (*Ber.*, 1912, **45**, 3713) and later by Schmidt and Grosser (*ibid.*, 1942, **75**, 826), although this alternative mode of synthesis does not appear to offer any advantages from the preparative point of view.

It recently became necessary to obtain a quantity of very pure dicinnamyl for spectroscopic and crystallographic examination in this laboratory, and the detection of a hitherto unsuspected trace impurity in the hydrocarbon, as well as the isolation of an interesting new crystalline isomer, led to a re-investigation of all aspects involved in the coupling reaction of cinnamyl halides.

Dicinnamyl.—In the work of all the authors cited above, dicinnamyl is described as a crystalline solid, m. p. 81°, characterised by a strong bluish or violet fluorescence. It is now found that the optical peculiarity is caused by the presence of a trace impurity, doubtless 1 : 6-diphenylhexatriene which is known to fluoresce strongly in dilute solution (Kuhn and Winterstein, *loc. cit.*) and to exhibit an intense absorption band at 3490 A. (Hausser, Kuhn, and Smakula, *Z. physikal. Chem.*, 1935, *B*, **29**, 384). Fluorescing samples of dicinnamyl all display selective absorption near 3500 A. with varying extinction coefficients corresponding to fractional percentages of diphenylhexatriene. Both absorption and fluorescence disappear on chromatographic purification, whereby pure white dicinnamyl of greatly improved crystallising properties is obtained (cf. Experimental). The hydrocarbon may also be prepared almost or entirely pure if it is isolated from the isomeric diphenylhexadiene mixture at the lowest possible temperature (distillation bath below 150°) in a high-vacuum still, and since pure dicinnamyl acquires fluorescence through heating in a vacuum at 250°, the trace impurity appears to be due to slight dehydrogenation taking place at elevated temperatures. Kuhn and Winterstein (*loc. cit.*) drew attention to the great stability and pronounced aromatic character of 1 : 6-diphenylhexatriene, the ready appearance of which in samples of dicinnamyl is paralleled by the formation of traces of stilbene whenever dibenzyl is prepared (Ramart-Lucas and Hoch, *Compt. rend.*, 1931, **192**, 53; Ley and Dirking, *Ber.*, 1934, **67**, 1331). The thermal dehydrogenation also finds an analogy in the behaviour of *cyclo*hexene, which gives rise to spectroscopically detectable amounts of *cyclo*hexadiene on simple distillation (Stücklen, Thayer, and Willis, *J. Amer. Chem. Soc.*, 1940, **62**, 1717; cf. Bateman and Koch, *J.*, 1944, 600).

Rather unexpectedly, it was not found possible to convert dicinnamyl into diphenylhexatriene by the action of *N*-bromosuccinimide under the conditions employed by Karrer and his collaborators, who thereby succeeded in dehydrogenating the 2 : 6-ethylenic end-groups of lycopene to the 2 : 4 : 6-unsaturated fully conjugated polyene structure (*Helv. Chim. Acta*, 1945, **28**, 793; 1946, **29**, 573). Dicinnamyl did not react with *N*-bromosuccinimide even after the addition of benzoyl peroxide, for reasons which are not understood. Both 1-phenylpropylene (Ziegler *et al.*, *Annalen*, 1942, **555**, 80) and diallyl (Karrer *et al.*, *loc. cit.*, 1946) form bromo-derivatives by substitution under these conditions.

No other modification of dicinnamyl is known to exist, and there cannot be any doubt (see this vol., p. 1123) that the hydrocarbon of m. p. 81° possesses the *trans-trans*-configuration.

meso-*αβ-Divinyldibenzyl.*—When the hydrocarbon mixture resulting from the coupling of cinnamyl halides was distilled in a high vacuum, the initial fractions deposited a new crystalline isomer, $C_{18}H_{18}$, of m. p. 87°. This hydrocarbon was found to be doubly unsaturated, giving rise to a *tetrabromide*, and its ultra-violet absorption spectrum, very similar to that of dibenzyl or allylbenzene, indicated that the two double bonds were out of conjugation with the benzene rings. The new isomer must therefore be formulated as 3 : 4-*diphenyl*-1 : 5-*hexadiene* (*αβ-divinyldibenzyl*) (III; R = Ph) which can theoretically exist in either the racemic DL- or the internally compensated *meso*-form. A determination of the crystallographic space-group (this vol., p. 1118) proved that the molecules were centrosymmetric and therefore necessarily of the *meso*-configuration. This structure was further confirmed by an isomorphous relationship with the *meso*-αβ-diethyldibenzyl examined by Carlisle and Crowfoot (*J.*, 1941, 6). The latter hydrocarbon has almost identical unit-cell dimensions, and a specimen failed to depress the slightly lower m. p. of the former on mixing. Through the courtesy of Professor E. C. Dodds it was also established that *meso*-αβ-divinyldibenzyl displayed weak oestrogenic activity comparable with that of *meso*-αβ-diethyldibenzyl, the hydrocarbon analogue of hexoestrol (this vol., p. 1116).

Since even the most carefully isolated αβ-divinyldibenzyl fractions always contained small amounts of an oily admixture, there appears to be evidence that the racemic DL-form was also produced during the coupling reaction. This stereoisomer would not be expected to crystallise, by analogy with DL-αβ-diethyldibenzyl which has been described as a liquid (cf. Carlisle and Crowfoot, *loc. cit.*). According to Liepins (*Chem. Abs.*, 1931, **25**, 3328), the coupling of phenylalkylmethyl halides over magnesium generally results in the formation of both DL- and *meso*-forms, although the respective rates may be different.

meso-αβ-Divinyldibenzyl undergoes rapid rearrangement when attempts are made to distil the hydrocarbon in a low vacuum. This phenomenon is no doubt responsible for the failure of previous authors to isolate it (cf. Gilman and Harris, *loc. cit.*) and will be further discussed below.

The Course of the Coupling Reaction.—Although the quantitative separation of αβ-divinyldibenzyl and dicinnamyl from the oily *iso*dicinnamyl (II; R = Ph) present in the coupled hydrocarbon mixture is impossible to achieve, the three isomers may be estimated in the product by ultra-violet absorption analysis of the fractions obtained on high-vacuum distillation. This method is based on the wide differences in maximum extinction near 2500 A. associated

$$\underset{\text{(I.)}}{\mathrm{CHR{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CHR}} \qquad \underset{\text{(II.)}}{\mathrm{CHR{:}CH{\cdot}CH_2{\cdot}CHR{\cdot}CH{:}CH_2}} \qquad \underset{\text{(III.)}}{\mathrm{CH_2{:}CH{\cdot}CHR{\cdot}CHR{\cdot}CH{:}CH_2}}$$

with the presence of 0, 1, or 2 conjugated styrene systems in the three hydrocarbons (ε = 370, 20,000, and 33,000, respectively). The result of such an analysis proves to be very similar to the composition of the analogous mixture produced by the coupling of crotyl halides which has been studied by Young, Roberts, and Wax (*J. Amer. Chem. Soc.*, **1945**, **67**, 841). The relevant data are given in the table below, where the figures in parentheses refer to the amounts of crystalline material which can actually be iolated in a pure state.

Coupling halide, $\mathrm{CHR{:}CH{\cdot}CH_2X}$.	Isomers, %.			Total hydrocarbon yield, %.
	(I).	(II.)	(III).	
Cinnamyl chloride (R = Ph, X = Cl)	20 (11)	75	3—5 (0·85)	85
Cinnamyl bromide (R = Ph, X = Br)	— (10)	—	— (1)	—
Crotyl chloride (R = Me, X = Cl)	12	82	6	72
Crotyl bromide (R = Me, X = Br)	10	88	2	—

The overall course of either coupling reaction may be formulated as

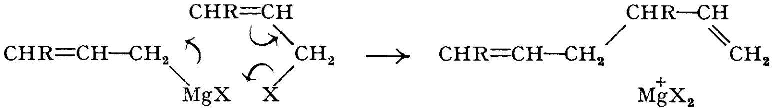
$$\mathrm{CHR{:}CH{\cdot}CH_2X} + \mathrm{Mg} \longrightarrow \left\{\begin{matrix}\mathrm{CHR{:}CH{\cdot}CH_2{\cdot}MgX}\ (a) \\ \text{and/or} \\ \mathrm{CHR(MgX){\cdot}CH{:}CH_2}\ (b)\end{matrix}\right\} \quad . \ . \ . \ . \quad (1)$$

followed by

$$\left\{\begin{matrix}\mathrm{CHR{:}CH{\cdot}CH_2{\cdot}MgX}\ (a) \\ \text{and/or} \\ \mathrm{CHR(MgX){\cdot}CH{:}CH_2}\ (b)\end{matrix}\right\} + \mathrm{CHR{:}CH{\cdot}CH_2X} \longrightarrow \text{(I), (II), and (III)} + \mathrm{MgX_2} \quad . \ . \quad (2)$$

The table shows that, for both cinnamyl and crotyl halides, the unsymmetrical *iso*-structure (II) is the main constituent of the product, which may therefore be regarded as formally derived from the " abnormal " secondary form (*b*) of the Grignard reagent. The yield of divinyl compound (III) is small in either case, but the proportion of the " normal " product (I) is significantly higher for cinnamyl than for crotyl halides. This difference may well be due to additional resonance stabilisation of (*a*) or (I) arising from conjugation in the cinnamyl residue. The percentages of dicinnamyl (I) and *iso*dicinnamyl (II) formed also correspond with the yields of 1-propenylbenzene (25%) and allylbenzene (75%) produced on hydrolysis of the Grignard reagent from cinnamyl halides (Young *et al.*, *ibid.*, 1939, **61**, 12; 1947, **69**, 688).

Recently, Young and Roberts (*ibid.*, 1946, **68**, 1472) have advanced strong arguments to support the view that the Grignard reagent from crotyl halides actually exists predominantly in the *primary* form (*a*), conclusions which might be expected to apply *a fortiori* to the resonance-stabilised cinnamyl compounds. On this basis, the preferential formation of (II) over (I) would appear to involve a bimolecular cyclic mechanism (cf. Gilman, " Organic Chemistry ", 2nd ed., 1943, p. 1880) as a facile alternative to the conventional " normal " mode of reaction :



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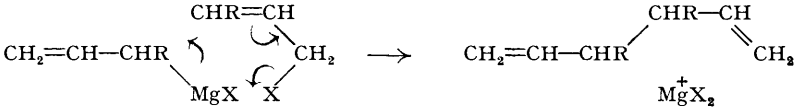
The small yield of $\alpha\beta$-divinyldibenzyl may be regarded as evidence *either* that resonating organic ions or radicals also appear during the coupling reaction *or* that at least a fraction of the Grignard reagent exists in the " abnormal " form (*b*), giving rise to the new isomer by a similar cyclic type of reaction :



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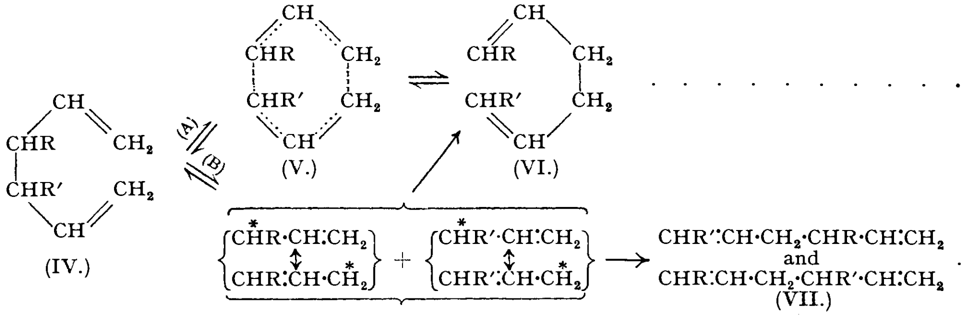
There is no reason to believe that the cinnamyl halides themselves may be partly isomerised to the secondary phenylvinylmethyl halides under the conditions of the synthesis.

Thermal Rearrangement of meso-$\alpha\beta$-*Divinyldibenzyl.*—The new crystalline isomer (IV; R = R′ = Ph) is stable at 100°, but on heating to 150° it is readily and quantitatively rearranged to an approximately 3 : 2 mixture of dicinnamyl and *iso*dicinnamyl. Two competing processes may be formulated to account for the initial step in the rearrangement of substituted hexa-1 : 5-dienes generally: an electron shift (A) giving rise to a cyclic transition complex (V), or dissociation (B) into free radicals which are stabilised by resonance involving two different positions of the unshared electron. Both mechanisms are unimolecular but distinguished by



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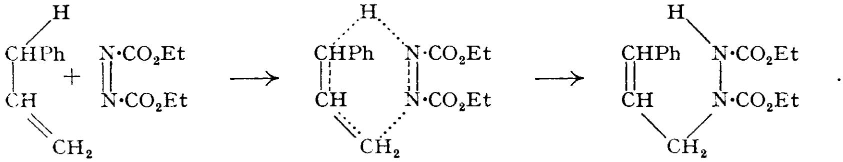
the fact that (A) cannot give more than one new isomer, whereas (B) is expected to yield two or three different products of radical recombination, depending on whether or not R = R′. Levy and Cope (*J. Amer. Chem. Soc.*, 1944, **66**, 1684) have established the general validity of the intramolecular cyclic scheme (A) by showing that (IV) could be incompletely and reversibly rearranged to pure (VI) when R = H and R′ = Me, by heating to 300°. Similar isomerisation to a single product occurred when R = Ph and R′ = Me, but in this case the reaction proceeded at a much lower temperature (165—185°) and rearrangement was complete and irreversible (*loc. cit.*), features which might be expected from the electronic activating effect of the phenyl substituent and the conjugated nature of the product. In the present work on αβ-divinyldibenzyl (IV; R = R′ = Ph), isomerisation was even more facile but the presence of *iso*dicinnamyl (VII) in the product indicates that the alternative process (B) must be operative at least in part. The further activating effect of the second phenyl group evidently assists the radical dissociation relatively more than the formation of the hypothetical cyclic transition complex. A rough calculation of the bond energies involved bears out the theoretical soundness of the free-radical reaction scheme. According to Orr (quoted by Bolland and Gee, *Trans. Faraday Soc.*, 1946, **42**, 244), the resonance energy of the divinylmethyl radical amounts to 30 kcals., and allowing for the small difference between the values recorded for allyl and benzyl radicals, the resonance energy of phenylvinylmethyl might be expected to be about 3 kcals. less than this, *i.e.*, near 27 kcals. The central bond of αβ-divinyldibenzyl would then be weakened by twice this amount below the normal single bond strength of 81 kcals. The resultant theoretical bond strength of approximately 81 − 2 × 27 = 27 kcals. is in good accord with the experimentally required isomerisation temperature. The resonance energy of the phenylvinylmethyl radical may therefore be regarded as the main driving force for a radical dissociation ultimately leading to the formation of the more stable molecular species of dicinnamyl and *iso*dicinnamyl. The central bonds of these two isomers are not weakened by the full amount of twice the radical resonance energy on account of the styrene conjugation already present in the undissociated molecules. Assuming this stabilisation to amount to 7 kcals. per styrene group, the dissociation temperature of *iso*dicinnamyl (II) might be expected to be about 100° higher than that of αβ-divinyldibenzyl (III), while dicinnamyl (I) should still be stable at 250°. This prediction was verified by experiment: (I) and (II) were unaffected by temperatures near 200°, but at 250° only dicinnamyl (I) remained unchanged while *iso*dicinnamyl (II) was largely transformed into a polymeric gum from which some dicinnamyl could be separated by vacuum distillation. Evidently free-radical dissociation leading to partial rearrangement of *iso*dicinnamyl had taken place at the higher temperature, affording indirect evidence in support of the analogous isomerisation mechanism proposed for αβ-divinyldibenzyl at 150°. More direct proof for the radical dissociation of αβ-divinyldibenzyl was also obtained by the fact that the hydrocarbon resembled dibenzoyl peroxide in catalysing the initial stages of autoxidation of ethyl linoleate (Bolland, *Proc. Roy. Soc.*, 1946, *A*, **186**, 218). In these experiments, divinyldibenzyl appeared to decompose by a heterogeneous process, with an activation energy in the neighbourhood of 30 kcals.

Attempts to shift the double bonds of αβ-divinyldibenzyl into conjugation to furnish 3 : 4-diphenylhexa-2 : 4-diene by treatment with hot alcoholic potassium hydroxide proved unsuccessful. No conjugative isomerisation could be observed before the competing thermal rearrangement removed the unconjugated isomer from the sphere of influence of the alkali.

Coupling of Phenylvinylmethyl Radicals.—In the thermal rearrangement of αβ-divinyldibenzyl a 67% yield of *iso*dicinnamyl and 33% of dicinnamyl might be expected if there were strict equivalence between the two alternative canonical forms of the coupling radicals. Since the relative yields of dicinnamyl are markedly higher than this (∼ 60%), it must be concluded either that the cinnamyl form is preferentially stabilised by conjugation or that some proportion of the dicinnamyl in the product arises from the non-dissociative intramolecular cyclic reaction (5) referred to above. Phenylvinylmethyl radicals were also prepared directly by decomposition of diacetyl peroxide in allylbenzene (cf. Kharasch, McBay, and Urry, *J. Org. Chem.*, 1945, **10**, 401), and on dimerisation they did produce *iso*dicinnamyl in excess of dicinnamyl, but the exact relative proportions of recombined phenylvinylmethyl and cinnamyl residues resulting from this reaction could not be ascertained on account of the formation of a considerable polymeric fraction of unknown composition. No trace of divinyldibenzyl could be isolated from the product, either on account of the high temperature required for the peroxide decomposition (near 120°) or because of preferential further attack by the reagent at the tertiary C–H group of the divinyldibenzyl, resulting in hydrocarbons of greater complexity which may form part of the polymeric fraction (cf. related observations of Kharasch *et al.*, *loc. cit.*). The formation of the diphenylhexadienes from allylbenzene and diacetyl peroxide offered no preparative advantages over the coupling of cinnamyl halides, and attempts to couple phenylvinylmethylsodium (sodio-allylbenzene) by the action of iodine proved completely abortive.

The intermediate appearance of phenylvinylmethyl radicals has been postulated by Alder, Pascher, and Schmitz (*Ber.*, 1943, **76**, 27) in order to explain the course of addition of maleic anhydride (at 200°) or azodicarboxylic ester (at room temperature) to allylbenzene. In either case the *only* isolable addition product was derived from the rearranged cinnamyl and not from the original phenylvinylmethyl residue of allylbenzene, and the double-bond shift was held to be due to primary dissociation of a C–H bond followed by conjugative isomerisation of the phenylvinylmethyl radical before combination with the addendum. Similar free-radical mechanisms were invoked to account for the products from hexa-1 : 5-diene for which again *exclusively* abnormal addition arising from double-bond shift was observed although no conjugation occurred here as a result of the rearrangement. Since it has been shown in the present work that the coupling of phenylvinylmethyl radicals invariably produces *iso*dicinnamyl as well as dicinnamyl, the mechanistic conclusions of Alder and his co-workers would not seem to be easily compatible with the dual reactivity of the phenylvinylmethyl radical. In the absence of special factors, the proposed scheme of addition of maleic anhydride or azodicarboxylic ester to allylbenzene should be expected to furnish a significant porportion of *normal* as well as abnormal products, just as the " abnormal " double-bond shift is incomplete during the addition of molecular oxygen to the (substituted) divinylmethyl radicals involved in ethyl linoleate oxidation (Bolland and Koch, *J.*, 1945, 445). If indeed Alder's observations on the quantitative completeness of the rearrangement-addition are well founded experimentally, they could equally well be accounted for by an intermolecular cyclic reaction mechanism analogous to the Diels–Alder *diene* addition and also somewhat reminiscent of the intramolecular rearrangements of type (5) :



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EXPERIMENTAL.

*Diphenylhexa-*1 : 5-*dienes from Cinnamyl Chloride.*—Dry hydrogen chloride was bubbled through melted *trans*-cinnamyl alcohol with ice-cooling to give cinnamyl chloride (80%), b. p. 106—112°/12 mm. (nitrogen), m. p. 8°. A stirred suspension of magnesium turnings (9 g.) in dry ether (50 c.c.) was activated by the addition of a few drops of methylmagnesium iodide solution, and cinnamyl chloride (111 g.) in dry ether (250 c.c.) was then added dropwise at such a rate that the mixture was kept spontaneously refluxing. After further heating on the water-bath for 30 mins., the contents of the flask were poured on ice and ammonium chloride, and the product obtained as a partly crystallised light yellow oil after working up in the usual manner. Slow distillation through a short Vigreux column at 10^{-3} mm. gave a small forerun, followed by ten separately collected fractions boiling between 80° and

135°, a final fraction being recovered from the residue in the distilling flask (total yield of hydrocarbon 72 g. = 85%; cf. Gilman and Harris, *loc. cit.*, 75%).

The small initial fractions (bath temp. 135—140°) soon deposited crystals of *meso*-*αβ*-divinyldibenzyl, while the higher fractions contained increasing amounts of solid dicinnamyl. Each fraction was weighed, and its approximate composition analysed by determining the maximum light absorption intensity in the region of 2500—2550 A., it being assumed that the first fractions consisted of the 3 : 4- and the 1 : 4-diphenyl-substituted hexa-1 : 5-dienes only, while the higher fractions were treated as mixtures of the 1 : 4- with the 1 : 6-isomer (cf. spectral data on pure compounds given below). The total hydrocarbon was accordingly estimated to contain about 3% of 3 : 4-diphenylhexa-1 : 5-diene (*αβ*-divinyldibenzyl) and 20% of 1 : 6-diphenylhexa-1 : 5-diene (dicinnamyl) after high-vacuum distillation. The amount of *αβ*-divinyldibenzyl actually formed during the coupling reaction may well have been somewhat greater than that collected in the distillate, on account of its thermal instability. The proportion of 1 : 4-diphenylhexa-1 : 5-diene (*iso*dicinnamyl) present in the reaction product is then estimated by difference to be about 75%.

By crystallisation from ethanol of the first semi-solid fractions, *meso*-*αβ*-divinyldibenzyl could be isolated in almost pure condition in a yield of 680 mg. (0·85% of the theoretical based on the cinnamyl chloride), and the higher fractions, after one redistillation, similarly gave 9·5 g. (11%) of crystalline *trans*-dicinnamyl (Gilman and Harris, *loc. cit.*, obtained 8·75%; Kuhn and Winterstein, *loc. cit.*, 10%).

meso-*αβ*-*Divinyldibenzyl* (3 : 4-*Diphenylhexa*-1 : 5-*diene*).—This *compound* formed small white monoclinic crystals from ethanol or by high-vacuum sublimation, m. p. 87—87·5° (Found : C, 92·3; H, 7·9. $C_{18}H_{18}$ requires C, 92·26; H, 7·74%). For crystallographic data, see this vol., p. 1118. A sample of *meso*-*αβ*-diethyldibenzyl kindly supplied by Dr. Crowfoot melted at 89·5—90° and did not depress the m. p. of the divinyl analogue. Light absorption in *n*-hexane: Max., 2600 A., $\epsilon = 370$ (stilbene-free dibenzyl has max., 2600 A., $\epsilon = 420$. For absorption of allylbenzene, cf. below). *Tetrabromide*: Microcrystalline powder from acetone, m. p. 241° (Found : Br, 57·6. $C_{18}H_{18}Br_4$ requires Br, 57·7%). No colour change or crystalline adduct was obtained on mixing either *meso*-*αβ*-divinyldibenzyl or *meso*-*αβ*-diethyldibenzyl with 2 mols. of *s*-trinitrobenzene in a small volume of chloroform, conditions under which stilbene-free dibenzyl forms a rather unstable colourless complex of m. p. 103° (cf. Sudborough, *J.*, 1916, **109**, 1339). *Oestrogenic assay* (data supplied by Professor Dodds) : the total dose of *meso*-*αβ*-divinyldibenzyl contained in 3 c.c. of sesame oil solution was given as six twice-daily injections of 0·5 c.c. each in spayed rats. Smears consisting entirely of cornified and/or epithelial cells were taken to indicate positive response. The E.D. 50 for the oestrogenic activity of the hydrocarbon by this technique was found to lie between 1 and 10 mg.

trans-*Dicinnamyl*.—This formed thin, irregular plates from ethyl or butyl alcohol, ethyl acetate, acetic acid, or light petroleum, b. p. 115°/0·005 mm.; m. p. 80·5—81° (lit., 81°), depressed to 75—77·5° on admixture with *meso*-*αβ*-divinyldibenzyl (Found : C, 92·3; H, 7·85. Calc. for $C_{18}H_{18}$: C, 92·26; H, 7·74%). Light absorption in *n*-hexane : Max., 2550 A., $\epsilon = 33{,}000$. Samples previously subjected to elevated reaction or distillation temperatures exhibit an absorption band near 3500 A. with ϵ values ranging up to 200, and a bluish or violet fluorescence in ordinary or ultra-violet light (cf. Rupe and Bürgin, *loc. cit.*; Schmidt and Grosser, *loc. cit.*). A sample obtained by distilling the diphenylhexadiene mixture from the coupling of cinnamyl chloride at the lowest possible temperature (wide-neck distilling flask with low side-arm attachment, bath at 150°, b. p. 105°/0·0005 mm.) was, however, free from the long-wave absorption and fluorescence characteristic of very dilute solutions of 1 : 6-diphenylhexatriene [cf. Kuhn and Winterstein, *loc. cit.*; Hausser, Kuhn, and Smakula (*loc. cit.*) found max. light absorption of diphenylhexatriene in ethanol at 3490 A., $\epsilon = 67{,}000$]. The trace impurity could also be removed by chromatographic adsorption from light petroleum (b. p. 40—60°) on alumina (Savory and Moore), on which dicinnamyl was only lightly held while the triene formed a rather broad band whose slow progress down the column could be conveniently followed by examination with ultra-violet light (fluorescence).

Single crystals of triene-free *trans*-dicinnamyl could be obtained from concentrated acetone solution as flat, transparent, monoclinic plates, characterised by a unit cell of dimensions $a = 15{\cdot}37$, $b = 7{\cdot}48$, $c = 6{\cdot}22$ A., $\beta = 103°$, containing two centrosymmetric molecules and having space-group symmetry of $P\,2_1/c$. The pure hydrocarbon forms an addition compound with 2 mols. of *s*-trinitrobenzene (needles, m. p. 145°, from chloroform) which is yellow with a greenish tinge, and not " light brownish-yellow " as described by Kuhn and Winterstein (*loc. cit.*) presumably because of contamination with traces of the intensely red complex formed by 1 : 6-diphenylhexatriene.

iso*Dicinnamyl* (1 : 4-*Diphenylhexa*-1 : 5-*diene*).—This isomer was obtained pure as a water-white liquid entirely devoid of fluorescence by threefold refractionation of the oily middle fractions of the diphenylhexadiene distillate; b. p. 100°/0·005 mm., $n_D^{13°}$ 1·5904 (cf. Gilman and Harris, *loc. cit.*, $n_D^{20°}$ 1·5890), light absorption in *n*-hexane, max., 2510 A., $\epsilon = 20{,}000$. A yellow colour but no compound crystals were obtained with *s*-trinitrobenzene in chloroform solution, and the addition of bromine resulted in formation of a gum. The hydrocarbon itself set to a glass on cooling.

Diphenylhexa-1 : 5-*dienes from Cinnamyl Bromide*.—Cinnamyl bromide (80 g.; b. p. 55—60°/0·02 mm.; m. p. 31°), prepared by refluxing cinnamyl alcohol with three parts of hydrobromic acid (*d* 1·48) for ½ hour, was brought into reaction with magnesium (5 g.) exactly as indicated under the chloride. *meso*-*αβ*-Divinyldibenzyl and dicinnamyl could be isolated by crystallisation from ethanol in yields of 550 mg. (1%) and 5·0 g. (10%), respectively.

Diphenylhexa-1 : 5-*dienes from Allylbenzene*.—Allylbenzene (b. p. 50·5—51°/17 mm.; $n_D^{15°}$ 1·5130; light absorption in *n*-hexane, max., 2600 A., $\epsilon = 210$) was prepared by reaction of phenylmagnesium bromide with allyl bromide and purified by a preliminary distillation from molten sodium, followed by rectification under reduced pressure in a Fenske–Whitmore apparatus.

(*a*) Sodio-allylbenzene was prepared in liquid ammonia solution by the method of Levy and Cope (*loc. cit.*), and the ammonia gradually replaced by dry ether and benzene. Rather less than half the theoretical amount of iodine required for a coupling reaction was absorbed fairly rapidly at room temperature and some salt was precipitated, but after addition of all the halogen, warming on the water-bath, and working up in the usual manner, only an unpleasant dark tar was obtained which was not further investigated.

(*b*) (cf. Kharasch, McBay, and Urry, *loc. cit.*). Sodium peroxide (20 g.) was weighed into a conical flask under dry ether (200 c.c.), acetic anhydride (40 g.) was added, and the whole cooled to − 15° in a freezing mixture. Ice (*ca.* 70 g.) was then added, with vigorous shaking, in traces at first and then more rapidly during 10—15 mins. After another 10 mins.' shaking in the cold, the ethereal layer was separated, dried ($CaCl_2$), and cooled to − 78° overnight, whereupon diacetyl peroxide crystallised out in long needles. The bulk of the ether was decanted from the crystals and the remainder evaporated at − 78° into a liquid-air trap by pumping on the high vacuum for 24 hours. The cold peroxide was then covered with allylbenzene (50 g.) and allowed to warm to room temperature and dissolve. This solution was added during 1½ hours below the surface to a further quantity of allylbenzene (30 g.) kept at 120° in a 500-c.c. flask. A regular stream of gas was evolved. The product was freed from low-boiling material and excess allylbenzene (52 g.) at the water-pump, and then subjected to careful distillation in a high vacuum. After a small unidentified forerun (0·5 g.), two roughly equal fractions of diphenylhexa-1 : 5-diene (total, 11 g.) were collected and a considerable polymeric residue remained in the flask. The first fraction (b. p. 110°/10^{-2} mm., $n_D^{14°}$ 1·58) consisted mainly of *iso*dicinnamyl and did not crystallise on cooling, while the second fraction (b. p. 115—140°/10^{-2} mm.) showed distinct fluorescence and soon began to deposit crystals of dicinnamyl which could be isolated in the usual manner after further fractionation. No trace of crystalline *meso*-$\alpha\beta$-divinyldibenzyl was detectable in the low-boiling fractions.

Thermal Rearrangement of meso-$\alpha\beta$-*Divinylbenzyl.*—(*a*) On attempting to distil *meso*-$\alpha\beta$-divinyldibenzyl at the water-pump, only a trace of solid sublimed over, followed by an oil which soon deposited crystals of dicinnamyl. (*b*) After the substance had been heated in a sealed tube under nitrogen for 2½ hours at 100°, it re-solidified almost unchanged (m. p. 84—86°). (*c*) When heated at either 150° or 200° under nitrogen for 2½ hours, *meso*-$\alpha\beta$-divinyldibenzyl produced a mixture of diphenylhexadienes of intense light-absorption characteristics (max. near 2500 A., ϵ = 27,000), and much dicinnamyl crystallised out soon after cooling. (*d*) A sample (500 mg.) of the crystalline hydrocarbon was heated at 200° in an atmosphere of nitrogen for 1 hour, and the product distilled at the water-pump. Four fractions of regularly increasing b. p., solidity after cooling, fluorescence, and light-absorption intensities (ϵ = 25,000—30,000 near 2550 A.) were collected.

Thermal Rearrangement of iso*Dicinnamyl.*—(*a*) When *iso*dicinnamyl was heated for 1 hour at 200° under nitrogen, no solid was produced, and the ultra-violet absorption characteristics remained unchanged. (*b*) On heating a sample of pure *iso*dicinnamyl (1·7 g.), sealed in a vacuum, at 250—260° for 3 hours, there resulted a yellow gum with a distinct greenish fluorescence. High-vacuum distillation of this product furnished (i) a colourless oil (400 mg.) at 105—130° which was mainly unchanged *iso*dicinnamyl but exhibited the typical bluish-violet fluorescence associated with the straight-chain isomer, and (ii) a further fraction (100 mg.) at 130—150° which largely crystallised and contained dicinnamyl, identified by its crystal form and fluorescence. An undistillable polymeric residue remained in the flask.

Thermal Treatment of Dicinnamyl.—Triene-free (non-fluorescent) dicinnamyl was sealed up in a high vacuum and heated for 3 hours at 250—260°. On cooling, the hydrocarbon recrystallised unchanged except for a distinct bluish-violet fluorescence.

Isomerisation of $\alpha\beta$-*Divinyldibenzyl in the Presence of Alkali.*—(*a*) *meso*-$\alpha\beta$-Divinyldibenzyl (50 mg.) was heated in a sealed tube with 10% ethyl-alcoholic potassium hydroxide solution (5 c.c.) overnight. After neutralisation with dilute acid, crystals of unchanged starting material (identified by m. p. and mixed m. p.) were isolated *via* ether. (*b*) The crystalline hydrocarbon (100 mg.) was sealed up with 10% ethyl-alcoholic potassium hydroxide solution (10 c.c.) and heated to 100°. The temperature was then gradually raised to 160° during 1 hour, and kept at this level for a further hour. On working up, the product was obtained as an almost colourless oil which largely crystallised in the cold. The crystals were identified as dicinnamyl by conversion into the addition compound with *s*-trinitrobenzene (m. p. and mixed m. p.).

Attempted Reaction of Dicinnamyl with N-*Bromosuccinimide* (cf. Karrer *et al.*, *loc. cit.*).—Dicinnamyl (1·4 g.; 0·006 mol.), *N*-bromosuccinimide (0·89 g.; 0·005 mol.), and recrystallised benzoyl peroxide (5 mg.) were refluxed together in dry carbon tetrachloride (2 c.c.) for 2 hours. The filtrate was evaporated and yielded unchanged dicinnamyl (1·0 g.) after one crystallisation from ethanol.

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