219. *Resolution of an Allene Hydrocarbon into Optical Antipodes by Asymmetric Catalysis.*

By PETER MAITLAND and WILLIAM H. MILLS.

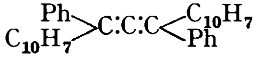
OF the various structural types of carbon compounds to which van 't Hoff's tetrahedral theory assigns molecular dissymmetry the unsymmetrically substituted allenes have proved the least amenable to experimental investigation. The prediction that enantiomorphism would be shown by allenes of the general formula $\begin{matrix}a\\b\end{matrix}{>}C{:}C{:}C{<}\begin{matrix}c\\d\end{matrix}$ was made by van 't Hoff in 1875 (" La Chimie dans l'Espace," p. 29) and many unsuccessful attempts to verify it have been recorded (Dimroth and Feuchter, *Ber.*, 1903, **36**, 2238; Lapworth and Wechsler, J., 1910, **97**, 38; Hurd and Webb, *J. Amer. Chem. Soc.*, 1927, **49**, 546; Faltis and Pirsch, *Ber.*, 1927, **60**, 1621; Faltis, Pirsch, and Bermann, *Ber.*, 1930, **63**, 691; Ziegler and Sauermilch, *Ber.*, 1930, **63**, 1851).

While the probability of van 't Hoff's view of the configuration of allene was almost universally admitted, the linking of the central carbon atom of the allene triad differs so considerably from the types of linking for which the tetrahedral theory has been shown to hold that its application in this case was necessarily subject to some uncertainty. Moreover the degree of configurational stability which allenes would exhibit was doubtful. The molecular configuration of this class of compounds was therefore a point of special interest in the stereochemistry of carbon, and we have been engaged for some time on its investigation.

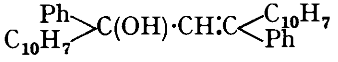
On account of the difficulty of preparing tetra-arylallenes containing the salt-forming groups required for resolution through combination with optically active acids or bases we tried other methods, and found in asymmetric catalysis a means of obtaining an allene in optically active forms.

In preliminary experiments on the synthesis of tetra-arylallenes we had discovered that *αγ-diphenyl-αγ-di-*1-*naphthylallene* (I) crystallised more readily than most hydrocarbons of this class.

(I.)



$$\begin{matrix}Ph\\C_{10}H_7\end{matrix}{>}C{:}C{:}C{<}\begin{matrix}C_{10}H_7\\Ph\end{matrix}$$



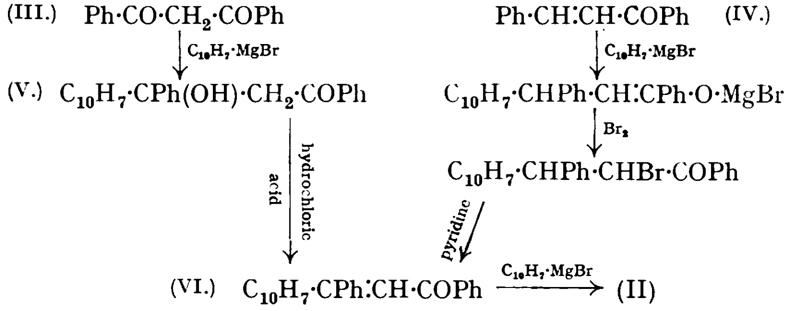
$$\begin{matrix}Ph\\C_{10}H_7\end{matrix}{>}C(OH){\cdot}CH{:}C{<}\begin{matrix}C_{10}H_7\\Ph\end{matrix}$$

(II.)

We therefore selected this compound for investigation * and studied its production by catalytic dehydration of *αγ-diphenyl-αγ-di-*1*-naphthylallyl alcohol* (II). We found that by the employment of optically active catalysts the dehydration could be conducted asymmetrically, and by this means we were able to isolate the two enantiomorphous forms of the allene.

The required diphenyldinaphthylallyl alcohol (II) was prepared in two ways based on methods employed by Vorländer and Siebert (*Ber.*, 1906, **39**, 1024) for the synthesis of tetraphenylallene.

Of these methods, one started with dibenzoylmethane (III) and the other (which was less advantageous) with benzylideneacetophenone (IV). Each of these substances could be converted through the employment of 1-naphthylmagnesium bromide, as indicated in the following schemes, into *phenyl β-phenyl-β-*1*-naphthylvinyl ketone* (VI) :



(III.) $Ph{\cdot}CO{\cdot}CH_2{\cdot}COPh \xrightarrow{C_{10}H_7{\cdot}MgBr}$ (V.) $C_{10}H_7{\cdot}CPh(OH){\cdot}CH_2{\cdot}COPh \xrightarrow{\text{hydrochloric acid}}$ (VI.)

$Ph{\cdot}CH{:}CH{\cdot}COPh$ (IV.) $\xrightarrow{C_{10}H_7{\cdot}MgBr} C_{10}H_7{\cdot}CHPh{\cdot}CH{:}CPh{\cdot}O{\cdot}MgBr \xrightarrow{Br_2} C_{10}H_7{\cdot}CHPh{\cdot}CHBr{\cdot}COPh \xrightarrow{\text{Pyridine}}$ (VI.)

(VI.) $C_{10}H_7{\cdot}CPh{:}CH{\cdot}COPh \xrightarrow{C_{10}H_7{\cdot}MgBr}$ (II)

Though this ketone should exist in two geometrically isomeric forms, only one modification was actually obtained, a bright yellow compound, m. p. 107—108°, which could be transformed, again with the aid of naphthylmagnesium bromide, into the required diphenyldinaphthylallyl alcohol (II). The alcohol thus obtained, like the ketone, was homogeneous in respect of the possible geometrical isomerism due to the presence of the ethylenic link. By the dehydration of the alcohol (II) diphenyldinaphthylallene was obtained as a colourless crystalline compound, melting at 242—244°, very sparingly soluble in the common organic solvents.

The dehydration of the alcohol is easily effected. It can be brought about, for example, by heating with acetic anhydride, and also, catalytically, by heating in benzene solution with a small proportion of *p*-toluenesulphonic acid, a method of dehydrating tertiary alcohols described by Wuyts (*Bull. Soc. chim. Belg.*, 1912, **26**, 304). To examine the possibility of asymmetric catalysis *d*-camphorsulphonic acid was used as the catalyst (compare Wuyts, *ibid.*, 1921, **30**, 30). The alcohol (II) was heated in benzene solution with 1% of its weight of the sulphonic acid. Under these conditions the dehydration is complete in about 15 minutes. At the high dilution employed, the rotation due to the added *d*-camphorsulphonic acid was too small to be measurable, but during the reaction the optical activity increased in a remarkable manner, and the final rotations, α_{5461}, observed (on the solution diluted to half its original concentration) were usually from + 1·25° to + 1·75°. After removal of the acid the strongly dextrorotatory solution contains, in addition to a minute amount of an unidentified yellow compound, two substances readily separable by fractional crystallisation. These are : (i) the inactive allene, m. p. 242—244°, and (ii) a smaller amount of a much more soluble compound separating in large well-formed crystals, m. p. 158—159°, having the same percentage composition as the allene, and showing in benzene solution the high specific rotation $[\alpha]_{5461}$ + 437°.

The catalytic dehydration of the alcohol (II) was then repeated, *l*-camphorsulphonic acid being used. The resulting phenomena were the counterpart of those observed with the *d*-acid. The solution became strongly lævorotatory and the products consisted of the inactive form of the allene, m. p. 242—244°, together with the lævo-antimer of the dextrorotatory compound of m. p. 158—159°. This lævorotatory compound melted at 158—159°,

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* It has long been recognised that the dissymmetry of the molecular type $^{a}_{b}\!\!>\!C{:}C{:}C\!<\!^{c}_{d}$ should persist when *a* becomes identical with *c* and *b* with *d*.

was found to have the percentage composition of the allene, and showed the specific rotation $[\alpha]_{5461}$ — 438° in benzene solution.

When saturated ethereal solutions of the *d*- and the *l*-antimer of m. p. 158—159° were mixed, the inactive allene of m. p. 242—244° was at once deposited. It was identified by its crystallographic characters as well as by its other properties. The inactive allene is therefore a racemic compound and the antimeric substances of m. p. 158—159° are its enantiomorphous components. Van 't Hoff's prediction of the enantiomorphism of unsymmetrically substituted allenes is thus verified.

The successful application of asymmetric catalysis in this case was made possible by a combination of various favourable circumstances : (i) the almost complete absence of by-products in the reaction, (ii) the crystallising power of the active and the inactive allene, combined with their great difference in solubility, and (iii) the high specific rotation of the active allenes, which greatly facilitated their detection.

Consideration of the catalytic dehydration of the alcohol allows certain conclusions to be drawn concerning the manner in which the active forms of the allene arise.

The alcohol (II), containing an asymmetric carbon atom, consists of an equimolecular mixture of *d*- and *l*-forms. If the removal of the water molecule took place exclusively, let us say, by *cis*-elimination,* the *d*-alcohol would be converted by dehydration into one only of the optically active forms of the allene, and the *l*-alcohol into the antimeric form. Complete dehydration of the inactive alcohol would then necessarily yield equal quantities of *d*- or *l*-allene, and the same would be true if the removal of water took place entirely by *trans*-elimination.

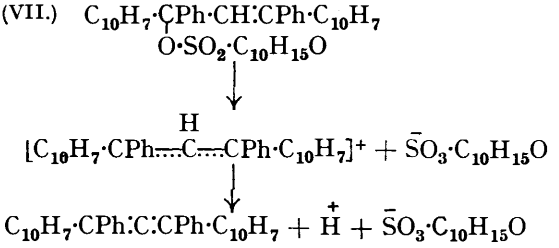
The possibility of obtaining an active product by complete dehydration therefore proves that the removal of water must take place partly by *cis*- and partly by *trans*-elimination.

When the catalytic dehydration of the *dl*-alcohol is carried out with an inactive catalyst, such as *p*-toluenesulphonic acid, the proportion of *cis*- to *trans*-elimination must be the same for the *d*-alcohol as for the *l*-alcohol. But when an optically active catalyst like camphorsulphonic acid is employed, the relative proportions of *cis*- and *trans*-elimination of water are different for the *d*- and the *l*-alcohol and unequal quantities of the enantiomorphous forms of the allene are produced. The optical rotation of the benzene solution of the products indicated that, with *d*-camphorsulphonic acid under the conditions employed, the antimeric forms were produced in the proportion of approximately 52·5% of *d*-allene to 47·5% of *l*-allene, the excess of *d*-allene amounting usually to 4—5% of the total allene formed.

d-Bromocamphorsulphonic acid was also tried as catalyst. Like the Reychler acid, it acted differently on the two antimeric components of the *dl*-alcohol, but to a less extent, the proportion of active allene resulting (in this case the *l*-antimer) being only 1·7% of the total.

When benzene solutions of the tertiary alcohol (II) are heated with camphorsulphonic acid, a purple coloration appears. This is probably due to the presence of a small quantity of the coloured (carbonium) form of the camphorsulphonate of the alcohol (II), since tetra-arylallyl alcohols, as has been shown by Ziegler (*Annalen*, 1923, **434**, 34), resemble triarylcarbinols in their behaviour, and form coloured derivatives with acids.

The intermediate formation of the alcohol camphorsulphonate would suggest that the mechanism of the catalytic dehydration consists of the following stages : (1) Esterification of the tertiary alcohol by the camphorsulphonic acid, (2) dissociation of the resulting ester (VII) into the camphorsulphonic ion and the coloured carbonium ion (VIII), (3) immediate



$$\begin{array}{lc} \text{(VII.)} & \mathrm{C_{10}H_7{\cdot}\underset{|}{C}Ph{\cdot}CH{:}CPh{\cdot}C_{10}H_7} \\ & \mathrm{O{\cdot}SO_2{\cdot}C_{10}H_{15}O} \\ & \downarrow \\ \text{(VIII.)} & \mathrm{[C_{10}H_7{\cdot}CPh{\cdots}\overset{H}{C}{\cdots}CPh{\cdot}C_{10}H_7]^+ + \bar{S}O_3{\cdot}C_{10}H_{15}O} \\ & \downarrow \\ & \mathrm{C_{10}H_7{\cdot}CPh{:}C{:}CPh{\cdot}C_{10}H_7 + \overset{+}{H} + \bar{S}O_3{\cdot}C_{10}H_{15}O} \end{array}$$

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* In applying the terms *cis*- and *trans*-elimination to saturated compounds the converse of *cis*- and *trans*-addition to the resulting ethylenic compounds is understood.

decomposition of the latter into a hydrogen ion (thereby regenerating the sulphonic acid) and the allene.

If this view of the mechanism of the dehydration is correct, it gives an indication of the reason why the reaction should proceed asymmetrically.

When the molecule of this camphorsulphonic ester is in the configuration necessary for the *trans*-elimination of camphorsulphonic acid, the general arrangement of the groups will be that represented in Fig. 1a. (It is not known which of the two possible geometrical isomers is represented by the only form of diphenyldinaphthylallyl alcohol obtained, but this scarcely affects the following considerations and the compound may be regarded provisonally as that in which the naphthyl group is in the *trans*-relationship to the asymmetric carbon atom as shown in the figure.)

FIG. 1a.

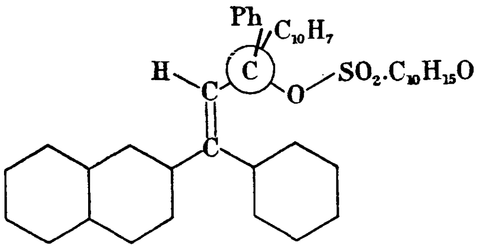
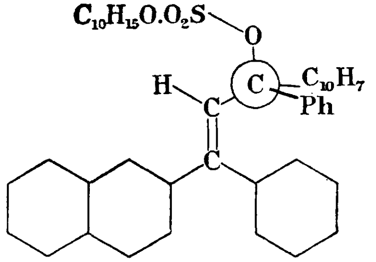


FIG. 1b.



In this configuration of the molecule the camphorsulphonic group is very closely surrounded by three rigid, widely extending aromatic groups. As is clearly seen from a model, these groups are in such proximity as to interfere greatly with one another's freedom of movement. Their most probable relative positions—and particularly the orientation of the camphorsulphonic group—will therefore be closely defined.

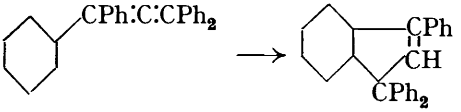
Under such conditions the dissymmetry of the camphorsulphonic group must cause its relationship to its immediate environment in the molecule to be considerably affected by an interchange of the phenyl and the naphthyl group on the asymmetric carbon atom. This implies that the rate of *trans*-elimination of water by the process suggested should be greater in one of the two antimeric forms of the alcohol than in the other.

In the configuration necessary for *cis*-elimination (Fig. 1b), however, the camphorsulphonic group is much less closely enveloped by aromatic groups, since it has only two of them as immediate neighbours, the space filled in the other configuration by a phenyl group now containing only a hydrogen atom. In this configuration, therefore, an interchange of the phenyl and the naphthyl group would be much less likely to cause an appreciable difference in the rate of elimination of the camphorsulphonic ion. Since the experimental results show that a considerable proportion of the water must be removed by *trans*-elimination, these considerations indicate in a general way how the difference in the relative amounts of *cis*- and *trans*-elimination from the *d*- and the *l*-form of the alcohol could be accounted for.

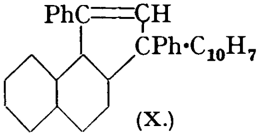
As has been stated, the optically active allenes show great configurational stability, and it is difficult to convert them by heating into the racemic modification. When the *d*-allene is heated to 190° in presence of air, it gradually loses its optical activity, but this is due to some chemical change other than simple racemisation, since very little of the racemic form can be isolated from the product. The *d*-allene, dissolved in decalin and heated to 190° in an indifferent atmosphere, could be recovered almost unchanged after 9 hours. By 48 hours' heating, however, under these conditions it was possible to effect the transformation of a considerable amount of the *d*- into the racemic form.

In the foregoing account of the hydrocarbon of m. p. 242—244° and its enantiomorphous components it has been assumed that the method by which it was synthesised sufficiently fixed its constitution. In order, however, to remove any doubt there might be as to its structure we have studied its reactions and these—particularly the transformation which it undergoes when treated with acids, and its behaviour on oxidation and reduction—show conclusively that it must be the diphenyldinaphthylallene (I).

Vorländer and Siebert showed (*loc. cit.*) that tetraphenylallene on treatment with acids was converted into an isomeric hydrocarbon which they regarded as 1 : 1 : 3-triphenylindene (IX) and the correctness of this formulation was afterwards established by Kohler (*Amer. Chem. J.*, 1908, **40**, 217).



(IX.)



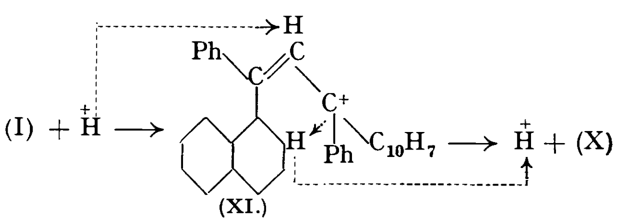
(X.)

Almost the only doubt there might have been about the structure of our hydrocarbon arose from the possibility that, since acidic reagents were used in its preparation, the allene primarily formed by dehydration of the alcohol (II) might have undergone a transformation analogous to the triphenylindene transformation of tetraphenylallene, and the product isolated—the hydrocarbon of m. p. 242—244°—might therefore conceivably have been the indene derivative (X).

This possibility is excluded by the fact that our hydrocarbon, when subjected to conditions corresponding with those which cause the transformation of the tetraphenylallene into triphenylindene, undergoes an evidently analogous transformation, yielding an isomeride of m. p. 233—234° to which we provisionally assign the structure (X) of a diphenylnaphthylbenzindene (although the alternative structure of a phenyldinaphthylindene, or even of a diphenylnaphthyl*peri*naphthindene, is not definitely excluded). Since the hydrocarbon of m. p. 242—244° is thus capable of undergoing the indene transformation, it cannot already have been subjected to it. It must therefore, from its method of synthesis, be the tetra-arylallene (I).

The optically active allenes of m. p. 158—159° can of course also be similarly transformed, but even under the mildest conditions of transformation optical activity could not be detected in the resulting indene.

This isomerisation of aryl allenes seems at first sight a somewhat surprising reaction, involving the apparent addition of the carbon and hydrogen of an aromatic CH group across a distantly situated pair of doubly linked carbon atoms. Consideration of the circumstances of the transformation gives an indication, however, of the manner in which it may take place. It is most readily effected by heating the allene with hydrogen chloride in acetic acid solution and a strong purple coloration then appears and persists until the conversion is complete. This coloration probably indicates, as in the catalytic dehydration of the tetra-arylallyl alcohol, the intermediate formation of the carbonium ion (XI) through the addition of a hydrogen ion to the central atom of the allene carbon triad. The three-carbon chain would thus be caused to assume an angular configuration, as is indicated in formula (XI), bringing the reactive carbonium carbon atom into a favourable position for combining with a β-carbon atom of the naphthyl group. The hydrogen atom thus displaced from the naphthyl group would be eliminated as a hydrogen ion, replacing that which had been absorbed from the solution and leaving a neutral benzindene molecule. Moreover the breaking of the double bond through the addition of the hydrogen ion would give the $C_{10}H_7\cdot\overset{+}{C}Ph$– complex freedom to rotate and cause the observed disappearance of the optical activity.



(XI.)

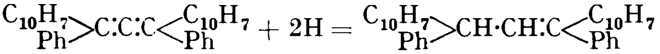
The allene structure of the hydrocarbon of m. p. 242—244° finds additional confirmation in its behaviour on oxidation and reduction. The allene is remarkably stable towards oxidising agents and, like tetraphenylallene (Vorländer and Siebert, *loc. cit.*), is resistant to potassium permanganate in acetone solution. In moist pyridine solution, however, potassium permanganate attacks it, giving, as would be expected, phenyl naphthyl ketone as the principal product, but a mixture of acids, somewhat greater in weight than the ketone, is also formed. This mixture contains phthalic and benzoic acids as its chief constituents and evidently comes from further oxidation of the ketone, since the latter is itself attacked by permanganate under the conditions employed and is oxidised to a similar mixture having phthalic and benzoic acids as chief components.

Hence, although the quantity of ketone that could actually be isolated was only 40% of that required by the equation

$$C_{10}H_7{\cdot}CPh{:}C{:}CPh{\cdot}C_{10}H_7 + 4O = 2Ph{\cdot}CO{\cdot}C_{10}H_7 + CO_2,$$

a considerable part of the initial yield of this compound must have been destroyed by its subsequent oxidation—which under the conditions used would necessarily occur—and the amount actually produced must have been much greater than that isolated.

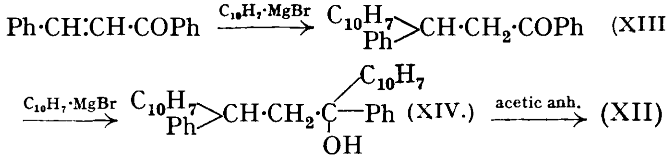
Reduction of the hydrocarbon yielded conclusive evidence of its structure. Of the various reducing agents used, hydriodic acid in presence of red phosphorus was the only one which gave a crystalline product. The reduction proceeds according to the equation



$${}^{C_{10}H_7}_{Ph}\!>\!C{:}C{:}C\!<\!{}^{C_{10}H_7}_{Ph} + 2H = {}^{C_{10}H_7}_{Ph}\!>\!CH{\cdot}CH{:}C\!<\!{}^{C_{10}H_7}_{Ph} \quad (XII.)$$

yielding a hydrocarbon which was proved to be the *diphenyldi-α-naphthylpropylene* (XII). [The corresponding tetraphenylpropylene was obtained by Vorländer and Weinstein (*Ber.*, 1923, **56**, 1122) by the action of the same reagent on tetraphenylallene, but in that case the reduction took place very much more rapidly and was readily carried further to tetraphenylpropane.]

The constitution of the reduction product (XII) was established by its synthesis through the following reactions, starting from benzylideneacetophenone. This unsaturated ketone gave with α-naphthylmagnesium bromide the saturated ketone (XIII), the reaction proceeding in the manner shown by Kohler to be the normal mode of interaction for αβ-unsaturated ketones. The ketone (XIII) with naphthylmagnesium bromide yielded the tertiary alcohol (XIV), which was not obtained crystalline, but was dehydrated by acetic anhydride, yielding a hydrocarbon $C_{35}H_{26}$. A hydrocarbon of this composition thus formed must necessarily have the constitution (XII), and it was found to be identical with the reduction product of the hydrocarbon of m. p. 242—244° which we have regarded as the allene. The latter compound, being converted by the addition of two atoms of hydrogen into diphenyldinaphthylpropylene (XII), can only have the allene structure (I) which we have assigned to it.



$$Ph{\cdot}CH{:}CH{\cdot}COPh \xrightarrow{C_{10}H_7\cdot MgBr} {}^{C_{10}H_7}_{Ph}\!>\!CH{\cdot}CH_2{\cdot}COPh \quad (XIII.)$$

$$\xrightarrow{C_{10}H_7\cdot MgBr} {}^{C_{10}H_7}_{Ph}\!>\!CH{\cdot}CH_2{\cdot}\overset{C_{10}H_7}{\underset{OH}{C}}{-}Ph \quad (XIV.) \xrightarrow{\text{acetic anh.}} (XII)$$

The existence of diphenyldinaphthylallene in enantiomorphous forms indicates clearly the correctness of van 't Hoff's view of the configuration of allene—the essential features of which are the linear arrangement of the three carbon atoms and the disposition of the external valencies of the terminal carbon atoms in planes at right angles to one another. This view was based on the representation of a pair of doubly linked carbon atoms by two tetrahedra in contact along an edge. According to the wave-mechanical view of the carbon valencies the formation of the ethylene molecule involves the trigonal wave-functions of carbon. These give three co-planar bonds of the Heitler–London type, involving three of the four valency electrons of the carbon atom, while the fourth, a $2p\pi$ electron, forms an electron cloud symmetrical about an axis perpendicular to the plane of the three single bonds.

In the ethylene molecule (Fig. 2a) one of the two bonds which make up the double link is thus a Heitler–London single bond. The other is of a different nature and arises through resonance between the two $2p\pi$ electrons. Maximum resonance, giving maximum binding energy, occurs when the axes *aa'* are parallel (thus the wave-mechanical view of the ethylene configuration corresponds closely with van 't Hoff's model). By applying this conception of the ethylenic link to allene and combining it with the knowledge of the configuration of this hydrocarbon (Fig. 2b) an indication is obtained of the structure of its characteristic central carbon atom. It would appear that two of the four valency electrons of this atom are concerned in the formation of two collinear ($s_1\sigma$) bonds directed towards the two outer atoms, while the other two are $2p\pi$ electrons with their axes *aa, a'a'* fixed at right angles to one another and to the ($6_1\sigma$) bonds. Resonance between these and the respective $2p\pi$ electrons of the outer carbon atoms brings about the configuration foreseen by van 't Hoff.

FIG. 2a.

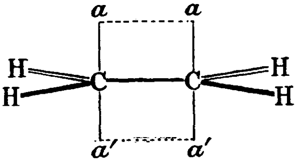
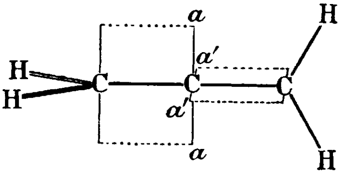


FIG. 2b.



Since our first publication of the preparation of optically active forms of diphenyldinaphthylallene (*Nature*, 1935, **135**, 994) the resolution of another unsymmetrically substituted allene—a glycollic acid derivative of the formula $C_{10}H_7\cdot CPh\!:\!C\!:\!CPh\cdot CO\cdot O\cdot CH_2\cdot CO_2H$—has been described by Kohler, Walker, and Tishler (*J. Amer. Chem. Soc.*, 1935, **57**, 1743). The resolution was effected by means of brucine. The enantiomorphism of the substituted allene type is therefore now well established.

EXPERIMENTAL.

β-*Hydroxy*-β-*phenyl*-β-1-*naphthylpropiophenone* (V).—This compound could not be obtained in the manner described by Vorländer, Osterburg, and Meye (*Ber.*, 1923, **56**, 1136) for the production of the corresponding diphenyl compound (hydroxydiphenypropiophenone). It is conveniently prepared by the following modification of their method, consisting in the use of a considerable excess of the Grignard reagent and the addition of sufficient benzene to prevent the formation of a precipitate during the reaction. To a solution of α-naphthylmagnesium bromide, prepared from magnesium (19·2 g.), α-bromonaphthalene (110·4 c.c.), and ether (480 c.c.), benzene (480 c.c.) was added and then dibenzoylmethane (40 g.), dissolved in benzene (200 c.c.), was dropped in with mechanical stirring during ½ hour, the temperature being kept at 5—10°. (In this, as in the other applications of Grignard reagents in this investigation, the solution of the reagent was poured off from undissolved magnesium before use.) After standing over-night at the ordinary temperature, the solution was poured on ice and dilute sulphuric acid, and the benzene–ether layer was separated, washed quickly with water (before crystallisation started), and steam-distilled. After removal of the solvents and naphthalene the water was poured away and the gummy product was dissolved in the minimum quantity of hot ethyl acetate (550—700 c.c.) and allowed to crystallise. Yield, 30·5—35·7 g., m. p. 166—167°. After recrystallisation from ethyl acetate the *compound* was obtained pure, m. p. 167—169° (Found: C, 85·0; H, 5·9. $C_{25}H_{20}O_2$ requires C, 85·2; H, 5·7%).* In one experiment, in which dibenzoylmethane was added to the boiling solution of the Grignard reagent, instead of the hydroxy-compound, a 20% yield of the unsaturated yellow ketone (VI) was obtained.

Phenyl β-*Phenyl*-β-1-*naphthylvinyl Ketone* (VI).—The crude hydroxy-compound (V), m. p. 166—167° (60 g.), was wetted by shaking with water (300 c.c.); concentrated hydrochloric acid (300 c.c.) was then added and the mixture was boiled for 3½ hours on a sand-bath with occasional shaking. After cooling to 50° the hydrochloric acid was poured off, and the light brown gum

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* This, like the other analyses recorded in this paper, was a micro-analysis, carried out in this laboratory by Mr. G. Purdie.

washed with water. The gum hardened quickly in ice and the water was then poured off as completely as possible. The moist gum was dissolved in acetic anhydride (60 c.c.), and the solution carefully warmed to decompose the residual water. On standing over-night, the *ketone* was deposited in bright yellow clusters (38—44 g.), m. p. 106—108°. Recrystallisation from alcohol gave the pure compound, m. p. 107—108° (Found: C, 89·6; H, 5·4. $C_{25}H_{18}O$ requires C, 89·8; H, 5·4%).

*αγ-Diphenyl-αγ-di-*1-*naphthylallyl Alcohol* (II).—To a solution of α-naphthylmagnesium bromide, prepared from magnesium (7·2 g.), α-bromonaphthalene (41·4 c.c.), and ether (180 c.c.), benzene (180 c.c.) was added and then, the temperature being kept below 0°, a solution of the ketone (VI, 25 g.) in benzene (180 c.c.) was run in gradually during 1 hour. After remaining over-night at the ordinary temperature, the solution was decomposed by pouring on ice and ammonium chloride. The benzene–ether layer was washed with water, dried with sodium sulphate, and concentrated to about 100 c.c. Ether (200 c.c.) was added and the solution was left for 2 days to crystallise. The solid deposited (24·7 g.) had m. p. 185—187° (softening at 180°). Recrystallised from benzene (100 c.c.), this gave the pure *compound* (16·3 g.) as a colourless microcrystalline powder, m. p. 187—189°. A second crop recrystallised gave a further 4 g. of pure product (Found: C, 90·7; H, 5·7. $C_{35}H_{26}O$ requires C, 90·9; H, 5·6%).

*αγ-Diphenyl-αγ-di-*1-*naphthylallene* (I).

1. *Racemic Form.*—(a) *With acetic anhydride.* Diphenyldinaphthylallyl alcohol (II) (0·5 g.) was boiled for 3 hours in acetic anhydride (3 c.c.). After 1½ hours the allene began to crystallise; m. p. 242—244° (softening at 240°). Yield, 0·35 g.

(b) *With* p-*toluenesulphonic acid.* To the alcohol (0·5 g.) in boiling ethyl acetate (12·5 c.c.) a trace of *p*-toluenesulphonic acid was added and the mixture was heated on the water-bath. A purple colour developed immediately, disappeared on shaking, and reappeared occasionally at the edge of the boiling solution. After 15 minutes a nucleus of the allene appeared and continued to increase as the heating proceeded. After ¾ hour the purple colour at the edge of the solution was replaced by brown. The heating was then stopped, and the *allene* (0·4 g.) collected after standing over-night. It was already pure; colourless tufts of feathery crystals, m. p. 242—244° (Found: C, 94·5; H, 5·3; *M*, 445. $C_{35}H_{24}$ requires C, 94·6; H, 5·4%; *M*, 444).

Crystallographic characters of the racemic form of dl-*diphenyldinaphthylallene.* We are indebted to Mr. J. D. Bernal and Miss F. O. Bell for the following report. This modification grows in short monoclinic prisms, with much tendency to parallel growths. The forms developed are (001), (101), (10$\bar{1}$), and (210). The approximate axial lengths are $a = 29{\cdot}4$, $b = 7{\cdot}7$, $c = 20{\cdot}6$ A., $\beta = 96°$. The space group is $C_{2h}^{6} - C2/c$ with eight asymmetric molecules in the cell. The birefringence is strong. No optic axial figure can be seen, but the *b* plane is the optical axial plane and γ lies ~ 10° from *c* in the obtuse angle. The sign is probably negative. Owing to the large number of molecules per cell and the absence of any point symmetry it is difficult to form any definite conclusion as to the arrangement of the molecules.

2. *The* d-*Form.*—A solution of diphenyldinaphthylallyl alcohol (32 g.) in hot anhydrous benzene (400 c.c.) was added quickly to a hot solution of *d*-camphor-β-sulphonic acid (0·32 g.) in the same solvent (400 c.c.) and the mixture was kept at the boiling point for ½ hour. A yellow colour appeared in the body of the solution and was sometimes preceded by a violet colour, but the edge of the solution always showed a violet colour until the reaction was complete. After cooling to about 40°, the benzene solution was poured off from the separated water (which contained most of the camphorsulphonic acid) and was left over-night to allow the racemic form of the allene to crystallise. The weight of this first crop of allene was 22·4 g. It was feebly dextrorotatory, but had m. p. 242—244° and was thus nearly pure racemate.

At the end of the heating a small portion of the solution (12·5 c.c.) was diluted to 25 c.c. and examined as quickly as possible in a 4 dcm. tube. In different experiments the observed rotations, α_{5461}, ranged from + 1·25° to + 1·75°, but in one the reading was as high as + 2·5°. In another experiment readings were taken at intervals during 1 hour. These showed that the dehydration proceeded rapidly. The activity reached a maximum in 15 minutes and then remained constant. By the end of the first 5 minutes two-thirds of the maximum activity had already been attained.

After removal of the first crop of racemic allene the benzene mother-liquor and the flask containing the separated water were washed with two portions (60 c.c.) of saturated sodium carbonate solution, each of which was then examined polarimetrically in a 4 dcm. tube. The readings, α_{5461}, were + 0·47° and + 0·05°. Since the quantity of camphorsulphonic acid employed as catalyst (0·32 g.) gave under the same conditions a reading α_{5461} of 0·51°, these observations show that the whole of the camphorsulphonic acid had been recovered; yet the benzene mother-liquor remained strongly dextrorotatory.

This mother-liquor was dried with potassium carbonate and evaporated to dryness, the residue was triturated with cold benzene, and the undissolved solid was collected and washed with more benzene (total 100 c.c.). The material so obtained (crop II, 5·8 g.) melted and behaved like the first crop and was thus again nearly pure racemic allene.

The benzene filtrate was evaporated, the residue, which solidified when scratched, was triturated with cold light petroleum (b. p. 60—80°) (60 c.c.), and the undissolved solid collected.* This solid (crop III) was a mixture of racemic and *d*-allene. It weighed 1·4 g. and melted at 157° (with slight softening at 110°) to a cloudy liquid clearing at 220°. It was heated with light petroleum (b. p. 100—120°) (60 c.c.), which left some racemate (m. p. 235—242°) and on standing over-night deposited more racemate (0·4 g.). The filtrate, concentrated to half its volume, deposited a slightly coloured solid, m. p. 158—159°, and this, recrystallised from light petroleum (b. p. 100—120°) (3 c.c.), yielded the pure d-*allene* (0·42 g.) in colourless aggregates of beautiful prisms, m. p. 158—159°. Further recrystallisation from light petroleum produced no change in the melting point or the specific rotation (Found : C, 94·6; H, 5·3. $C_{35}H_{24}$ requires C, 94·6; H, 5·4%). 0·04415 G. in 30 c.c. of benzene solution showed $\alpha^{17°}_{5461}$ $+$ 2·57° ($l = 4$); whence $[\alpha]^{17°}_{5461} = +\ 437°$; $[M]^{17°}_{5461} = +\ 1940°$.

Rotatory dispersion. The exceptionally high value of the molecular rotation of the allene suggested that the absorption band with which the circular double refraction was associated was not very far removed from the visible region of the spectrum. Dr. C. B. Allsopp kindly measured the rotatory dispersion of the *d*-allene in *cyclo*hexane at 20° over the range λ6708 to λ3400.

Preliminary readings gave the following results :

100 C.c. of solution contain 0·0356 g.; length of column = 6 dm.

	Visual readings.			Photographic readings.		
	λ.	$\alpha_{obs.}$.	$[\alpha]^{20°}$.	λ.	$\alpha_{obs.}$.	$[\alpha]^{20°}$.
Li	6708	0·47°	220°	4310	2·00°	936°
Cd	6438	0·52	243	4190	2·20	1030
Li	6104	0·66	309	4070	2·40	1120
Na	5893	0·75	351	4020	2·50	1170
Hg	5780	0·81	379	3940	2·70	1260
Hg	5461	0·94	440	3880	3·00	1410
Cu	5219	1·07	501	3840	3·30	1550
Cd	5086	1·16	543	3800	3·60	1690
Cd	4800	1·30	609	3730	4·00	1870
Cd	4678	1·44	674	3640	4·50	2110
Li	4603	1·64	768	3590	5·00	2340
Hg	4358	2·01	941	3400	6·00	2810

On account of the low solubility of the material in *cyclo*hexane solution the observed rotations are very small, even with a 6 dm. column, and the experimental error is therefore proportionately large.

The high value 2·14 for the ratio $\alpha_{4358}/\alpha_{5461}$ indicates the marked influence of an absorption band. The specific rotations in the visible region can nevertheless be represented with fair accuracy by the simple equation

$$[\alpha]^{20°} = 83/[\lambda - (0{\cdot}316)^2]$$

and this points to the presence of a band concerned with the origin of the activity in the neighbourhood of λ3160.

Dr. Allsopp then examined the absorption spectrum of the hydrocarbon. This examination presented experimental difficulties, since the substance was extraordinarily rapidly decomposed by ultra-violet light. The active radiations were, however, of shorter wave-length than λ = 2300 and the extinction coefficient of the allene could be measured up to this limit in *cyclo*-

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* The filtrate from crop III was evaporated and the residue was crystallised from ethyl acetate. A substance was thus isolated which crystallised in bright yellow, lustrous platelets, m. p. 242—244°, mixed m. p. with the racemic allene *ca.* 225°, and gave a violet solution in concentrated sulphuric acid (the allene gives a red solution). This is evidently the substance which gives rise to the yellow colour that always appears when the alcohol (II) is dehydrated. The quantity obtained was not sufficient for further investigation.

hexane when 0·1—0·2% of carbon disulphide was added to absorb the light of shorter wavelength. The absorption spectrum showed an extraordinarily intense band beginning about λ3500 and rising to a maximum ($\varepsilon = 320{,}000$) at $\lambda = 2600$. There is a shallow minimum at $\lambda = 2550$, followed by a rise in the extinction coefficient to nearly complete opacity.

We are indebted to Mr. Bernal and Miss Bell for the following account of the crystallographic characters of *d*-diphenyldinaphthylallene. This compound grows in well-developed brilliant crystals. The habit is that of a short prism terminated by dome faces, the forms being (110), (100), and (101). The axial lengths are approximately $a = 25{\cdot}6$, $b = 11{\cdot}3$, $c = 8{\cdot}46$ A. The probable space group is $D^4 - P2_1\,2_1\,2_1$ with four asymmetric molecules in the cell. The birefringence is strong. α, β, γ lie along *c*, *a*, and *b* respectively. The optic axial angle is large and the sign probably positive. It is difficult to deduce the molecular positions. The molecules may be bent towards a plane and piled in two layers in the *ab* planes.

3. *The* l-*Form.*—Diphenyldinaphthylallyl alcohol (8 g.) in benzene (100 c.c.) was added to a solution of *l*-camphorsulphonic acid (0·08 g.) in benzene (100 c.c.), and the mixture kept at the boiling point for ½ hour. The l-*allene* (0·08 g.), m. p. 158—159°, was isolated from the product in the same way as had been used for the *d*-allene (Found : C, 94·5; H, 5·4%). 0·01182 G. in 30 c.c. of benzene solution showed $\alpha_{5461}^{17^\circ} - 0{\cdot}69^\circ$ ($l = 4$), whence $[\alpha]_{5461}^{17^\circ} = -438^\circ$; $[M]_{5461}^{17^\circ} = -1944^\circ$.

Production of l-*allene with* d-*bromocamphorsulphonic acid.* A solution of diphenyldinaphthylallyl alcohol (0·5 g.) and *d*-bromocamphorsulphonic acid (0·005 g.) in benzene (12·5 c.c.) was kept at its boiling point for 1 hour. The intense violet coloration which was immediately produced disappeared when the reaction was complete, leaving a yellow solution. This was washed with aqueous sodium carbonate, dried with potassium carbonate, made up to 25 c.c. with benzene, and examined in a 4 dcm. tube. A rotation $\alpha_{5461} - 0{\cdot}58^\circ$ was observed. Assuming that the *l*-allene was the only optically active substance in the solution, this indicates the presence of 0·0083 g. of the lævo-form, implying the production of an excess of 1·74% of this modification.

Combination of the d- *and the* l-*Modification to form the Racemate.*—The *d*-allene (0·01040 g.), m. p. 158—159°, dissolved in cold absolute ether (3 c.c.), was added to *l*-allene (0·01041 g.), m. p. 158—159°, also in ether (3 c.c.), and the mixture was left at room temperature. Crystallisation began in 2 minutes and was soon complete. The ether was gently removed by heating. The product was the pure racemic allene. It melted at 242—244° alone or admixed with authentic racemate. Mixed with the indene of m. p. 233—234°, it melted at 212—222°. Comparison by Mr. Bernal and Miss Bell of the crystallographic measurements made on the racemate prepared directly and that produced by combination of the *d* and the *l*-modification showed the identity of the two products. The *X*-ray diffraction diagrams of the two products were also identical.

Racemisation of the d-*Allene by Heating.*—The *d*-allene (0·025 g.) in decalin (0·5 c.c.) was heated to 190° in a small sealed tube from which the air had been displaced by carbon dioxide. After 9 hours' heating, the optically active compound was recovered almost unchanged.

The experiment was repeated, but the heating was extended to 48 hours. On cooling, crude racemic allene (0·01 g.), m. p. 242° with preliminary softening at 210°, crystallised. Recrystallised from ethyl acetate, it gave pure racemic allene, m. p. 242—244° alone or admixed with authentic racemate.

Heated in boiling decalin solution without exclusion of air, the *d*-allene retained its optical activity unchanged for 1½ hours, but the activity then began to diminish and had practically disappeared after 9½ hours. However, only a minute amount of crude racemate could be obtained from the solution.

1 : 3-*Diphenyl*-1-α-*naphthyl*-4 : 5-*benzindene* (X).—The indene transformation of diphenyldinaphthylallene is less readily effected than that of tetraphenylallene (cf. Vorländer and Siebert, *loc. cit.*). It is not brought about by boiling with concentrated hydrochloric acid and takes place exceedingly slowly in boiling glacial acetic acid. It is, however, easily carried out by the two following methods.

(a) *With acetic acid and hydrogen chloride.* Dry hydrogen chloride was led into a boiling solution of the racemic allene (0·2 g.) in the minimum quantity of boiling acetic acid (200 c.c.). A pale purple colour appeared immediately, deepened, and then disappeared after 4 minutes (cf. Kohler, *loc. cit.*). The solution was heated 1 minute longer and poured into excess of sodium carbonate solution, and the product extracted with ether. The crude substance obtained on evaporation of the ether had m. p. 232—233° and gave the pure indene derivative, m. p. 233—234°, on recrystallisation from ethyl acetate (mixed m. p. with the racemic allene 212—222°)

(Found : C, 94·8; H, 5·4. $C_{35}H_{24}$ requires C, 94·6; H, 5·4%). The *compound* is phototropic, becoming yellow on exposure to light and colourless again when kept in the dark.

(b) *With iodine.* The racemic allene (0·5 g.), iodine (0·05 g.), and benzene (7·5 c.c.) were heated for 1 hour on the water-bath (cf. Vorländer and Siebert, *loc. cit.*, p. 1030). The product obtained, after removal of the iodine with sodium thiosulphate solution and evaporation of the benzene, gave on crystallisation from ethyl acetate the pure indene derivative, m. p. 233—234° alone or mixed with the product obtained by the foregoing method.

Experiments (a) and (b) repeated with the *d*-allene in place of the racemic modification gave an optically inactive product.

Oxidation of Diphenyldinaphthylallene.—To a hot solution of the racemic allene (1·0 g.) in pyridine (120 c.c.) and water (20 c.c.), finely powdered potassium permanganate (5 g.) was added. The permanganate colour disappeared after 20—30 minutes' boiling. Sulphurous acid was then added to dissolve the precipitated manganese dioxide, the solution was poured into excess of dilute sulphuric acid, and the mixture exhaustively extracted with ether in a continuous extraction apparatus. After being washed with sodium carbonate solution and then with sodium hydroxide solution, the ether was dried (potassium carbonate) and evaporated. The residue (0·42 g.) rapidly crystallised and was nearly pure phenyl α-naphthyl ketone (m. p. 72—74°, softening at 70°). Recrystallised from methyl alcohol, it gave the pure ketone, m. p. 73—75° alone or mixed with a specimen prepared by the method of Acree (*Ber.*, 1904, **37**, 628) (Found : C, 87·9; H, 5·3. Calc. for $C_{17}H_{12}O$: C, 87·9; H, 5·2%).

The sodium carbonate extract yielded on acidification and ether-extraction a mixture of acids (0·50 g.), from which light petroleum (b. p. 60—80°) extracted crude benzoic acid (0·19 g.), leaving a residue of crude phthalic acid. Both fractions sublimed completely except for slight gummy residues when heated gradually at 0·1 mm. The benzoic acid was identified by m. p. and mixed m. p. (120°), and the phthalic acid by m. p. and mixed m. p. of the anhydride (128—131°) as well as by the fluorescein reaction.

When phenyl α-naphthyl ketone (0·5 g.) was treated with potassium permanganate (5 g.) under conditions similar to those employed for oxidation of the allene, only 0·25 g. of the ketone could be recovered unchanged and 0·20 g. of an acidic product was obtained consisting mainly of a mixture of benzoic and phthalic acids.

*Reduction of Diphenyldinaphthylallene. αγ-Diphenyl-αγ-di-*1*-naphthyl-*Δ^{α}*-propylene* (XII).—The allene (racemic form, 12 g.), acetic acid (240 c.c.), hydriodic acid (*d* 1·7, 18 c.c.), and red phosphorus (6 g.) were boiled together for 6 hours, and the filtered solution was poured into excess of sodium carbonate solution and extracted with chloroform. After drying over potassium carbonate, the chloroform was evaporated, and the residue dissolved in ether; the solution, allowed to evaporate slowly in air for several days, deposited 8 g. of colourless prisms, m. p. 165—167°, which after recrystallisation from ethyl acetate melted at 167—169° (Found : C, 93·8; H, 6·1. $C_{35}H_{26}$ requires C, 94·2; H, 5·8%). The analytical data do not distinguish between the formula $C_{35}H_{26}$ and that of diphenyldinaphthylpropane, $C_{35}H_{28}$, but the identity of the hydrocarbon with the product of dehydration of diphenyldinaphthylpropyl alcohol (XIV) shows that it must be the *propylene* derivative (XII).

*Synthesis of αγ-Diphenyl-αγ-di-*1*-naphthyl-*Δ^{α}*-propylene.*—β-Phenyl-β-1-naphthylpropiophenone (XIII) was prepared by the following modification of the method described by Kohler and Johnstin (*Amer. Chem. J.*, 1905, **33**, 44). Into the boiling Grignard solution prepared from magnesium (4·8 g.), α-bromonaphthalene (27·6 c.c.), ether (120 c.c.), and benzene (120 c.c., added when the magnesium had ceased reacting) was dropped during ½ hour a solution of benzylideneacetophenone (18 g.) in ether (100 c.c.) and benzene (50 c.c.). After pouring into ice and dilute sulphuric acid, the benzene–ether layer was separated, washed with water, dried over potassium carbonate, and concentrated to very small bulk. Hot alcohol (500 c.c.) was added, and, when cold, acetone (100 c.c.) to prevent the precipitation of an oil. After 4 hours the solid (14·7 g., m. p. 118—120°) was collected. Recrystallised from ethyl acetate (50 c.c.; charcoal), it gave 9·1 g., m. p. 120—121° (Found : C, 88·7; H, 6·0. Calc. for $C_{25}H_{20}O$: C, 89·3; H, 6·0%).

To the above ketone (16·8 g.), suspended in ether (100 c.c.), was added the Grignard solution prepared from magnesium (4·8 g.), α-bromonaphthalene (27·6 c.c.), and ether (200 c.c.). The ketone dissolved quickly and the whole was boiled for 4 hours and poured into ice and dilute sulphuric acid; the ether layer was separated, washed with water, and steam-distilled to remove naphthalene. The residue was redissolved in ether and dried over calcium chloride, and the ether removed. The gum, which was probably the alcohol (XIV), could not be obtained crystalline. It was therefore heated with acetic anhydride (200 c.c.) for 8 hours. To the cooled solution, water (40 c.c.) was added and the mixture was carefully warmed to convert the acetic anhydride into acetic acid. More acetic acid (100 c.c.) was then added and the solution was scratched and left for several days. A solid (5·2 g.), m. p. 130—160°, was deposited which, recrystallised thrice from ethyl acetate, gave beautiful colourless prisms (1·2 g.), m. p. 167—169° (Found : C, 93·9; H, 5·8. Calc. for $C_{35}H_{26}$: C, 94·2; H, 5·8%). This hydrocarbon appeared to be identical with that obtained by reduction of the allene, the mixed m. p. (167—169°) showing no depression.

Since we felt that the method of mixed melting points might not distinguish with certainty between two compounds so closely related as diphenyldinaphthylpropylene and the corresponding propane, we asked Mr. Bernal and Miss Bell to make a crystallographic comparison of the synthetical propylene (*A*) with the hydrocarbon (*B*) obtained by reduction of the allene. They reported : The optics and facial angles were the same in crystals of *A* and *B*. The *X*-ray oscillation photographs were identical; they showed the same layer line spacing and the same spots appeared with the same relative intensities on both photographs. The crystals of *A* and *B* are therefore identical, or at any rate, more alike than those of any known compounds of different chemical constitution.

The same hydrocarbon was obtained when the gummy alcohol was boiled with hydriodic acid, acetic acid, and red phosphorus under the conditions employed for the reduction of the allene.

Alternative Method of Preparation of Phenyl β-*Phenyl*-β-1-*naphthylvinyl Ketone* (VI).—α-*Bromo*-β-*phenyl*-β-1-*naphthylpropiophenone* (cf. Kohler, *Amer. Chem. J.*, 1904, **31**, 652). Into the boiling Grignard solution prepared from magnesium (4·8 g.), α-bromonaphthalene (27·6 c.c.), and ether (200 c.c. + 500 c.c. added after 1 hour), a solution of benzylideneacetophenone (18 g.) in ether (480 c.c.) was dropped during 1 hour. To the hot solution bromine (11 c.c.) was then added in 2 minutes with vigorous stirring. After 15 minutes the bluish solution was added to ice and dilute sulphuric acid. Crystallisation in the ethereal layer commenced and the whole was left for 2 days for the ether to evaporate. The sticky mass was triturated with ether (100 c.c.), and the purple solid filtered off (11 g., m. p. 190—195°). It was recrystallised from acetic acid (250 c.c.; charcoal); or dissolved in chloroform (200 c.c.), boiled gently until the violet coloration disappeared, and then alcohol (200 c.c.) added. Colourless stout needles (8·8 g.), m. p. 196—198° (darkening) were obtained (Found : C, 72·2; H, 4·5. $C_{25}H_{19}OBr$ requires C, 72·3; H, 4·6%). When the *bromo*-derivative (1 g.) was reduced with a mixture of acetic acid (10 c.c.), hydriodic acid (*d* 1·7; 2 c.c.), and red phosphorus (0·5 g.), it gave β-phenyl-β-1-naphthylpropiophenone.

Phenyl β-*phenyl*-β-1-*naphthylvinyl ketone* (VI). The above bromo-ketone (15 g.) was heated in pyridine (150 c.c.) for 48 hours. The mixture was then poured into excess of dilute hydrochloric acid and extracted with ether. The yellow ethereal solution, filtered from much colourless undissolved material, dried over potassium carbonate, and evaporated, left a yellow oil (7 g.), which was dissolved in acetic acid (60 c.c.). Over-night 2·3 g. of crystals, m. p. 106—108°, were deposited, and after concentration of the filtrate a further 1·3 g., m. p. 105—108°. Recrystallisation from acetic acid or alcohol gave the pure compound, m. p. 107—108° alone or mixed with a sample prepared by the method described on p. 993, which is much the better way of obtaining this compound.

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