223. *Absorption Spectra of Dicinnamyl and Some Related Compounds.*

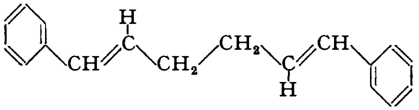
By H. P. Koch.

Comparative measurements are presented of the ultra-violet absorption spectra of both solutions and oriented crystals of 1 : 6-diphenylhexa-1 : 5-diene (dicinnamyl) and 1 : 10-diphenyldeca-1 : 9-diene, and of solutions of 1-propenylbenzene and 1 : 4-diphenylhexa-1 : 5-diene. All these hydrocarbons exhibit high-intensity absorption characteristic of *trans*-substituted styrenes. Two main wave-length regions of selective absorption may be recognised, one (2950—2750 A.) apparently associated with light vibrating in the plane of the benzene ring at right angles to the long axis of the styrene chromophore, and the other (2700—2300 A.) due to light vibrations in the same plane but normal to the above, *i.e.*, parallel to the direction of greatest extension of the styrene chain. The perpendicular 2950—2750 A. absorption exhibits characteristic fine-structure which is completely unaffected in the solution spectra by the second-order differences between the structural environments of the above hydrocarbon chromophores, although the band-heads are shifted to slightly longer wave-lengths in the crystalline state. The longitudinal 2700—2300 A. absorption region displays minor variations among the different compounds which must be attributed, at least in part, to weight or chain-length effects. Chromophore interaction across the three central single bonds of dicinnamyl is either non-existent or slight, precluding any kind of conjugation between the two styrene systems in the molecule.

The marked colour difference between lycopene and β-carotene is ascribed, not to incomplete electronic insulation of 1 : 5-spaced double bonds in lycopene, but to steric hindrance of conjugation in β-carotene.

X-Ray evidence recently presented by Jeffrey (*Proc. Roy. Soc.*, 1947, *A*, **188**, 222) has demonstrated the existence of abnormal bond-character associated with systems of two unsaturated groups separated by three single bonds. In both geranylamine hydrochloride and dibenzyl a significant shortening of the central single bonds was observed, and some degree of electronic interaction between the unsaturated groups was believed to accompany the unusual effect (cf. Bateman and Jeffrey, *Nature*, 1943, **152**, 446; Jeffrey, *Proc. Roy. Soc.*, 1945, *A*, **183**, 388). It was therefore to be expected that the peculiar bond structure would be reflected in the first ultra-violet absorption region of these compounds, which is generally considered highly characteristic of the energy levels of unsaturation electrons. No such correlation between abnormal bond length and absorption spectra could, however, be detected. Neither geranylamine hydrochloride (Bateman and Koch, *J.*, 1944, 600) nor dibenzyl (Ley and Dirking, *Ber.*, 1934, **67**, 1331; cf. Jones, *Chem. Reviews*, 1943, **32**, 1) exhibits quartz-ultra-violet absorption in any way suggestive of imperfect insulation between the unsaturated chromophores. Similarly negative evidence is obtained on comparing the absorption of αβ-divinyldibenzyl (a derivative of hexa-1 : 5-diene as well as of dibenzyl) with that of allylbenzene in the same spectral region (cf. this vol., p. 1116). These spectroscopic facts appear to be incompatible with the view that the bond abnormality is associated with a gain in resonance energy due to conjugation across three single bonds. Since the first *intense* ($N \longrightarrow V$) absorption bands of all the above compounds have their actual peaks located in the region of 2000 A. or beyond where precise quantitative measurement becomes difficult, it was felt desirable to confirm this result with systems giving rise to well-defined maxima of intense absorption within the range of the usual spectrophotometric equipment. Accordingly, the ultra-violet survey has now been extended to dicinnamyl and similar molecules, and the observed electronic spectra have been considered in some detail.

Dicinnamyl (I) is structurally derived from dibenzyl by substitution of styryl groups for the two benzene rings, and the greater degree of conjugation of the styrene system over benzene causes the first intense absorption band of dicinnamyl to occur at considerably longer wave-lengths in the quartz-ultra-violet region. In order to ascertain the presence or otherwise of chromophore interaction in the molecule, it is necessary to relate the spectrum of dicinnamyl to that of other β-substituted styrenes of different intramolecular environment, with due attention to the possible influence of steric factors. Complexities of geometrical isomerism hardly exist, since the styrene system differs from the analogous butadiene chromophore in the important respect that it does not admit of spectrally significant *cis-trans* isomerism about the single bond linking the two conjugated unsaturated centres (cf. Sugden and Walsh, *Trans. Faraday Soc.*, 1945, **41**, 76) : only one form of styrene is possible. Again, only one stable modification of dicinnamyl (m. p. 81°), usually prepared from the crystalline *trans*-cinnamyl halides, is known (cf. this vol., p. 1112), and this may undoubtedly be assigned the *trans-trans*-configuration (I) with regard to the double bonds. An extended zigzag chain formulation is in accord with the centrosymmetrical character and unit-cell dimensions of the molecule in the crystalline state, and the solution spectra plotted on a logarithmic scale in Fig. 1 show that the two styrene

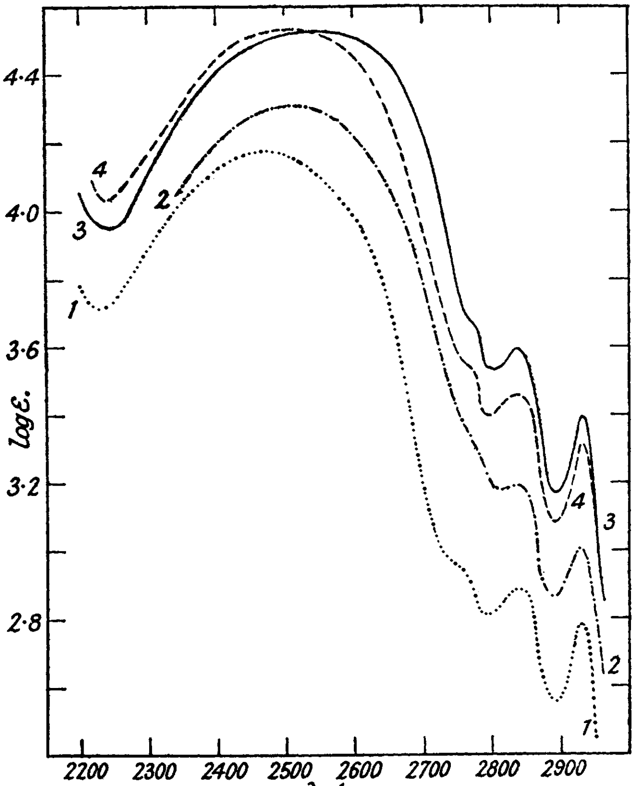


(I.)

chromophores in dicinnamyl together absorb rather more than twice as strongly as one styrene system in propenylbenzene or styrene itself (for the latter, cf. Jones, *loc. cit.*). These spectroscopic relationships are incompatible with a *cis*-structure of dicinnamyl in which the styrene-type conjugation would be considerably weakened by the steric interference between an aromatic *ortho*-carbon and a methylene group in the coplanar form required for full electronic resonance. According to the relevant scale models already examined in the preceding paper and also by Zechmeister and LeRosen (*J. Amer. Chem. Soc.*, 1942, **64**, 2755), in similar contexts, a *cis*-substituted styrene demands appreciable rotation of the benzene ring out of the molecular plane for the removal of such interference between the van der Waals radii of non-bonded groups; and reference to such spectra as those of stilbene and αβ-dimethylstilbene (Jones, *ibid.*, 1943, **65**, 1818) provides a good illustration of the well-known fact that steric incompatibility of the geometrical type under discussion always produces a marked reduction in light-absorption properties.

FIG. 1.

Absorption spectra in n-*hexane solution.*



1, 1-*Propenylbenzene.*
2, 1 : 4-*Diphenylhexa*-1 : 5-*diene.*
3, 1 : 6-*Diphenylhexa*-1 : 5-*diene* (*dicinnamyl*).
4, 1 : 10-*Diphenyldeca*-1 : 9-*diene.*

The same arguments may be applied to the ultra-violet spectrum of the homologous hydrocarbon 1 : 10-diphenyldeca-1 : 9-diene (II) of m. p. 53°, which is also shown in Fig. 1.

This absorption strongly resembles that of dicinnamyl, and the *trans-trans*-structure of the higher homologue cannot therefore be in doubt. By analogy, the two liquid hydrocarbons 1-propenylbenzene (III) and 1 : 4-diphenylhexa-1 : 5-diene (*iso*dicinnamyl; IV) of Fig. 1 are likewise regarded as the *trans*-isomers.

Although the light-absorption characteristics of styrene itself are well known, 1-propenylbenzene (III) is the only example of the substituted styrenes illustrated in Fig. 1 for which the spectrum has been determined previously (cf. Jones, *loc. cit.*). This hydrocarbon was obtained by alkaline isomerisation of allylbenzene. 1 : 10-Diphenyldeca-1 : 9-diene (II) was prepared by standard methods, and the preparation of spectroscopically pure (non-fluorescent) samples of dicinnamyl (I) and *iso*dicinnamyl (IV) has been described in a preceding paper (this vol., p. 1111). It should be mentioned that Smakula (*Angew. Chem.*, 1934, **47**, 657) has reported maximum extinction data for 3 : 4-dihydroxy-1 : 6-diphenylhexa-1 : 5-diene (V) which suggest a close resemblance between the ultra-violet absorption of this dihydroxydicinnamyl ($\lambda_{max.}$ = 2560 A., ε = 28,000 in ethanol) and that of dicinnamyl itself.

$CHPh:CH\cdot[CH_2]_6\cdot CH:CHPh$ (II.)

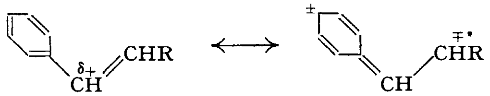
$CHPh:CH\cdot CH_3$ (III.)

$CHPh:CH\cdot CH_2\cdot CHPh\cdot CH:CH_2$ (IV.)

$CHPh:CH\cdot CH(OH)\cdot CH(OH)\cdot CH:CHPh$ (V.)

$CHPh:CH\cdot CH(OH)\cdot CH_3$ (VI.)

All the spectra reproduced in Fig. 1 exhibit two main regions of selective absorption, the first between 2950 and 2750 A. with well-defined vibrational fine-structure peaks at 2930 and 2840 A., and the second between 2700 and 2300 A. with a rather broad band-head more than ten times as intense as the long-wave region. Such light-absorption properties are apparently characteristic of all β-alkyl-substituted styrenes (cf. Ramart-Lucas and Amagat, *Bull. Soc. chim.*, 1932, **51**, 965; Braude, Jones, and Stern, *J.*, 1946, 396) and also similar to those of benzaldehyde (Walsh, *Trans. Faraday Soc.*, 1946, **42**, 62), and their origin may be explained as follows : The 2700—2300 A. region is almost certainly analogous to the intense $N \longrightarrow V$ transition of butadiene around 2200 A. and therefore to be associated with resonance of the type (A), the absorption being polarised in the plane of the styrene chromophore with the light vibrations in a direction parallel to its long axis. The 2950—2750 A. region, on the other hand, with a fine-structure separation of 1010 cm.$^{-1}$ corresponding to the symmetrical " breathing " frequency of the benzene ring, is analogous to the " forbidden " benzene absorption near 2600 A., facilitated in the derivatives by the decreased symmetry resulting from substitution in the aromatic ring. This absorption is presumably polarised in the same plane but with the electric vector normal to the above, so that the two absorption systems correspond to the mutually perpendicular " *x* " and " *y* " bands believed to be associated with all complex aromatic hydrocarbons and similar chromophores (Lewis and Calvin, *Chem. Reviews*, 1939, **25**, 273; Jones, *ibid.*, 1947, **41**, 353).

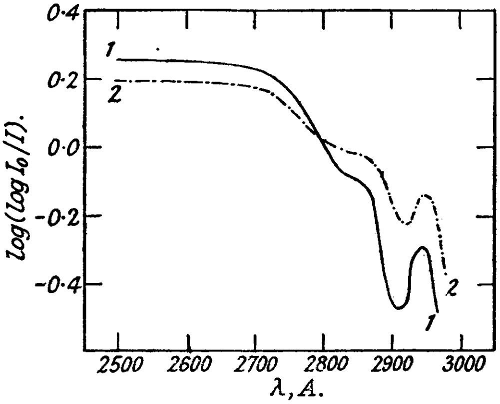


(and two *o*-quinonoid structures) (A.)

Interesting confirmation of the above directional assignment of absorption bands is obtained on measuring the ultra-violet transmission of a thin oriented layer of dicinnamyl or 1 : 10-diphenyldeca-1 : 9-diene in the crystalline state. Dicinnamyl generally crystallises in thin flakes; and preliminary *X*-ray crystallographic examination by Mr. S. C. Nyburg, together with trial packing experiments and observations on diffuse thermal reflections kindly carried out by Dr. K. Lonsdale, have shown that the long axis of the molecules lies almost at right angles to the face of the flakes. When molten and squeezed between plates of glass or quartz to a thickness of the order of 1 μ, the resultant film of dicinnamyl gives rise on freezing to a number of crystalline regions accounting for at least 90% of the bulk according to *X*-ray photographs, each region being essentially a single flake-like crystal with its face roughly parallel to the containing surface. To a first approximation, therefore, the hydrocarbon may be regarded as oriented with the length of the molecule and also the long axis of the styrene chromophores roughly normal to the flat surface of the resulting sandwich structure. Similar orientation was observed by Scheibe, Hartwig, and Mueller (*Z. Elektrochem.*, 1943, **49**, 372; cf. also Krishnan and Seshan, *Proc. Indian Acad. Sci.*, 1938, *A*, **8**, 487), who found that hexamethylbenzene crystallised between quartz plates with the aromatic ring planes of the molecules perpendicular to the plane of the optical flats. On passing a beam of unpolarised ultra-violet light across the dicinnamyl film at a right angle, all the electric vectors, being directed at right angles to the direction of propagation of the light, will then be polarised in the plane of the flat face, *i.e.*, more or less *normal* to the orientation of the long axis of the styrene chromophore. Consequently, selective absorption in the 2700—2300 A. region associated with the resonance (A) depicted above and requiring vector polarisation *parallel* to this axis should be greatly weakened or suppressed. Analogous optical phenomena were encountered by Krishnan and Seshan (*loc. cit.*) in their experiments on crystals of chrysene which did not absorb ultra-violet light vibrating at right angles to the molecular planes.

The observed spectrum of the dicinnamyl " sandwich " is plotted as curve (1) of Fig. 2 and may be compared with the corresponding solution spectrum, although absolute extinction coefficients could not be determined owing to the uncertain losses incurred through scattering and reflection. The characteristic first absorption region at 2950—2750 A. is still clearly discernible, but the high-intensity maximum between 2700 and 2300 A. has disappeared and been replaced by considerably reduced and apparently continuous extinction which may be attributed in part to both anomalous and Rayleigh scattering in the crystalline film, the latter being slightly opaque to visible light. Relative to the long-wave bands as an internal standard, the short-wave absorption attributed to excitation associated with the resonance (A) is evidently much weaker in the oriented crystal flat than in solution, in accordance with expectation. The 2950—2750 A. absorption of the film is quite strong and therefore presumably polarised in perpendicular directions where electric vectors are available for the requisite excitation *normal* to the long axis of the styrene chromophore. At the same time, the vibrational fine-structure peaks are shifted from 2930 and 2840 A. in solution to 2945 and 2860 A. in the crystal, their characteristic separation being maintained at 1010 wave-numbers, the " breathing" frequency of the benzene ring. Like shifts of 15—20 A. take place between the ultra-violet absorption bands of hexamethylbenzene as measured in solution and in the crystalline state (Scheibe *et al.*, *loc. cit.*).

FIG. 2.



1, ——— 1 : 6-*Diphenylhexa*-1 : 5-*diene* (*dicinnamyl*).
2, —·— 1 : 10-*Diphenyldeca*-1 : 9-*diene*.

Curve (2) of Fig. 2 represents the transmission of a crystalline film of 1 : 10-diphenyldeca-1 : 9-diene (III), set up analogously to the above. The spectrum is extremely similar to that of dicinnamyl and it may be presumed that here, too, the long axes of the styrene chromophores are oriented more or less at right angles to the characteristic flat face of the crystals which is doubtless developed in a direction parallel to the quartz plates.

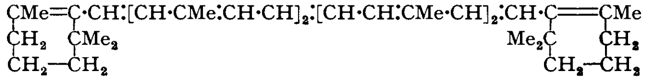
On careful comparison of the solution spectra of the four β-substituted styrenes plotted in Fig. 1, the location of the perpendicular benzenoid maxima was found to be remarkably constant at 2930 and 2840 A. On the other hand, significant second-order variations do occur between the centres of the longitudinal styrene absorptions in the short-wave region. At first sight it seemed, in fact, that intramolecular electronic interaction in the 1 : 5-unsaturated systems was indicated by the gradual shift from 2470 to 2550 A. and simultaneous intensification of the extinction calculated per styrene group in the series propenylbenzene <*iso*dicinnamyl <dicinnamyl. These small shifts appeared to be the more significant in view of the work of Ramart-Lucas and Amagat (*loc. cit.*), who compared styrene and β-octylstyrene and claimed that the length of chain attached had no influence on the ultra-violet absorption

properties. Subsequent examination of the 1 : 9-unsaturated diphenyldecadiene, however, strongly supported the view that the observed bathochromic effects must be due, in part at least, to other causes. The absorption of this higher homologue [curve (4) of Fig. 1] is so similar to the dicinnamyl spectrum, particularly as regards the short-wave slope of the main band and its peak intensity, that the remaining relative shift between the respective absorption centres (located at 2505 and 2550 A.) may scarcely be considered sufficient spectroscopic evidence for electronic interaction of the two styrene systems in the dicinnamyl molecule. If anything, the spectra suggest that there is a definite small weight or chain-length effect which causes the styrene chromophores in diphenyldecadiene to absorb relatively more strongly and at longer waves than they do in propenylbenzene; and it must remain an open question in how far the displacements of the *iso*dicinnamyl and dicinnamyl absorptions from the propenylbenzene position are due to similar weight effects or to slight interaction of the unsaturation electrons across the three central single bonds as envisaged by Bateman and Jeffrey (*loc. cit.*).

Walsh (*Proc. Roy. Soc.*, 1947, *A*, **191**, 32) has examined the absorption of styrene in the vapour phase and found that the broad short-wave maximum was split into two distinct humps with a separation of 1650 cm.$^{-1}$ corresponding to the carbon–carbon double-bond stretching frequency (cf. Hausser, *Z. tech. Physik*, 1934, **15**, 10). There can be little doubt that all the strong continua between 2700 and 2300 A. shown in the spectral curves of Fig. 1 arise from the superposition of discrete vibrational sub-levels, and Braude, Jones, and Stern (*loc. cit.*) have in fact resolved the solution spectrum of styrylmethylcarbinol (VI) into two band-heads at 2510 and 2480 A., although the dicinnamyl maximum could not be resolved in the present work with the aid of a Hilger medium spectrograph. The rather unsymmetrical broadening and displacement of the styrene-type spectra of *iso*dicinnamyl, dicinnamyl, and diphenyldecadiene may therefore conceivably be due to changes in the energy or relative importance of their separate vibrational levels rather than to a genuine shift of electronic activation. If indeed the three central bonds of dicinnamyl are shortened for whatever cause, the unusual valency orbital hybridisation involved might be expected to have some effect also on the vibrational characteristics of the adjacent double bonds, in both ground and excited states. So-called chain-length effects may well be similarly correlated with weighting effects on the valence vibration determining the contour of the electronic bands.

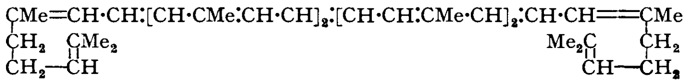
Attention should also be drawn to the fact that the styrene-analogous butadiene absorption region around 2200 A. is equally subject to second-order chain-length effects. Thus, the well-known conjugated linoleic compounds which may be regarded as terminally long-chain di-substituted butadienes all absorb maximally near 2320 A., whereas simple hexa-2 : 4-dienes are characterised by more short-wave absorption peaks in the region of 2275 A. (cf. Bolland and Koch, *J.*, 1945, 445). These shifts are small but nevertheless significant.

To conclude this spectral survey of 1 : 5-spaced hydrocarbon chromophores, an apparent exception to the general failure to detect appreciable interaction effects remains to be discussed. A well-known and striking colour change (band-shifts from 4835 and 4520 A. to 5060 and 4740 A.) accompanies the structural change from β-carotene (VII) to lycopene (VIII); and since the two isomeric pigments are based on the same system of eleven double bonds in conjugation, the deeper colour of lycopene might be thought to be due to electronic interaction across three single bonds with the additional terminal double bonds of this molecule. The absorption bands of γ-carotene, which has one of the two end groups cyclised and the other terminally unsaturated, lie intermediate between those of (VII) and (VIII). A recent comparison of the ultra-violet spectra of phytal (IX) and citral (X), however, does not lend support to the above interpretation of the spectral shifts in terms of a 1 : 5-interaction effect. The double-bond structure of the two open-chain αβ-unsaturated aldehydes (IX) and (X) differs exactly as (VII) differs from (VIII) by the absence or presence respectively of a terminal double bond in a position 1 : 5 to a conjugated chromophore, and yet both citral and phytal display maximum absorption at precisely



$$\mathrm{CMe{=}C{\cdot}CH{:}[CH{\cdot}CMe{:}CH{\cdot}CH]_2{:}[CH{\cdot}CH{:}CMe{\cdot}CH]_2{:}CH{\cdot}C{=}CMe}$$

(VII.)



$$\mathrm{CMe{=}CH{\cdot}CH{:}[CH{\cdot}CMe{:}CH{\cdot}CH]_2{:}[CH{\cdot}CH{:}CMe{\cdot}CH]_2{:}CH{\cdot}CH{=}CMe}$$

(VIII.)

$$\mathrm{CHMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}[CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2]_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH{:}O} \qquad \text{(IX.)}$$

$$\mathrm{CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH{:}O} \qquad \text{(X.)}$$

the same wave-length of 2380 A. (Burawoy, *J.*, 1941, **23**; and unpublished work). The colour change between lycopene and β-carotene must evidently find its true explanation in terms of the cyclisation, as may be readily understood by reference to steric scale models. Although resonance stabilisation undoubtedly induces a fully coplanar zigzag arrangement of the entire system of eleven conjugated double bonds in lycopene (VIII), yet the scale model of β-carotene (VII) does not admit of coplanarity with respect to the two terminal double bonds forming part of the cyclic portion of the molecule on account of steric interference between the planar central chain and the methyl groups on the rings. The effective electronic conjugation of the cyclic double bonds of β-carotene is therefore reduced and the light absorption shifted to shorter wave-lengths relative to the lycopene pigment. Similar spectral abnormalities have been recorded for β-ionone, β-*cyclo*citral, and their crystalline semicarbazones (cf. Koch, *Chem. and Ind.*, 1942, **61**, 273); and the relatively small spectral shift associated with displacement out of conjugation of the two cyclic double bonds (from 4835 and 4520 A. in β-carotene to 4780 and 4475 A. in α-carotene) may be cited as further evidence of the small conjugating power of these double bonds due to inhibition by unfavourable steric conditions.

EXPERIMENTAL.

All spectra were recorded with the aid of a Spekker photometer attached to a Hilger small quartz spectrograph. Through the courtesy of Dr. D. M. Simpson, a Hilger medium spectrograph was also made available at the University of Cambridge for the examination of dicinnamyl, without, however, achieving any resolution of the broad absorption maximum. A detailed description of the *X*-ray work on dicinnamyl will be given elsewhere, but preliminary data are contained in a preceding communication (this vol., p. 1111).

1-*Propenylbenzene*.—Allylbenzene (5 g.; cf. this vol., p. 1116) was heated with potassium hydroxide (10 g.) in ethylene glycol solution (100 g.) for 1 hour at 160° in an atmosphere of nitrogen. After the addition of water and ether, the isomerised hydrocarbon was isolated from its ethereal solution in the usual manner and distilled at 171°/763 mm.; $n_D^{13\cdot5°}$ 1·5510. 1-Propenylbenzene differs from allylbenzene in giving a yellow colour with *s*-trinitrobenzene in chloroform solution.

1 : 10-*Diphenyldeca*-1 : 9-*diene* (cf. Borsche and Wollemann, *Ber.*, 1911, **44**, 3185; Schmidt and Grosser, *ibid.*, 1942, **75**, 826).—Sebacophenone (48 g., prepared by Friedel–Crafts reaction between sebacyl chloride and benzene; m. p. 92·5—93·5°) was reduced in a boiling molar solution (300 c.c.) of aluminium *iso*propyl alcohol. After completion of the reaction (no more acetone distilling over) the bulk of the solvent was taken off at reduced pressure and the residue hydrolysed by addition of dilute hydrochloric acid. The resulting oil gradually solidified, and the colourless solid was crystallised from benzene after being washed with dilute acid and water. The purified 1 : 10-dihydroxy-1 : 10-diphenyldecane was only obtained as an amorphous powder, m. p. 63·5—69° (lit., 70—72°; needles, m. p. 72°), insoluble in petrol and extremely soluble in ethanol (Found: C, 80·9; H, 9·3. Calc. for $C_{22}H_{30}O_2$: C, 80·95; H, 9·25%) (this alcohol would hardly be expected to be homogeneous but rather a mixture of equal proportions of the DL- and the *meso*-form). Facile dehydration took place over potassium hydrogen sulphate at 160—180° under reduced pressure, and the resulting 1 : 10-diphenyldeca-1 : 9-diene began to crystallise soon after distillation at 150°/10^{-3} mm. The hydrocarbon was obtained in thin irregular plates from ethanol, m. p. 53·5° (lit., needles, 53°). It gave a yellow colour but no compound crystals on mixing with 2 mols. of *s*-trinitrobenzene in concentrated chloroform solution.

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