ISOMERIZATION OF UNSATURATED HYDROCARBONS[1]

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Of all the isomerizations of hydrocarbons, only those of unsaturated ones allow a clear formulation, and even here there exist certain reactions, occurring under rather abnormal conditions of pressure and temperature, which are far from being describable by the usual valency scheme, e.g., the conversion of butene into isobutene (3, 52, 80). This article deals exclusively with the isomerization reactions of unsaturated hydrocarbons, which may be divided into two groups: (I) isomerization of open-chain hydrocarbons into other open-chain hydrocarbons; (II) isomerization of open-chain hydrocarbons into cyclic hydrocarbons. The reversal of the latter process is rare,—a case in point is the thermal conversion of cyclopropane into propene (6, 68),—and the reactions that we shall discuss under this heading cannot be reversed at all.

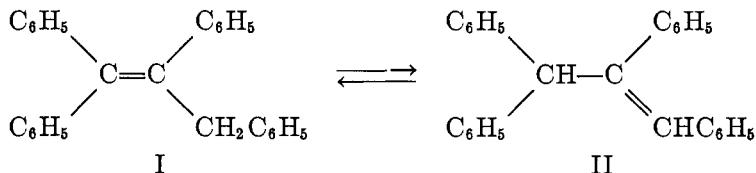## I. ISOMERIZATION OF OPEN-CHAIN HYDROCARBONS INTO OTHER OPEN-CHAIN HYDROCARBONS

Among these reactions, which proceed through the migration of a hydrogen atom in a triad system (C=C—C), the direction of the isomerization is generally determined by the tendency to form a conjugated system. Thus, the alkaline conversion of allylbenzene into propenylbenzene (5) and similar reactions (60a) are obviously provoked by the stability of the phenyl–double bond system in the end product:

| Allylbenzene | Propenylbenzene |
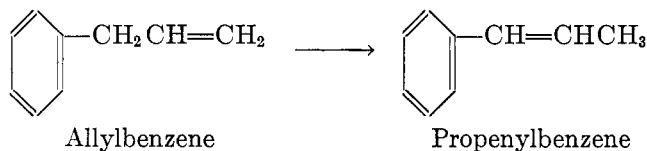
A similar case is the isomerization of 1,4-pentadiene into 1,3-pentadiene (57, 87). In view of the olefinic character of the 9,10-double bond in phenanthrene, the isomerization of 9-allylphenanthrene into 9-propenylphenanthrene (11) may also be quoted here. While in these cases the
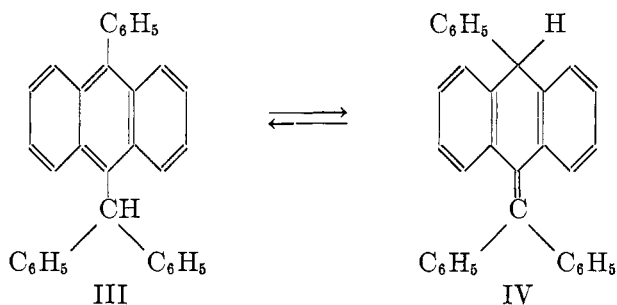
reaction is practically non-reversible, all those systems in which both compounds contain conjugated systems are reversible (mobile in both reactions), as in the cases of indene and of 1,3-diphenylpropene, both of which have been studied extensively by Ingold and coworkers (2). Other examples studied are the following: (a) the pair 1,1,2-triphenyl-2-benzylethylene (I) and 1,2-diphenyl-1-benzhydrylethylene (II) (20);

$$
\begin{array}{ccc}
\underset{C_6H_5}{\overset{C_6H_5}{\diagdown}}C=C\underset{CH_2C_6H_5}{\overset{C_6H_5}{\diagup}} & \rightleftarrows & \underset{C_6H_5}{\overset{C_6H_5}{\diagdown}}CH-C\underset{CHC_6H_5}{\overset{C_6H_5}{\diagup}}
\end{array}
$$

I   II

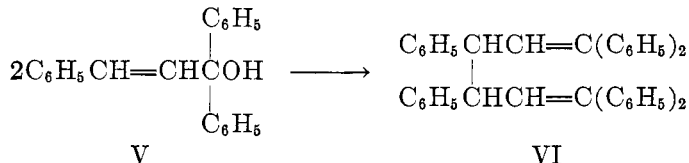1,1,2-Triphenyl-2-benzylethylene   1,2-Diphenyl-1-benzhydrylethylene

(b) the pair 9-benzhydryl-10-phenylanthracene (III) and 9-benzhydrylidene-10-phenyl-9,10-dihydroanthracene (IV) (7);

III   IV
9-Benzhydryl-10-phenyl-   9-Benzhydrylidene-10-phenyl-
anthracene   9,10-dihydroanthracene

(c) the spontaneous formation of 1,1,3,4,6,6-hexaphenyl-1,5-hexadiene (VI) on the reduction of diphenylstyrylcarbinol (V) (61):

$$
2C_6H_5CH=CH\underset{\overset{|}{C_6H_5}}{\overset{\overset{|}{C_6H_5}}{C}}OH \longrightarrow \begin{array}{l} C_6H_5CHCH=C(C_6H_5)_2 \\ \;\;\;\;| \\ C_6H_5CHCH=C(C_6H_5)_2 \end{array}
$$

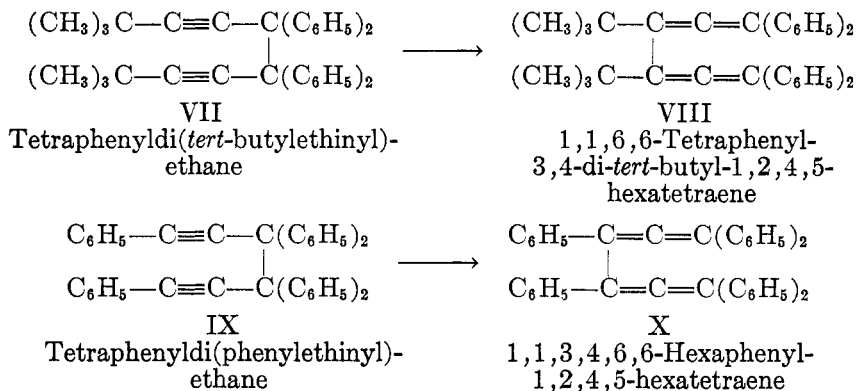V   VI
Diphenylstyrylcarbinol   1,1,3,4,6,6-Hexaphenyl-1,5-
        hexadiene

The genetic relationship between methylacetylene and allene (4), which also appears in their substitution products (53), should be mentioned here:

$$
CH_3C{\equiv}CH \qquad \rightleftarrows \qquad CH_2=C=CH_2
$$

Methylacetylene   Allene
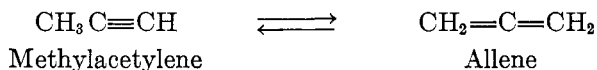
In recent years an analogous transformation has been observed by Marvel and coworkers (47, 48, 62, 66, 82, 83, 88) in a series of highly substituted

acetylenic hydrocarbons which rearrange irreversibly into the isomeric allenes: tetraphenyldi(*tert*-butylethinyl)ethane (VII) gives 1,1,6,6-tetraphenyl-3,4-di-*tert*-butyl-1,2,4,5-hexatetraene (VIII) (47); tetraphenyldi-(phenylethinyl)ethane (IX) gives 1,1,3,4,6,6-hexaphenyl-1,2,4,5-hexatetraene (X) (66), which had been obtained previously by Moureu, Dufraisse, and Houghton (65):

$$(CH_3)_3 C—C≡C—C(C_6H_5)_2$$
$$(CH_3)_3 C—C≡C—C(C_6H_5)_2$$

$$\longrightarrow$$

$$(CH_3)_3 C—C=C=C(C_6H_5)_2$$
$$(CH_3)_3 C—C=C=C(C_6H_5)_2$$

VII
Tetraphenyldi(*tert*-butylethinyl)-
ethane

VIII
1,1,6,6-Tetraphenyl-
3,4-di-*tert*-butyl-1,2,4,5-
hexatetraene

$$C_6H_5—C≡C—C(C_6H_5)_2$$
$$C_6H_5—C≡C—C(C_6H_5)_2$$

$$\longrightarrow$$

$$C_6H_5—C=C=C(C_6H_5)_2$$
$$C_6H_5—C=C=C(C_6H_5)_2$$

IX
Tetraphenyldi(phenylethinyl)-
ethane

X
1,1,3,4,6,6-Hexaphenyl-
1,2,4,5-hexatetraene

## II. ISOMERIZATION OF OPEN-CHAIN HYDROCARBONS INTO CYCLIC HYDRO-CARBONS

The cases in which the rearrangement of an open-chain hydrocarbon consists in a "cycloisomerization" are much more frequent, various types of reaction being known.

A. *Cycloisomerization of a vinylbenzene system*

The only two cases of the cycloisomerization of a vinylbenzene system known at present are (*a*) the isomerization of *as*-phenyl-*o*-biphenylethylene (XI) into 9-phenyl-9,10-dihydrophenanthrene (XII), observed under the influence of phosphorus pentachloride (11, 14),


XI
as-Phenyl-*o*-
biphenylethylene

XII
9-Phenyl-9,10-dihydro-
phenanthrene
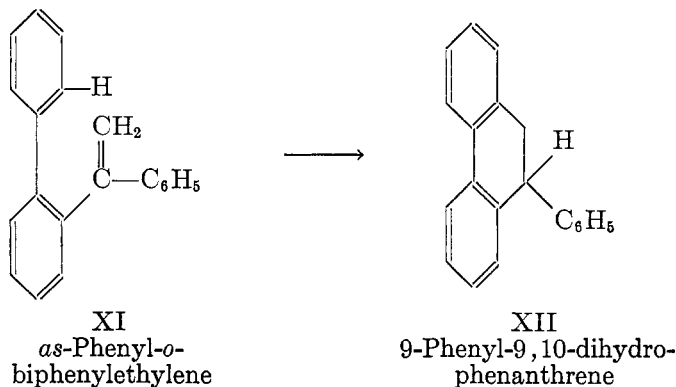
and (b) the isomerization of 1-methyl-2-α-naphthyl-1-cyclohexene (XIII), which, by cyclization and subsequent dehydrogenation, gives fluoranthene (XIV) (41):

XIII
1-Methyl-2-α-naphthyl-1-
cyclohexene

XIV
Fluoranthene
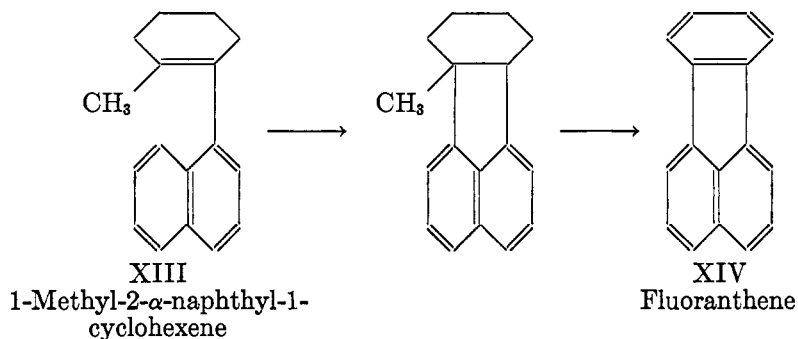
### B. *Cycloisomerization of an allylbenzene system*

The first cases of this type studied were (a) the conversion, by means of concentrated sulfuric acid, of 1,1-diphenyl-2-benzylethylene (XV) into 1,3-diphenylhydrindene (XVI) (77), a change which obviously involves two isomerization reactions,—namely, the migration of hydrogen in the open chain and subsequent cycloisomerization,—

XV
1,1-Diphenyl-2-
benzylethylene

XVI
1,3-Diphenyl-
hydrindene
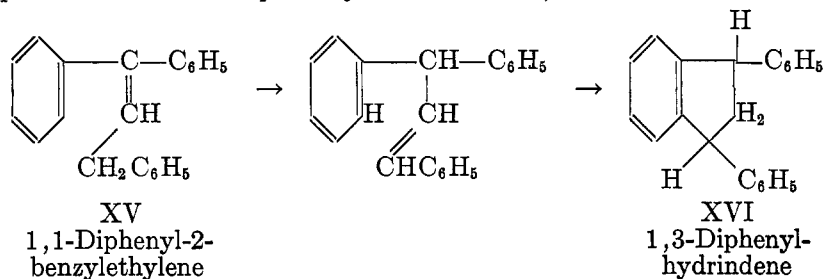
and (b) the isomerization of the unsaturated isomer of *as*-diphenyl-ethylene (1,1,3,3-tetraphenyl-1-butene) (XVII) into the saturated isomer, 1,1,3-triphenyl-3-methylhydrindene (XVIII) (18):

XVII
1,1,3,3-Tetraphenyl-
1-butene

XVIII
1,1,3-Triphenyl-3-
methylhydrindene
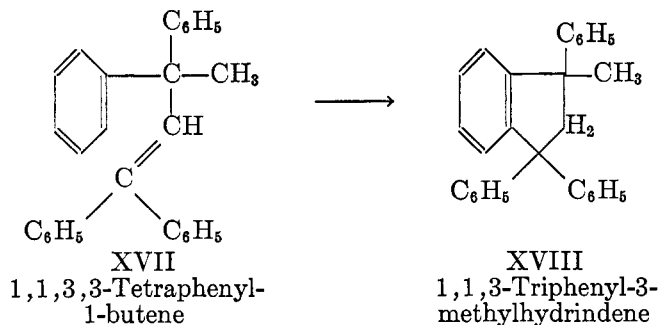
Other cases are the isomerization of the unsaturated dimer of anethole into 6-methoxy-1-(p-methoxyphenyl)-2-methyl-3-ethylhydrindene (2a), the cycloisomerization of α-benzylstilbene (19), the cycloisomerization of 2,2-diphenyl-4-methyl-3-pentene (17), and the cycloisomerization of 9-allylphenanthrene (XIX), which is transformed into 9,10-cyclopentenophenanthrene (XX) (12a):

XIX
9-Allylphenanthrene

XX
9,10-Cyclopentenophenanthrene
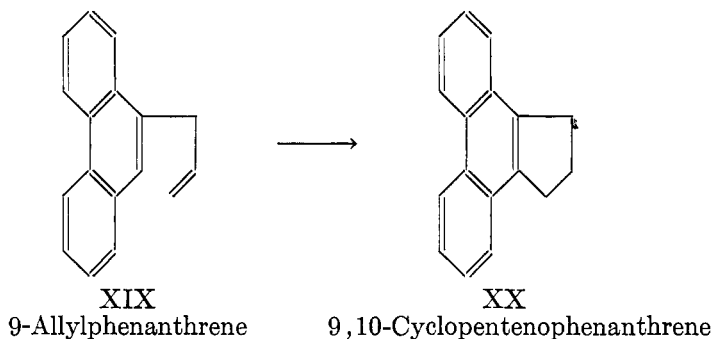
It has been further discovered (24) that a whole group of compounds, the alkylhydrobenzoins, are converted into indene hydrocarbons by dehydrating agents according to a similar scheme. An example is the conversion of methylhydrobenzoin (XXI) into 2-phenylindene (XXII).

XXI
Methylhydrobenzoin

XXII
2-Phenylindene
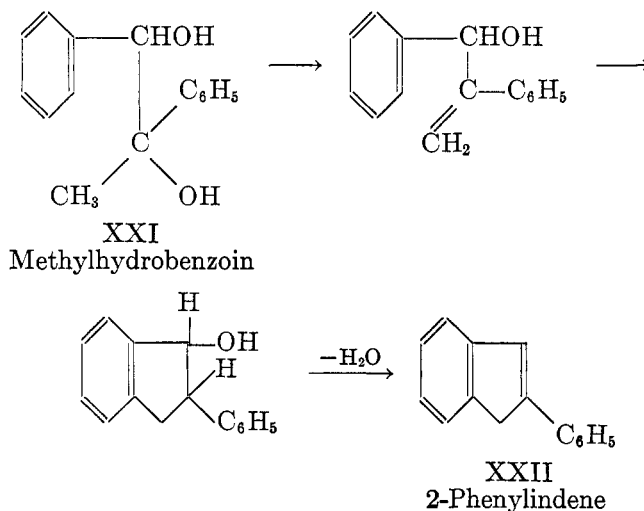
This isomerization has subsequently found much use in the synthesis of compounds related to sterols (33, 37, 38; 27, 28a; 59; 12, 13, 51, 78),—the sterol molecule contains a hydrindene system,—but could not be

extended by Cook and coworkers (1, 35, 37, 40) to include the building up of fluorene derivatives, e.g.,
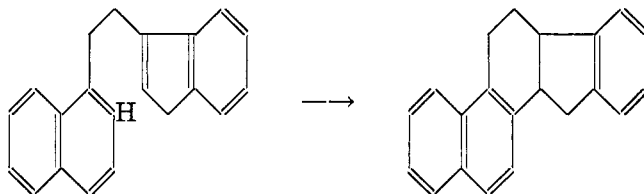
in general.   In the case of benzylcyclohexene, Cook and Hewett (39) have shown that no fluorene derivative is obtained, but, rather unexpectedly, a substance of the following structure:
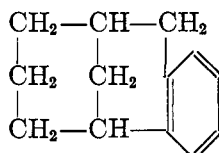
A curious isomerization which converts the red rubrene (9,10,11,12-tetraphenylnaphthacene, XXIII) into the colorless so-called pseudoru-brene[2] (XXIV) (45, 46, 64) may well be explained by a similar cycloiso-merization.


XXIII
Rubrene

XXIV
Pseudorubrene
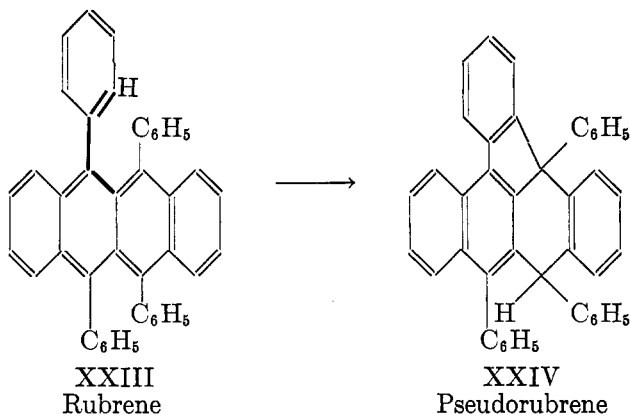
[2] Moureu and his coworkers, however, prefer another formula for pseudorubrene, in which a benzene ring with two ortho carbon atoms forms a bridge between the positions 11 and 12:
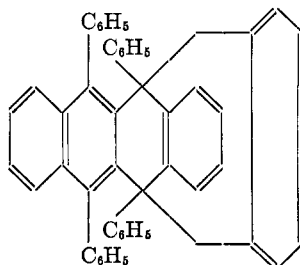
This formula seems to be in contradiction with the known stability of ring valencies toward deflection.

The molecule contains the system of an allylbenzene (marked in heavy type), which is isomerized as usual except that the hydrogen atom does not remain at the central atom of the allyl system; it subsequently undergoes an allylic rearrangement and the hydrogen appears therefore in position 12. An analogous observation has been made in the case of 1,4,9,10-tetra-phenylanthracene (90). It may be added that *formally* the isomerization of *as*-phenyl-*o*-biphenylethylene, mentioned above, may also be regarded as a case of allylbenzene isomerization, the single bond of the allylic system being located in the benzene nucleus.

A similar, but still more complicated, case of cycloisomerization is the conversion of 1,2,3-triphenylnaphthalene (XXV) into 9-phenyl-9,10-dihydro-1,2,3,4-dibenzanthracene (XXVI), which, according to Schlenk and Bergmann (76; see 10, 23), takes place under the influence of metallic lithium. The following scheme assumes an intermediate transfer of hydrogen along a system of conjugated double bonds:

XXV
1,2,3-Triphenyl-
naphthalene

XXVI
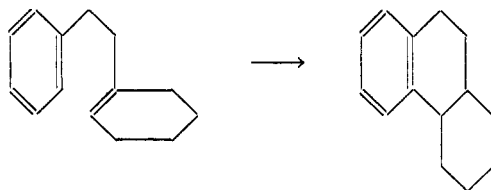9-Phenyl-9,10-dihydro-
1,2,3,4-dibenzanthracene
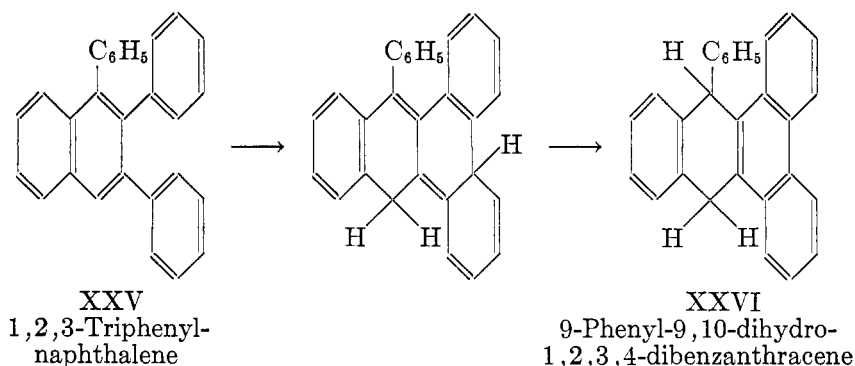
*C. Cycloisomerization of a butenylbenzene system*

Bogert and coworkers (25, 26, 28, 67, 70, 71) were the first to synthesize hydrogenated naphthalenes and phenanthrenes from butenyl-substituted benzenes (or the corresponding alcohols): for example,
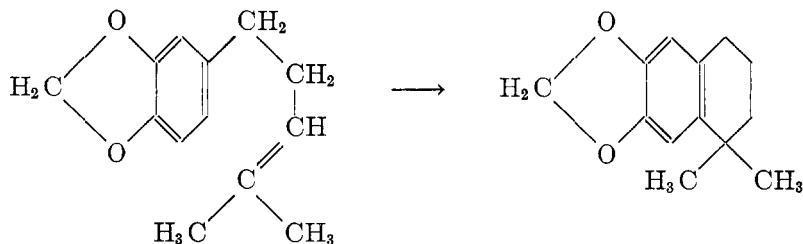

and

Subsequently, this method was also used by other investigators for various syntheses: e.g., (*a*) for the preparation of 1,2,5,6-dibenzphenanthrene from 4-(β-phenylethyl)-1,2-dihydrophenanthrene (8), (*b*) for the preparation of 1-methyl-6-isopropylphenanthrene (79a), (*c*) for the synthesis of triphenylene derivatives (e.g., triphenylene itself from 1-phenyl-2-cyclohexenylcyclohexanol (71a)), and (*d*) for the synthesis of dodecahydro-1,2-benzanthracene from 2-(β-phenylethyl)octalin (42; for further references see 70). The following case, in which a more unsaturated cyclization product is formed, may also be cited (21): the condensation product (XXVII) resulting from the reaction of 2,3-dimethyl-2-cyclohexen-1-one and β-phenylethylmagnesium chloride is converted, through cyclization and subsequent dehydrogenation, into 1,2-dimethylphenanthrene (XXVIII).

XXVII

XXVIII
1,2-Dimethyl-
phenanthrene
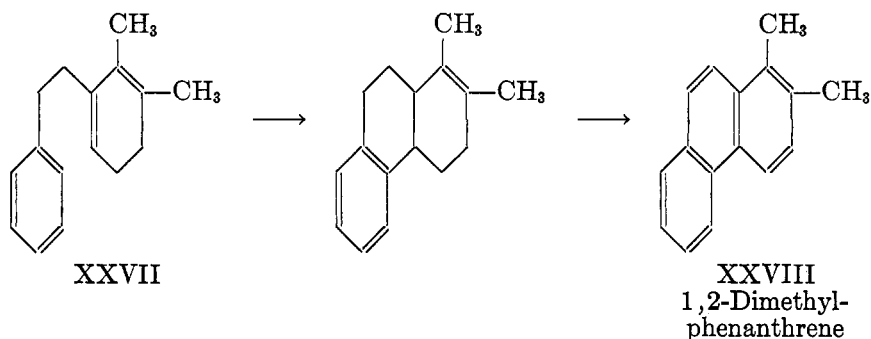
In all these cases (see page 539) the usefulness of the reaction is sometimes decreased by the formation of spirans. These spirans can easily be detected, as they remain unchanged under suitable dehydrogenation conditions; their structure can be elucidated by oxidation experiments. It has been reported that methyl groups in the γ-position of the butenyl side chain favor the "normal" ring closure in this series (69, 70).

With regard to the cyclization proper, the Bogert synthesis is identical with the method reported by Bardhan and Sengupta (2b) a short time before; in the preparation of the initial butenylbenzenes, the two methods are different and complementary to each other.

Another variation of the above cycloisomerization is provided by the Darzens (44) synthesis of naphthalene- and phenanthrene-carboxylic acids from benzylallyl- and naphthomethylallyl-acetic acids, respectively, which are isomerized under the influence of concentrated sulfuric acid, most probably by way of the isomeric propenyl compounds which contain the butenylbenzene system; e.g.,
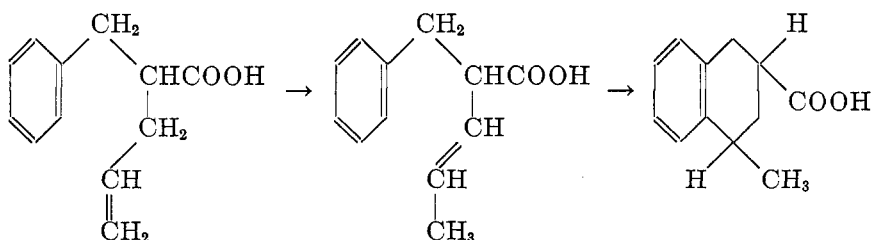
The migration of the double bond appears to be directed by the tendency to approach the carboxyl group.

C(a). Cycloisomerization of the phenylbutadiene system

A special instance of the cycloisomerization discussed in the preceding section is the case of the phenylbutadienes, in which the butenylbenzene system to be isomerized contains an additional (conjugated) double linkage. No such reaction is known for pure hydrocarbons (the pertinent case of 1,2,3,4-tetraphenylbutadiene is discussed on page 539), but undoubtedly the formation of 2,3,4-tribromo-1-phenylnaphthalene (XXX) upon the bromination of diphenyldiacetylene (XXIX) (85) must be formulated in the following manner, involving cycloisomerization of the primary tetrabromide and subsequent loss of one molecule of hydrobromic acid:

XXIX
Diphenyl-
diacetylene

XXX
2,3,4-Tribromo-1-
phenylnaphthalene
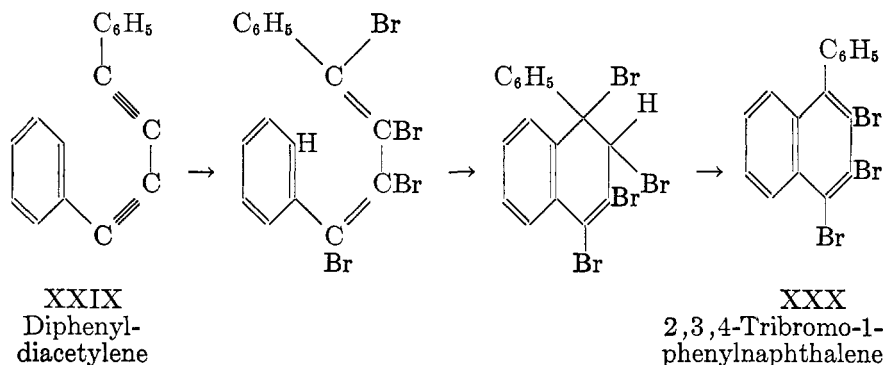
The same mechanism is involved in the photochemical isomerization of triphenylfulgide (XXXI) (84), which is catalyzed by iodine:


XXXI
Triphenylfulgide

XXXII

XXIII
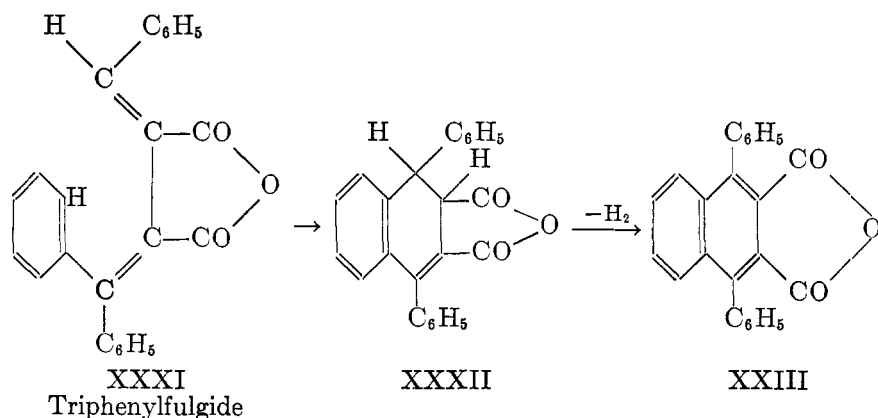
The intermediate dihydronaphthalene (XXXII) stage can be isolated if the photoisomerization is carried out in the absence of oxygen.

1. Mechanism of the isomerization

These isomerizations, which are usually brought about by reagents like concentrated sulfuric acid, aluminum chloride, stannic chloride (in the presence or the absence of hydrochloric acid), have been formulated so far—merely for the sake of simplicity—as involving the transfer of a hydrogen atom from the benzene nucleus to the central atom of the unsaturated side chain. It is quite possible that the actual mechanism of the reaction is addition of the catalyst (e.g., $H—OSO_3H$, $H—HSnCl_6$, etc.) to the double bond and splitting off of the catalyst molecule, the ortho hydrogen atom of the benzene nucleus now being involved:
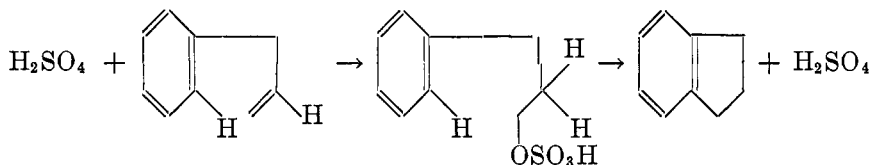
Whether the additional hydrogen atom appearing in the newly formed ring is that of the aromatic nucleus or derives from the sulfuric acid may perhaps be decided in every case by using heavy sulfuric acid as the catalyst, but, even on the basis of the existing experimental evidence, it may be maintained that both mechanisms may actually occur (quite as in the similar case of dimerization by the transfer of hydrogen, not within the molecule but from one molecule to another). In the case of 1,2,3,4-tetraphenyl-1-butene, for example, it has been observed (22) that metallic sodium may produce the isomerization, which would seem to be a purely catalytic reaction. On the other hand, observations made in the case of 1,1-diphenylpropene (XXXIV) point definitely to a participation of the agent in the reaction. When concentrated sulfuric acid acts upon this hydrocarbon, a sulfur-containing compound[3] of the formula $C_{15}H_{12}O_2S$ is obtained (9); according to its properties this compound has the structure of a thio-α-pyran derivative (4-phenyl-5,6-benzothio-α-pyran-1-dioxide) (XXXV) and owes its formation to the following reaction:

XXXIV

1,1-Diphenylpropene

XXXV
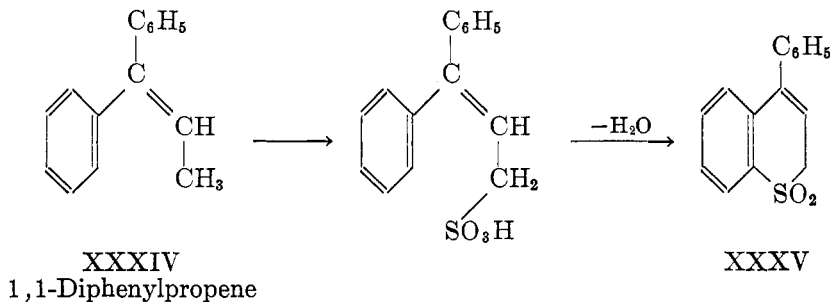
[3] The substance has a melting point of 114°C. and on catalytic hydrogenation gives a dihydro compound melting at 169–170°C.

The above reaction resembles[4] the course that bromination takes in the case of $(C_6H_5)_2C\!\!=\!\!C(CH_3)_2$, when the ω-derivative, $(C_6H_5)_2C\!\!=\!\!C(CH_3)(CH_2Br)$, is produced (91).

2. Influence of substituents on the cycloisomerization

Cook and his coworkers (33, 39, 40, 41, 43) have observed that a methyl group in the 2-position of the allyl group generally enhances the ring closure in the desired sense and suppresses side reactions, such as the formation of spiran derivatives. This is probably due to (a) a favorable valency deflection, caused by the more complete substitution on one side of the double bond, and (b) to the $+I$ effect of the methyl group, which causes an attraction of the nuclear protons by the neighboring unsaturated carbon atom, as shown in the following diagram:[5]
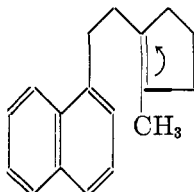

The influence of substituents in the aromatic nucleus on ring formation has never been studied, but it may be safely assumed that it is the same as for the cyclization reaction of phenylated fatty acids, as studied by v. Braun, Manz, and Reinsch (32); an unsubstituted phenyl nucleus reacts more easily than a m-tolyl system and less easily than a p-tolyl system (meta and para with regard to the hydrogen atom to be split off).

Also the question as to which of the two rings, cyclohexane or cyclopentane, is formed when the structural possibility for the formation of both is present has not yet been answered definitely. For the phenylated acids, Leuchs (60) and v. Braun and Manz (31) have shown that the six-membered ring is formed in preference to the five-membered ring, but in the hydrocarbon series the only case so far known points to the contrary. 1,2,3,4-Tetraphenylbutadiene (XXXVI) might cyclize to give either 1,2,3-triphenyl-1,4-dihydronaphthalene (XXXVII) or 1,2-diphenyl-3-benzylidenehydrindene (XXXVIII):

[4] It is possible that the reaction consists in the well-known addition of the acid as $HO\!\!-\!\!SO_3H$, followed by dehydration and allylic rearrangement.

[5] In the reaction of 2-methylcyclopentanone with β-(9-phenanthryl)ethylmagnesium chloride, the methyl group does not show this favorable effect (13; cf. 36, 51).

XXXVI
1,2,3,4-Tetraphenylbutadiene

XXXVII
1,2,3-Triphenyl-1,4-dihydro-
naphthalene

XXXVI
1,2,3,4-Tetraphenylbutadiene

XXXVIII
1,2-Diphenyl-3-benzylidene-
hydrindene
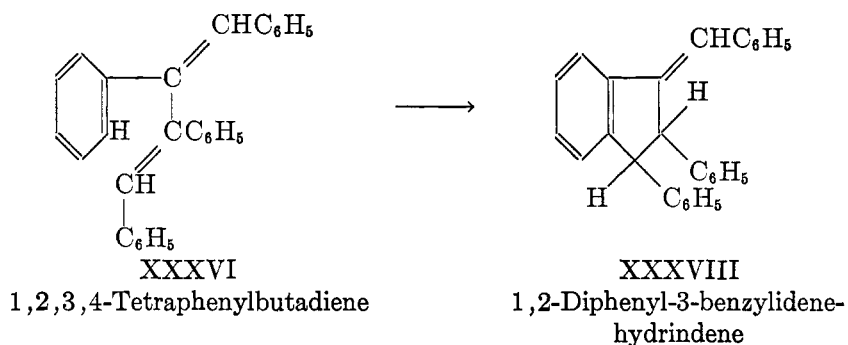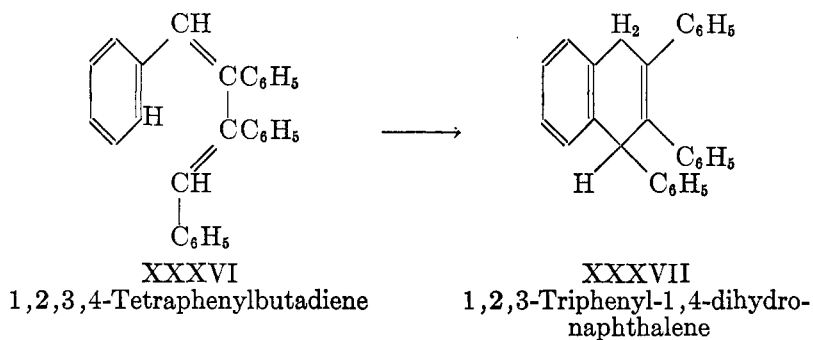
Actually, only the indene derivative is obtained (22). It may be that steric influences—not yet clear—play a certain part in these cyclization processes. This view is supported by the following general observation (34): The diarylitaconic acids, on cyclization, form indene derivatives, a change which involves the α-carboxyl group,
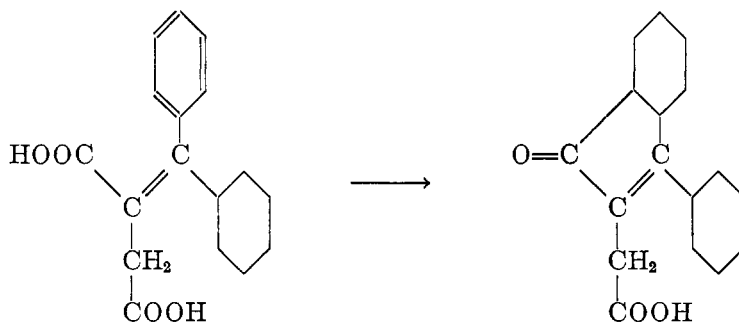
while the corresponding hydrogenated diarylmethylsuccinic acids, on dehydration, yield α-aryltetralones with the β-carboxyl group:
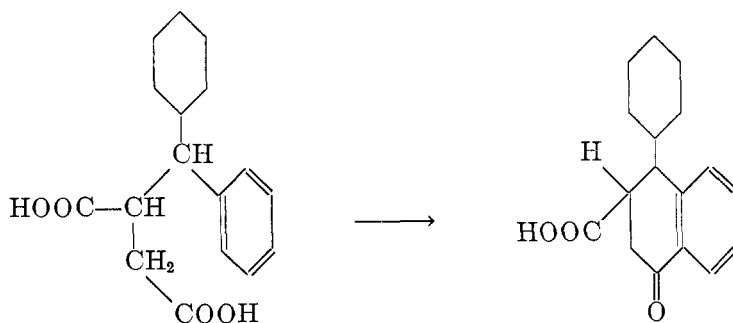
In the unsaturated acid, obviously, the aryl and the α-carboxyl groups are sterically close to each other, and, owing to the rigidity of the ethylene system, five-membered ring formation is preferred to the other possible cyclization, which is not preformed in the same sense.

D. Cycloisomerization of arylated allenes

The isomerization of allenes into indenes presents a very clear-cut case. Tetraphenylallene (XXXIX) is isomerized by strong acids into 1,1,3-triphenylindene (XL) (58, 89), according to the following scheme:

| XXXIX | XL |
| Tetraphenylallene | 1,1,3-Triphenylindene |
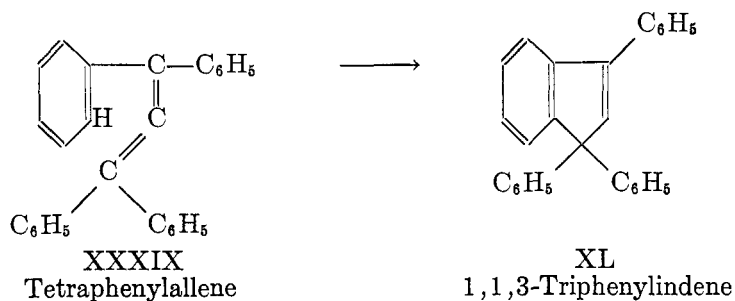
One assumes, in general, that the deeply colored halochromic compound which is formed and disappears in the course of this reaction is the intermediate A, from which the acid is split off again, removing the ortho

A   B

hydrogen atom from the benzene nucleus. This is, however, not in accordance with the behavior of 1,1-diphenyl-3-diphenyleneallene (XLI) (56). As the diphenylmethyl system seems to be more basic than the fluorenyl group, one would expect the occurrence of the following reaction:

XLI

1,1-Diphenyl-3-diphenyleneallene

XLII

However, this reaction does not occur, possibly owing to the difficulty[6] of formation of such a condensed ring system.

There is, however, another possibility. The addition of the acid to the allene system, yielding the halochromic compound, may have nothing to do with the cycloisomerization, but may only enhance this reaction by giving the rigid allene derivative a mobility which is required for the transition into a state which is geometrically apt to undergo cyclization. The intermediate product would therefore be of type B, the cycloisomerization of allene would be a special case of that of allylbenzenes, and the isomerization of 1,1-diphenyl-3-diphenyleneallene (XLI) would follow another course:

XLI   XLIII

[6] This difficulty has already been pointed out by v. Braun and Anton (30); recently, however, Koelsch (55) has actually isolated a substance of this complicated type.

Formula XLIII shows the correct structure of the final product. A decision between the two explanations is not yet possible.

Many similar cycloisomerizations have been observed (15, 92, 93), but the structure of the isomerization product has been elucidated only in the case of the dimeric triphenylallene (86) and of tetraphenylbutatriene (XLIV) (29), which gives 1-benzhydrylidene-3-phenylindene (XLV) according to the following scheme:

| XLIV	XLV
Tetraphenylbutatriene	1-Benzhydrylidene-3-phenylindene
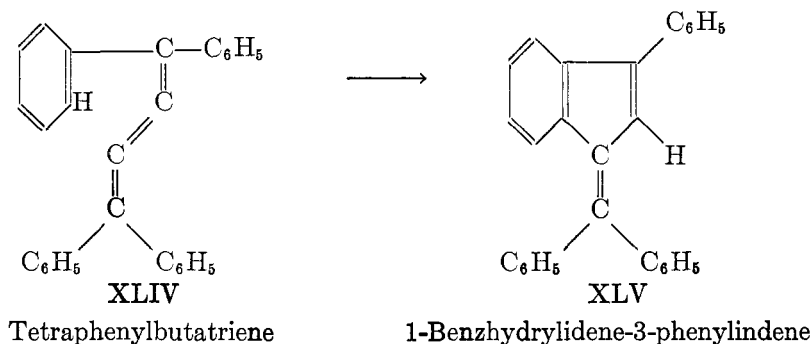
The arylated diallenes, obtained by Marvel and coworkers (47, 48, 62, 66, 83, 88; see page 531), are also apt to isomerize, but it is not yet clear which course this cycloisomerization takes. For example, the product obtained from 1,1,6,6-tetraphenyl-1,3-di-*tert*-butyl-1,2,4,5-hexatetraene (VIII) under the influence of mineral acids or by treatment with metallic sodium and subsequent removal of the sodium from the organometallic compound formed is not 3,3'-diphenyl-1,1'-di-*tert*-butyl-1,1'-diindenyl (XLVI), which might be expected according to the above schemes, as it does not show any tendency to dissociate into free radicals (49, 50), but it is also not 2,8-diphenyl-6b,12b-di-*tert*-butyl-6b,12b-dihydrochrysene (XLVII), as has been shown by Marvel and Peppel (62) on the basis of spectroscopic evidence.

VIII

1,1,6,6-Tetraphenyl-1,3-di-*tert*-butyl-1,2,4,5-hexatetraene
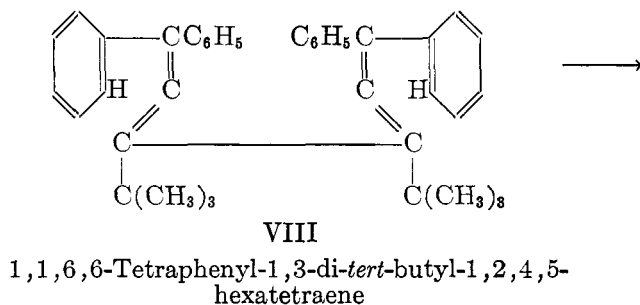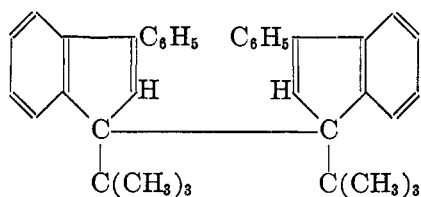
XLVI

3,3'-Diphenyl-1,1'-di-*tert*-butyl-1,1'-diindenyl
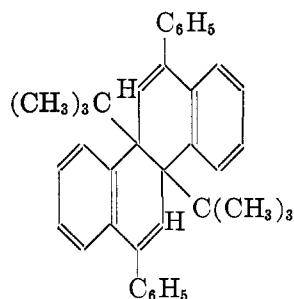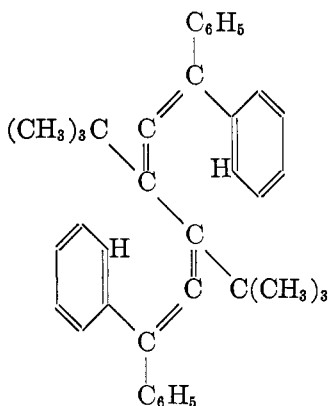
XLVII

An interesting example of the effect of steric influences on cyclization reactions of this type has been studied by Koelsch (54).   Pentaphenylallyl alcohol (XLVIII) splits off water to give 1,1,2,3-tetraphenylindene, while the analogous 3-diphenylene-1,1,2-triphenylallyl alcohol (XLIX) is unable to do so, but behaves as 2,3,3-triphenyl-1-diphenyleneallyl alcohol, giving 1-diphenylene-2,3-diphenylindene.
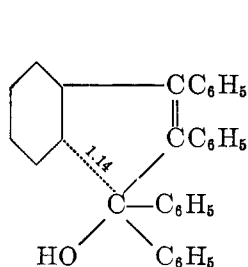
XLVIII
Pentaphenylallyl alcohol
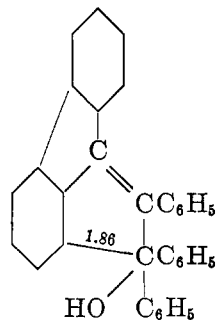
XLIX
3-Diphenylene-1,1,2-
triphenylallyl alcohol

On the basis of certain assumptions, Koelsch calculates that the distances between the carbinol carbon atom and the nuclear carbon atom which are involved in the cyclization reactions are 1.14 and 1.86 Å., respectively, for the two different cases.

E. Cycloisomerization of terpene compounds

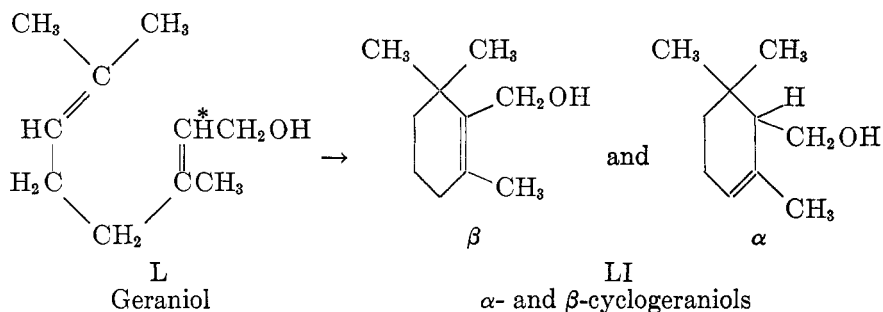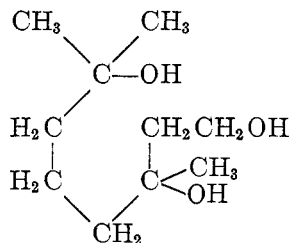It is to be expected that the tendency toward cycloisomerization would not be confined to a convenient unsaturated chain linked with an aromatic nucleus, but that the latter could be substituted by other suitable olefinic systems. In this way doubly unsaturated chains, especially in the terpene group, are likely to form ring compounds possessing one remaining double bond. Geraniol (L), for example, is converted into α- and β-cyclogeraniols (LI),

$$
\begin{array}{ccc}
\underset{\substack{\text{L}\\ \text{Geraniol}}}{
\begin{array}{c}
CH_3 \quad CH_3 \\
\diagdown \diagup \\
C \\
HC \quad\quad \overset{*}{C}HCH_2OH \\
\| \quad\quad\quad \| \\
H_2C \quad\quad CCH_3 \\
\diagdown \diagup \\
CH_2
\end{array}}
\quad \longrightarrow \quad
\underset{\beta}{
\begin{array}{c}
CH_3 \quad CH_3 \\
CH_2OH \\
CH_3
\end{array}}
\quad \text{and} \quad
\underset{\alpha}{
\begin{array}{c}
CH_3 \quad CH_3 \\
H \\
CH_2OH \\
CH_3
\end{array}}
\end{array}
$$

L — Geraniol; LI — α- and β-cyclogeraniols

and the same is true of the corresponding aldehyde (citral) and the corresponding acid (geranic acid). The formation of the α-compound, which involves not only the migration of the hydrogen atom marked with an asterisk, but also that of the double bond, may be due to a partial allylic rearrangement during or after cyclization—or perhaps to the fact that the cycloisomerization, under the influence of strong acids, is preceded by hydration processes and is actually a "cyclodehydration", e.g., of a compound like

$$
\begin{array}{c}
CH_3 \quad\quad CH_3 \\
\diagdown \diagup \\
C\text{—}OH \\
\diagup \\
H_2C \quad\quad CH_2CH_2OH \\
| \quad\quad\quad | \\
H_2C \quad\quad C{<}^{CH_3}_{OH} \\
\diagdown \diagup \\
CH_2
\end{array}
$$

in which the final dehydration can give rise to both the α- and the β-forms.

In the same way hydrocarbons may be cyclized. The heterodimeriza-

tion product of isoprene and myrcene, the so-called cycloisoprenemyrcene
(LII), is isomerized by means of strong acids to form bicycloisoprenemyr-
cene (LIII) (73, 79),

| LII | LIII |
| Cycloisoprenemyrcene | Bicycloisoprenemyrcene |
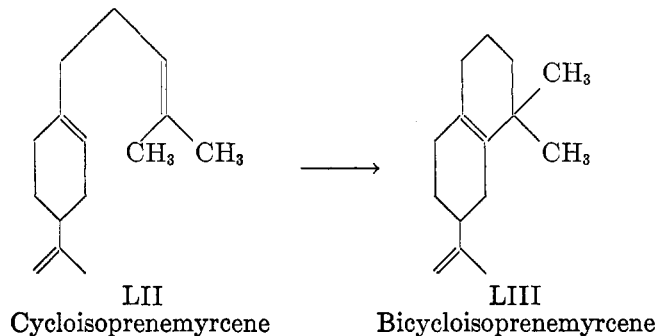
in which the location of the double bonds is somewhat arbitrary. This
reaction parallels the Bogert synthesis of hydrogenated naphthalene deriv-
atives (see page 535). Even cases similar to the Darzens synthesis are
known, involving the migration of the double bond in the initial product
before cyclization; for example, in the isomerization of zingiberene (75):
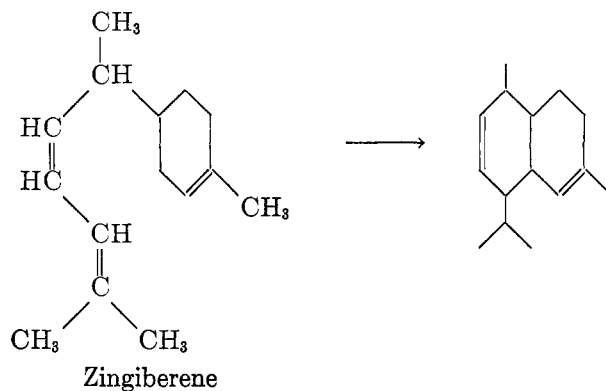

Zingiberene

This cycloisomerization is energetically so favored that it sometimes occurs
even in the absence of acid, e.g., under the conditions of dehydrogenation,
under which zingiberene yields cadalene (1,6-dimethyl-4-isopropylnaph-
thalene) (72, 74).

F. Bimolecular cycloisomerization of phenylacetylenes and related reactions

It is obvious that phenylacetylene (like phenylethylene) cannot undergo
simple cycloisomerization, as this would lead to benzocyclobutadiene deriv-

atives.   For a long time, however, it has been known (63) that two mole-
cules of phenylpropiolic acid (LIV) are apt to combine to yield (the
anhydride of) 1-phenylnaphthalene-2,3-dicarboxylic acid (LV) under the
influence of such reagents as acetic anhydride.

$$C_6H_5$$

LIV
Phenylpropiolic acid

LV
1-Phenylnaphthalene-
2,3-dicarboxylic acid
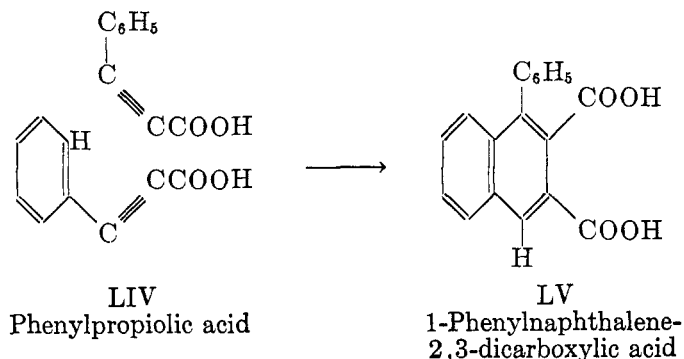
This reaction appears to reflect the existence of a certain molecular affinity
between two molecules of the acetylenic compound.   Recently the anal-
ogous reaction of tolane (diphenylacetylene) (LVI) was observed by
Schlenk and Bergmann (76).   When tolane was treated with metallic
lithium in the presence of ether, various derivatives of 1,2,3-triphenyl-
naphthalene (LVII) were obtained.

$$C_6H_5$$

LVI
Tolane

LVII
1,2,3-Triphenyl-
naphthalene
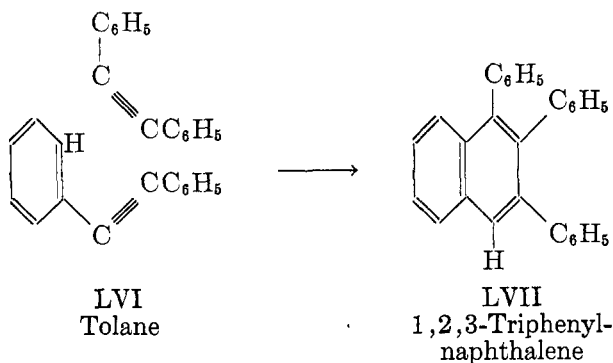
In spite of additional research (10, 22, 23), the intrinsic mechanism of this
reaction has not become quite clear.   Bergmann and Zwecker (23) put
forward the suggestion that a dilithiostilbene, C_6H_5CLi=$CLiC_6H_5$, is
formed at first and then reacts with a molecule of unchanged tolane.
There are many possibilities of explaining on this basis the formation of
the two organometallic compounds (LVIII and LIX) assumed to be present
in the solution obtained from lithium and tolane but, whatever the intimate

mechanism of the reaction, the similarity in the behavior of phenyl-propiolic acid and of tolane is evident.
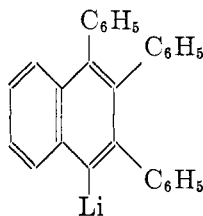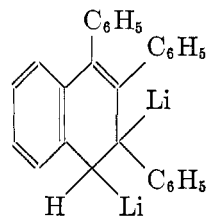
LVIII   LIX

An equally surprising case of dimolecular cyclization is the formation of rubrene (XXIII) from diphenyl(phenylethinyl)chloromethane (LX), although this reaction is not actually an isomerization. According to Dufraisse (45; *cf.* 81) the chloromethane reacts in its isomeric form (for similar rearrangements see page 530), as follows:

LX   XXIII
Diphenyl(phenylethinyl)-   Rubrene
    chloromethane
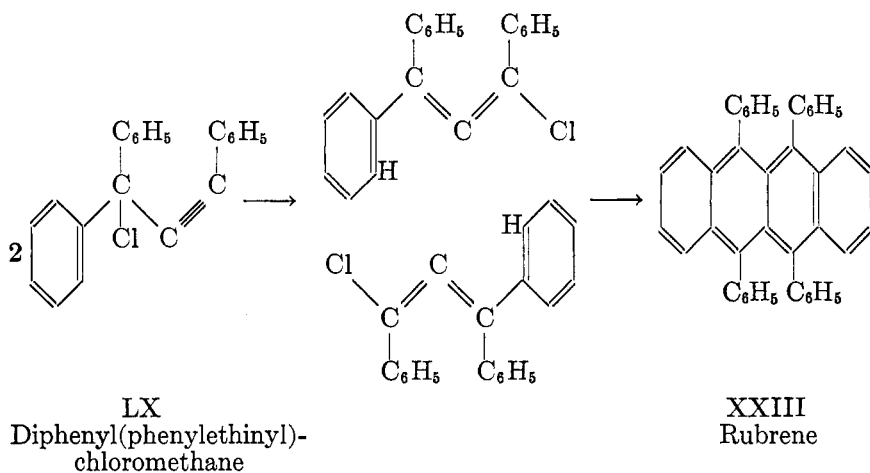
Here again, a peculiar intermolecular interaction—between the two central carbon atoms—appears to play an important rôle.

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