Summary

A synthesis of 1,1-dimethyl-2-phenylindene is described, and it is shown that a hydrocarbon previously believed to have this structure is actually 1,1-dimethyl-3-phenylindene. The finding of Kohler and Heritage that the reaction between methylmagnesium iodide and methyl α-phenylcinnamate involves 1,2-addition is confirmed.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Thermal Isomerization of Some Indene Derivatives

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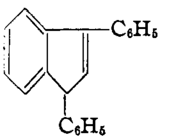
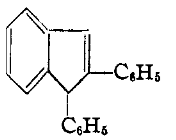
In a previous paper[1] it was shown that the pyrolysis of α,α,γ-triphenylpropylene yielded, among other products, 1,3-diphenylindene (I), 1,2-diphenylindene (II), and 2,3-diphenylindene (III). The 1,3-compound obviously resulted from dehydrogenation of the propylene with accompanying cyclization. Data were presented which rendered it likely that the formation of 1,2- and 2,3-diphenylindenes was not a result of isomerization followed by cyclization, but was instead a result of these processes in the reverse order.



I



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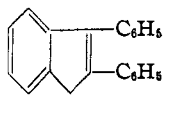


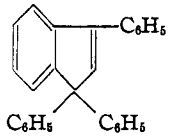
III

In the present paper it is shown that I is transformed into a mixture of II and III at 450°, and that therefore the mechanism previously outlined is at least possible. Of considerably greater interest is the discoveiy that the isomerization is reversible. Any of the three compounds mentioned yielded the same mixture of products on pyrolysis; in a large number of runs on each of the indenes, the products were I (8–20%), II (4–6%), and III (47–65%). An indene mixture containing the three substances in approximately the ratios indicated, passed through the pyrolysis tube five times without any change in composition.

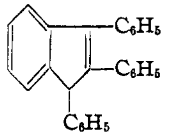
Reversibility in the present example indicates that the failure of v. Braun and Manz[2] to detect any 1(or 3)-phenylindene in the pyrolysis product of 2-phenylindene was caused by an unfavorable equilibrium, the reverse rearrangement having been demonstrated.

Since II and III are interconvertible under conditions much milder than those involved in pyrolysis, it was not possible to tell whether the phenyl from position 3 or that from position 1 was involved in the isomerization of I. In order to gain some insight into this question, the pyrolysis of more highly substituted indenes was studied. That migration from position 1 was possible was shown in three examples.

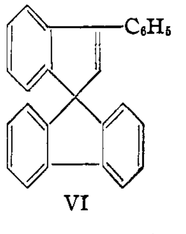
1,1,3-Triphenylindene (IV) gave 1,2,3-triphenylindene (V) at 490° in an 86% yield; the remainder of the product was a red gummy substance. 3′-Phenyl-*spiro*-[fluorene-9,1′-indene](VI) gave 13-phenyl-(13)-dibenzo[ac]fluorene (VII) in an 80% yield, and 17% of the starting material was recovered. The question of reversibility in these two cases is of particular interest. The results are best interpreted as showing that the point of equilibrium, assuming reversibility in the reaction, is far toward the side of the products V and VII, for in the case of IV, no starting material was found in the products, and in the case of VI, the presence of starting material in the product was probably a result of the special conditions necessary for carrying out the pyrolysis. Under the usual conditions VI was largely



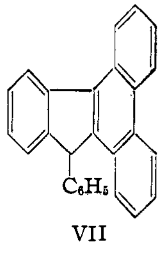
IV



V



VI



VII

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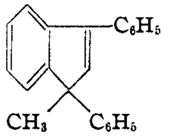
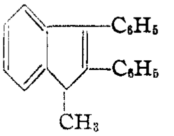
(1) Koelsch and Johnson, *J. Org. Chem.*, **6**, 534 (1941).

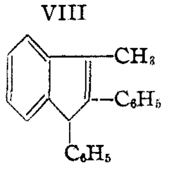
(2) v. Braun and Manz, *Ber.*, **62**, 1059 (1929).

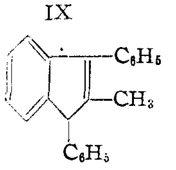
carbonized, and only when the tube filling was removed and the compound was swept through the furnace by a very rapid stream of nitrogen could carbonization be avoided. Incidentally, this was the only substance among all the indenes pyrolyzed which showed any tendency to undergo deep-seated decomposition. It is of interest that the same isomerizations of IV into V, and VI into VII are brought about by alkali metals under conditions totally different from pyrolysis.[3]

The third example illustrating migration from position 1 involved the pyrolysis of 1,3-diphenyl-1-methylindene (VIII). This hydrocarbon gave an 82% yield of crystalline isomerization products, consisting of a mixture of 2,3-diphenyl-1-methyl- (IX) and 1,2-diphenyl-3-methylindene (X). The oily remainder of the product on oxidation gave sufficient *o*-benzoylbenzoic acid to account for 7.5% of the original substance and sufficient *o*-dibenzoylbenzene to account for an additional 7.5% of the original substance.


VIII

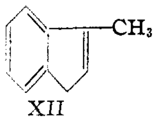

IX

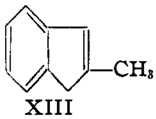

X

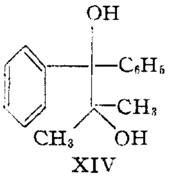

XI

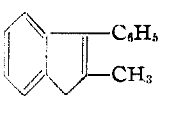
Two questions arise in connection with this pyrolysis: first that of the point of equilibrium in the isomerization, and second that of the migration of a methyl group. The isomerization is probably quite complete, for neither VIII nor its oxidation product, *o*-benzoyl-α,α-diphenylpropionic acid,[4] was isolated. The non-formation of VIII from IX and X was also shown by pyrolysis of a mixture of IX and X and oxidation of the crude product; no *o*-benzoyl-α,α-diphenylpropionic acid or even *o*-dibenzoylbenzene (formed from VIII on vigorous oxidation) was isolated. The methyl group in VIII probably migrates to a small extent, for although 1,3-diphenyl-2-methylindene (XI), m. p. 108°,[5] was not isolated, the dibenzoylbenzene formed in the oxidation is considered to represent this substance, since the oxidation was carried out under mild conditions. The benzoylbenzoic acid is formed from IX and X.

The probable migration of a methyl group in the pyrolysis of VIII made it necessary to re-investigate the behavior of 3-methylindene (XII), since it had been reported[6] that this substance was unchanged under conditions which brought about isomerization of 3-phenylindene. This report was confirmed, and in order to eliminate the possibility that the thermal stability of the methyl group was only apparent, caused by an equilibrium unfavorable to the formation of XIII, the pyrolysis of 2-methylindene (XIII) was also investigated. The compound, however, was not isomerized. These results are remarkable for a number of reasons. First, that isomerization of neither hydrocarbon took place was unexpected, for it has been shown[7] that α-methylnaphthalene yields the β-isomer at 420–430°. Second, that ring enlargement did not occur was also unexpected, for 9-methylfluorene changes into phenanthrene[8] on passage through a hot tube, and more recently it has been found that both 2- and 3-methylindenes are converted into naphthalene[9] by palladium black at 450°. Third, the results indicate that the migration of the methyl group in VIII is made possible only by the presence of the phenyl groups on the five-membered ring. In this connection, an observation of Blum-Bergmann[10] should be noted. This investigator found that when 2 - methyl - 1,1 - diphenylpropanediol - 1,2 (XIV) was passed over silica gel at 500°, it was converted into 3-methyl-2-phenylindene (XVI), and it was suggested that the product was formed through isomerization of the primary product XV. Such an isomerization involves the migration of


XII


XIII


XIV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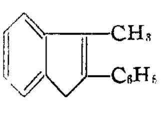
XVI

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[3] Ziegler and Crössman, *Ber.*, **62**, 1768 (1929); Koelsch, This Journal, **56**, 480 (1934).

[4] Koelsch, *ibid.*, **56**, 1605 (1934).

[5] Ingold and Wilson, *J. Chem. Soc.*, 1493 (1933).

[6] Mayer, Sieglitz and Ludwig, *Ber.*, **54**, 1397 (1921).

[7] Mayer and Schiffner, *ibid.*, **67**, 67 (1934).

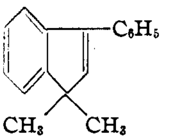
[8] Graebe, *ibid.*, **37**, 4145 (1904).

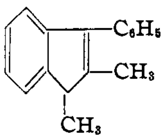
[9] Ruzicka and Peyer, *Helv. Chim. Acta*, **18**, 676 (1935).

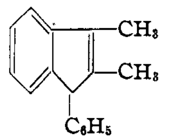
[10] Blum-Bergmann, *Ber.*, **65**, 109 (1932).

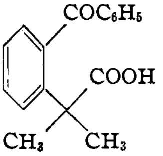
a methyl group, but here as in the case of VIII, the five-membered ring carries a phenyl as well as the methyl.

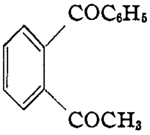
Further support for the suggestion that a methyl group can migrate only when a phenyl is present was found in two additional cases studied in the present investigation. When 1,1-dimethyl-3-phenylindene (XVII) was pyrolyzed, it yielded an oily product from which no pure substance could be isolated. Oxidation of the product gave both *o*-benzoyl-α,α-dimethylphenylacetic acid (XX) and *o*-acetylbenzophenone (XXI), whereas oxidation of the starting material (XVII) gave only XX. When 2,3-dimethyl-1-phenylindene (XIX) was pyrolyzed, it likewise gave an oily mixture of products, and this mixture, like that from XVII, on oxidation yielded both XX and XXI, whereas oxidation of XIX gave only XXI. Thus it appears that the pyrolysis of either XVII or XIX gives qualitatively the same mixture containing XVII, XVIII and XIX.

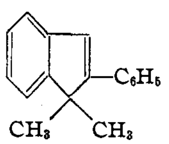

XVII


XVIII


XIX


XX


XXI


XXII

It is surprising that in the two pyrolyses just discussed no evidence for the migration of the phenyl group was obtained. If migration takes place only from the 1 position, the phenyl group in XVII should not move, but after XVIII $\rightleftarrows$ XIX is formed, the phenyl should be free to move just as it does in the isomerization of XV into XVI. The stability of the phenyl in the 1 (or 3) position may be caused by the ability of the two methyls in XVII, XVIII, and XIX to absorb vibrational energy and thus prevent it from accumulating in the bond holding the phenyl.

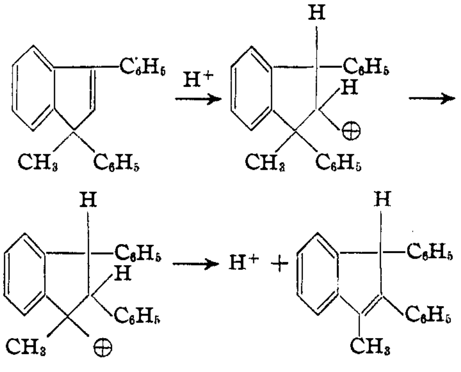
A mechanism suggested below indicates that migrations to the 3 position should be possible, In order to test this possibility, the pyrolysis of 1,1-dimethyl-2-phenylindene (XXII) was studied. This indene proved rather resistant to isomerization. At 490° it was largely (60%) unchanged, and the unchanged substance was the only crystalline material obtainable from the products. However, oxidation of the oily fraction gave benzoylbenzoic acid, indicating that the phenyl must have migrated from the 2 position. Evidence of the presence of XX among the oxidation products was obtained, which may identify XVII, but unfortunately the acid could not be isolated in quantity sufficient for its complete purification. Benzoylbenzoic acid in the oxidation products indicated that, as expected, XVII rearranged to XVIII $\leftrightarrows$ XIX almost as fast as it was formed.

Discussion.—Consideration of the data presented leads to the following conclusions:

1. Alkyl or aryl groups substituted on the five-membered ring of indene undergo reversible migration to an adjacent position under the influence of heat.
2. The presence of an aryl group on the indene ring is necessary for the migration of a methyl.
3. Migration from the 1 to the 2 position takes place if the latter is not already substituted.
4. Migration from the 2 to the 3 position takes place if the 1 position is completely occupied, but secondary rearrangement occurs.
5. A mobile hydrogen on the indene ring is not necessary for the migration.

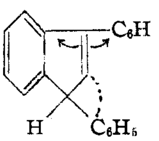
A free radical mechanism for the rearrangement does not appear to be applicable, for if free radicals (*e. g.*, phenyl) were formed, their hydrogenation products (benzene) should be isolable, and if any coupling were possible, some products of the coupling of like radicals (biphenyl) should be formed.

An ionic mechanism appears unlikely. Such a course would be formulated

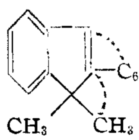


The final product contains a potential proton, but until some rearrangement has occurred, the source of the original proton is obscure. A greater difficulty with the ionic mechanism is found when it is applied to the isomerization of 1,1-dimethyl-3-phenylindene, for here methyl and not phenyl migrates, and as has often been found in ionic rearrangements (*e. g.*, pinacol), aryl groups migrate more easily than alkyl groups.

The remaining possibility is that an activated complex is formed in which the migrating group is neither detached completely from the rest of the molecule nor attached to either of the positions which it may finally occupy. If the proper electronic distribution is present, the group which is to migrate will find itself, after the bond holding it has accumulated sufficient vibrational energy, in a state where it is attracted equally by two adjacent positions on the nucleus. Depending on the relative stabilities of the structures concerned, a new valence bond may form. This picture leads to an explanation of the necessity for the presence of a phenyl in the migration of a methyl group; without the phenyl, resonance will be insufficient to release electrons to bind the methyl to a new position. Migrations from the 1 to the 2 position (but not the reverse), and from the 2 to the 3 position are also explained, as illustrated in XXIII and XXIV.



XXIII



XXIV

Experimental

The apparatus used has been described.[1] In most of the pyrolyses, the temperature was 490° and the rate of passage of the indene through the tube was 2–8 g. per hour. Nitrogen (5–10 ml./min.) was used as a carrier. Some runs were made using a tube filling of clay plate, others using pumice; in many cases it was demonstrated that the nature of the contact agent had no effect on the course of the reaction.

1,2-, 1,3- and 2,3-Diphenylindenes (II, I, III).—The preparations of the starting materials have been described.[1] Six pyrolyses of 1,3-diphenylindene (4–8 g.), and four of 2,3-diphenylindene (3–7.5 g.) were made. Analysis of the products in each case showed the presence of the same substances in nearly the same ratios. In some experiments the three compounds were isolated by crystallization (*e. g.*, 1,2- 4%, 2,3- 47%, 1,3- 20%). Greater analytical accuracy was attained by crystallizing the 1,2- and 2,3- compounds and oxidizing the remaining oil. The amount of 2,3- and 1,3- compounds in the oil could be estimated by the amounts of benzoylbenzoic acid and dibenzoylbenzene obtained, since the oxidation of the pure indenes has been studied[1] semi-quantitatively (*e. g.*, crystallized 1,2- and 2,3-, 67%; 1,3- by oxidation, 19.5%). Separation of the 1,2- and 2,3-diphenylindenes as the benzal derivative from 1,3-diphenylindene was found to be possible but not useful for quantitative work.

1,1,3-Triphenylindene (IV).—Diphenylvinylmagnesium bromide[11] and benzophenone gave tetraphenylallyl alcohol[12] in 50% yield; crystallized from acetic acid this alcohol gave tetraphenylallene quantitatively, and boiling this hydrocarbon with acetic acid containing sulfuric acid gave IV, m. p. 132–134°[13] in a yield of 64%. Pyrolysis of the product (4 g.) gave 3.05 g. of pure 1,2,3-triphenylindene (86%) and 0.25 g. of a red gummy substance.

For comparison, 1,2,3-triphenylindene (V) was synthesized from phenylmagnesium bromide and 2,3-diphenylhydrindone[14] (2.7 g.). The intermediate carbinol was dehydrated by boiling in acetic acid containing one drop of sulfuric acid, giving 1.25 g. of V, which melted at 130–132° (reported[15] 132–134°) alone or mixed with the above pyrolysis product.

3'-Phenyl-*spiro*-fluorene-9,1'-indene (VI).—This compound was obtained by the published method[16] in a yield of 45%.

Pyrolysis under the usual conditions was accompanied by deposition of carbonaceous material on the tube filling and gave a black tarry product from which no pure substance could be isolated. In order to avoid extensive decomposition, the indene (4.5 g.) was dropped rapidly (4–6 drops/min.) into the heated (490°) tube from which all the porcelain chips except one at the top had been removed. The speed of the nitrogen stream was not regulated by a Mariotte bottle, but was increased so that the solid pyrolysis product could just be retained in the first receiver. The crude brown product melted at 194–197° (the melting point of a mixture of the pure product with 17% of the starting material), and crystallization from xylene (charcoal) gave 3.25 g. (72%) of VII, identified by comparison with an authentic specimen.

1-Methyl-1,3-diphenylindene (VIII).—The indene was prepared in a 53% yield from phenylmagnesium bromide and 3-methyl-3-phenylindanone-1[17] (13 g.). The crude product from the Grignard reaction was dehydrated by warming it in acetic acid containing a little sulfuric acid, then distilled (b. p. 205–210° at 7 mm.) and crystallized from methanol-ether. It melted at 59–60° alone or mixed with a sample prepared in a different way.[4]

A description of one of three checking pyrolyses is given. Four grams of VIII passed through the tube over pumice at 470° gave 3.9 g. of a viscous clear yellow oil. Solution in methanol-ether followed by cooling gave 1.03 g. of white crystals (m. p. 78–86°) which after further crystallization from acetic acid melted at 91° alone or mixed with an authentic sample of 3-methyl-1,2-diphenylindene (X) (see below). The oil remaining in the mother liquor, after readjustment of the solvent, cooling, and scratching,

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[11] Lipp, *Ber.*, **56**, 571 (1923).

[12] Vorländer and Siebert, *ibid.*, **39**, 1034 (1906).

[13] Schlenk and Bergmann, *Ann.*, **463**, 223 (1928).

[14] Koelsch, THIS JOURNAL, **56**, 1338 (1934).

[15] Koelsch, *ibid.*, **54**, 2045 (1932).

[16] Koelsch, *ibid.*, **55**, 3394 (1933).

[17] Koelsch, Hochmann and Le Claire, *ibid.*, **65**, 59 (1943).

gave 2.24 g. of yellow crystals (sint. 73°, m. p. 87°) which on further crystallization (ligroin, then acetic acid) melted at 105–106° alone or mixed with an authentic sample of 1-methyl-2,3-diphenylindene (IX) (see below). Oxidation with chromic anhydride in cold acetic acid of the oil remaining in the mother liquors (2.25 g. from three pyrolyses) gave 0.2 g. of benzoic acid (steam distilled), 0.4 g. of pure *o*-benzoylbenzoic acid, and 0.5 g. of pure *o*-dibenzoylbenzene.

Synthesis of 1-Methyl-2,3-diphenylindene (IX).—Crotonic acid (17 g.) in 100 ml. of dry ether was treated with the calculated amount of bromine at 10–15°, and the solvent was then removed under reduced pressure. The resulting crude 2,3-dibromobutyric acid was covered with 300 ml. of benzene and 42 g. of aluminum chloride was added. The mixture was boiled for a short time, then poured into water. The solvent was removed with steam, and the remaining solid was purified by solution in aqueous sodium carbonate. Crystallization from benzene gave 10 g. of 2,3-diphenylbutyric acid which melted at 182–183°. Prepared in a different way,[18] this acid has been reported to melt at 180–181°. Eight grams of diphenylbutyric acid was boiled for a few minutes with 7 g. of phosphorus pentachloride in 50 ml. of benzene, and then 7.25 g. (70% excess) of aluminum chloride was added. The mixture was boiled for twenty minutes and then decomposed with iced hydrochloric acid. The product was distilled, giving 6 g. (70%) of **3-methyl-2-phenylindanone,** which boiled at 196–200° at 13 mm. and after crystallization from methanol melted at 84.5–86°.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.4; H, 6.4. Found: C, 86.5; H, 6.4.

Three grams of this indanone was added to a solution of phenylmagnesium bromide prepared from 0.62 g. of magnesium, and the mixture was stirred for ten minutes. The product was isolated in the usual way, dehydrated by warming in acetic acid containing 1% of sulfuric acid, and crystallized from acetic acid. There was obtained 3 g. (79%) of 1-methyl-2,3-diphenylindene, which formed light yellow needles that melted at 105–106°. The yellow color was removed when the compound was crystallized repeatedly from abs. alcohol, and the product then melted at 106.5°.

Anal. Calcd. for $C_{22}H_{18}$: C, 93.6; H, 6.4. Found: C, 93.3; H, 6.4.

This indene was partially isomerized to 3-methyl-1,2-diphenylindene when it was boiled with 10% alcoholic potash for a few minutes.

Synthesis of 3-Methyl-1,2-diphenylindene (X).—A solution of 2.3 g. of 2,3-diphenylindanone[14] in 10 ml. of dry benzene was added to ethereal methylmagnesium iodide prepared from 0.255 g. of magnesium. Hydrolysis of the complex and removal of the solvents left an oil, which was dehydrated in acetic acid containing sulfuric acid. The product separated from acetic acid in the form of colorless transparent rhombs that melted at 91°; yield, 1.6 g., 70%.

Anal. Calcd. for $C_{22}H_{16}$: C, 93.6; H, 6.4. Found: C, 93.5; H, 6.7.

The indene was partially isomerized to 1-methyl-2,3-diphenylindene when it was distilled or when it was boiled for a few minutes with alcoholic potash.

3-Methylindene (XII).—The hydrocarbon was prepared from α-hydrindone and methylmagnesium iodide.[19] When it was allowed to stand for several days in acetic acid containing 1% of sulfuric acid, it was converted into a brown oily polymer. The polymer was not volatile at 280° and 24 mm., but it was depolymerized by distillation at atmospheric pressure from a few drops of sulfuric acid. The depolymerized product boiled at 91–92° at 24 mm. and had n^{23}D 1.5598 (reported,[9] b. p. 70° at 10 mm., n^{25}D 1.5595). It gave an anisal derivative that melted at 114–115° (reported[20] 113°) and an unstable picrate that melted at 76–77° (reported 76–78°).

Pyrolysis of 15 g. of 3-methylindene over pumice at 490° during three hours gave 13.65 g. of a liquid product. Distillation of this gave 2.5 g. that boiled at 77–81° at 14 mm., n^{27}D 1.5535; 8.0 g. that boiled at 81–83° at 14 mm., n^{27}D 1.5590, and 2.7 g. of a red viscous residue. The distilled fractions were characterized as unchanged indene by conversion to the anisal derivative and the picrate.

2-Methylindene (XIII).—β-Hydrindone was prepared by the method of Porter and Suter[21] (20% over-all yield in each of two preparations) and by the method of Pope and Read[22] (54% over-all yield). Treatment of the ketone with methylmagnesium iodide gave 2-methylindanol-2, m. p. 52–53° (reported[23] 52°) in a yield of 73%, but in each of two preparations the carbinol was accompanied by two by-products, removed by treatment with petroleum ether, in which they were insoluble. The by-products were separated by crystallization from alcohol; one melted at 173–176° and was identified as anhydro-bis-β-hydrindone by comparison with an authentic sample[24]; the other melted at 156–157° and probably was a product from methylmagnesium iodide and anhydrobishydrindone.

Dehydration of 2-methylindanol-2 with sulfuric acid in acetic acid was unsatisfactory, large amounts of polymeric material being formed; phosphorus pentoxide gave better results. A mixture of 20 g. of phosphorus pentoxide, 100 ml. of benzene, and 16 g. of the carbinol was boiled for thirty minutes. The organic layer was removed, washed, and distilled, giving 8 g. (55%) of 2-methylindene which boiled at 97–99° at 24 mm. and had n^{23}D 1.5646 (reported[9] b. p. 79° at 10 mm., n^{19}D 1.5650). No crystalline anisal derivative of 2-methylindene could be obtained. The hydrocarbon formed a picrate that melted at 79–79.5° which although too unstable to be purified for analysis was nevertheless suitable for characterization, since a mixture of it with the picrate of 3-methylindene melted at 64–78°.

The pyrolysis of 3 g. of 2-methylindene at 490° during forty-five minutes over pumice gave a pale orange liquid (2.95 g.) which yielded a picrate identical with that obtained from the starting material. On fractionation, the pyrolysis product distilled almost completely, leaving only a minute residue. The first fraction boiled at 94–96° at 24 mm. and had n^{23}D 1.5645, the second boiled at 96–97° at 24 mm. and had n^{23}D 1.5645, indicating that no pyrolytic change had occurred.

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(18) Ramart-Lucas, *Ann. chim.*, (8) **30**, 424 (1913).

(19) Stoermer and Laage, *Ber.*, **50**, 989 (1917).

(20) Thiele and Buhner, *Ann.*, **374**, 266 (1906).

(21) Porter and Suter, THIS JOURNAL, **57**, 2025 (1935).

(22) Pope and Read, *J. Chem. Soc.*, **121**, 2550 (1922).

(23) v. Braun, Kruber and Danziger, *Ber.*, **49**, 2653 (1916).

(24) Heusler and Schieffer, *ibid.*, **32**, 32 (1899).

1,1-Dimethyl-3-phenylindene (XVII).—The indene was prepared from 3,3-dimethylindanone-1[17] by the method of Bergmann, Taubadel and Weiss[25] in a yield of 67%. It boiled at 184–185° at 27 mm. and melted at 50–51°.

Nitration of the indene (0.4 g.) in acetic acid (5 ml.) with nitric acid (0.15 ml., d. 1.42) at 100° for thirty minutes gave 1,1-dimethyl-2(?)-nitro-3-phenylindene (0.3 g.) which crystallized from alcohol in the form of yellow needles that melted at 141–142°.

Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 76.9; H, 5.7. Found: C, 77.1; H, 5.9.

Oxidation of the indene (0.5 g.) in acetic acid (10 ml.) with chromic anhydride (1.34 g.) at 25–30° for fifteen hours gave as the only acidic product *o*-benzoyl-α,α-dimethylphenylacetic acid (0.4 g.) identified by comparison with an authentic sample.[26,27] In several oxidations under even more drastic conditions, benzoylbenzoic acid was not formed from the indene, and it could be obtained in only a very small amount from the keto acid, treated with chromic acid in acetic acid at the boiling point. No solid neutral product was obtained from the indene on oxidation under any conditions.

Three pyrolyses of 1,1-dimethyl-3-phenylindene were carried out, one of which is presented in detail. Twenty-nine grams of the hydrocarbon passed over pumice at 490° during five hours gave 29 g. of crude oily product. Distillation of 16 g. of this at 27 mm. gave: (1) 0.5 g. boiling at 155–180°; (2) 1.5 g. boiling at 180–185°; (3) 12.0 g. boiling at 185–187°; (4) 1.4 g. of residue. Treatment of fraction (2) with methanol–ether at −80° gave a small amount of crystalline starting material and an oil. Similar treatment of fraction (3) gave 4.65 g. of starting material, and an oil. One gram of this oil in 60 ml. of acetic acid was treated with 2 g. of chromic anhydride at room temperature for forty hours; the oxidation products were: *o*-benzoyl-α,α-dimethylphenylacetic acid (0.43 g.) which melted at 187–190° without recrystallization; and oily neutral products (0.47 g.) from which there was obtained 0.15 g. of *o*-acetylbenzophenone, m. p. 95–97° (described in detail under XIX). From these data, which were approximately checked in several duplicate experiments, and from those obtained by the oxidation of pure 1,1-dimethyl-3-phenyl- and 2,3-dimethyl-1-phenylindenes, it can be calculated that the pyrolysis products contain roughly 63% of unchanged XVII and 26% of XVIII and XIX.

2,3-Dimethyl-1-phenylindene (XIX).—The hydrocarbon was prepared from benzalpropiophenone by the method of Smith and Hanson[28] in a yield of 50%; it melted at 68–69° in agreement with the reported value.

Oxidation of 0.2 g. of the indene by treatment with 0.33 g. of chromic anhydride in 10 ml. of acetic acid at 30° during twenty hours gave 0.184 g. of oily neutral products, from which by treatment with ether–ligroin there was obtained 0.068 g. of **o-acetylbenzophenone** (XXI), m. p. 95–96.5°. After several crystallizations from alcohol, the diketone melted at 99°.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.3; H, 5.4. Found: C, 80.3; H, 5.5.

The **disemicarbazone,** prepared from 0.2 g. of the diketone in 5 ml. of alcohol in the presence of aqueous sodium acetate, formed a colorless powder that sintered above 200° and melted with decomposition at 214–216°. It became green in an acid atmosphere, and gave a deep blue solution in hot acetic acid.

Anal. Calcd. for $C_{17}H_{18}N_6O_2$: C, 60.3; H, 5.4. Found: C, 60.3; H, 5.4.

When the indene was warmed for ninety minutes with 10% alcoholic potash it was converted into an oily mixture of XVIII and XIX from which no solid product could be isolated.

Pyrolysis of the indene (6 g.) over pumice at 490° during ninety minutes gave 6 g. of crude product; cooling this at −80° in methanol–ether gave 1.6 g. of crystalline starting material. Quantitative oxidation of a 1-g. portion of the remaining oil indicated that it consisted mainly of the allyl isomers XVIII and XIX. Only about 5 mg. of *o*-benzoyl-α,α-dimethylphenylacetic acid (indicating migration) was obtained.

A second pyrolysis of 5.7 g. of the indene carried out by repassing the substance six times through the furnace (5 g. per hour) gave 3.9 g. of crude oily product, the comparatively large loss being occasioned by mechanical difficulty in returning the product quantitatively to the pyrolysis chamber The product was separated into 1.2 g. of crystalline starting material and 2.7 g. of yellow oil. The latter, oxidized in the usual way, gave 2.05 g. of neutral products from which 0.7 g. of *o*-acetylbenzophenone was obtained; the acidic oxidation products were *o*-benzoylbenzoic acid (0.3 g., pure), and *o*-benzoyl-α,α-dimethylphenylacetic acid (0.1 g. crude, 0.05 g. pure) identified by comparison with an authentic sample and by conversion into the anilide.

1,1-Dimethyl-2-phenylindene (XXII).—The preparation and oxidation of this hydrocarbon have been described.[29] Pyrolysis of 2.5 g. of the indene over pumice at 490° during forty minutes gave 2.45 g. of a yellow oily product which, on cooling in methanol, yielded 1.5 g. of unchanged starting material. A solution of 0.9 g. of the remaining oil in 50 ml. of acetic acid containing 2 g. of chromic anhydride was warmed at 100° for ten hours and then poured into water and extracted repeatedly with ether. The solid (0.2 g.) extracted from the ether solution with dilute sodium carbonate was heated at 100° under reduced pressure for two hours, giving a few mg. of a sublimate consisting of benzoic acid; the residue was nearly pure *o*-benzoylbenzoic acid (identified by m. p. and by conversion into anthraquinone). The solid (0.55 g.) not extracted from ether by sodium carbonate was crystallized from acetic acid, giving 0.3 g. of pure α,α-dimethyldesoxybenzoin-*o*-carboxylic acid, identified by comparison with an authentic sample.[29]

Summary

The pyrolysis of 1,3-diphenylindene at 490° yields a mixture containing 1,3-diphenylindene, 1,2-diphenylindene, and 2,3-diphenylindene.

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(25) Bergmann, Taubadel and Weiss, *Ber.*, **64**, 1493 (1931).

(26) Koelsch and Le Claire, *J. Org. Chem.*, **6**, 516 (1941).

(27) The anilide of this acid, prepared with thionyl chloride and crystallized from alcohol melted at 202–202.5°. *Anal.* Calcd. for $C_{23}H_{21}NO_2$: C, 80.4; H, 6.2. Found: C, 80.3; H, 6.1.

(28) Smith and Hanson, THIS JOURNAL, **57**, 1326 (1935).

(29) Koelsch and Johnson, *ibid.*, **65**, 565 (1943).

Since the same mixture is obtained by pyrolysis of any of these three compounds, the isomerization is reversible. It is suggested that isomerizations of other indene derivatives under similar conditions are likewise reversible, and that an apparently complete isomerization is a result of an equilibrium very favorable for one product.

Other hydrocarbons whose pyrolyses are reported are 1,1,3-triphenylindene, 3-phenyl-*spiro*-[fluorene - 9, 1 - indene], 1 - methyl - 1,3 - diphenylindene, 1,1 - dimethyl - 3 - phenylindene, 2,3 - dimethyl - 1 - phenylindene, 1,1 - dimethyl - 2-phenylindene, 2-methylindene, and 2-methylindene. All of these substances except the last two yielded the rearrangement products expected. In some cases the isomerization products were isolated and in others their presence was shown by oxidative degradation of inseparable mixtures.

An interpretation of the migration is given.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Synthesis of an Epimeric Pair of Trisaccharides Containing Mannose Units[1]

BY EUGENE A. TALLEY AND WM. LLOYD EVANS

The preparation of acetobromomannosidoglucose,[2] led to the synthesis of a trisaccharide of the type proposed by Nishida and Hashima[3] as a unit in the structure of the mannan from the tubers of *Amorphophallus konjac.* Condensation of the acetobromo compound with β-D-glucose-1, 2,3,4-tetraacetate and with β-D-mannose-1,2,3, 4-tetraacetate by the Koenigs and Knorr reaction gave the two epimeric trisaccharides, 12-β-D-mannosido-β-gentiobiose hendecaacetate and 12-β-D-mannosido-β-*epi*-gentiobiose hendecaacetate, respectively. The trisaccharide acetates do not contain an orthoester grouping as shown by the fact that all eleven acetyl groups are removed by an alkaline deacetylating agent in both cases.

Although 12-mannosido-*epi*-β-gentiobiose hendecaacetate is made up of two mannose units and one glucose unit, it was not thought that the compound would be identical with the trisaccharide of Nashida and Hashima[3] as pointed out in another contribution from this Laboratory.[4] Nashida and Hashima reported that their trihexose could be broken down to give two disaccharides, of which one (mannosido-mannose) was hydrolyzed only to mannose and the other (mannosido-glucose) was hydrolyzed into one molecule of mannose and one molecule of glucose. Such a result could not be obtained from our mannosido-*epi*-gentiobiose. But after preparing it, the properties found for 12-mannosido-*epi*-β-gentiobiose hendecaacetate did seem to be comparable with those of two fractions reported by the Japanese workers.[3] The properties are given in Table I.

TABLE I

Material	M. p., °C.	Acetic acid, %	$[\alpha]_D$ in $CHCl_3$	Molecular weight (in benzene)
10-B[a]	105–115	68.69	+10.8°	1134
11-B[a]	102–115	68.76	+12.3°	1413
MGM[b]	113–114	68.0, 67.0 (68.3 calcd.)	+11.2°	1015, 1005 (967 calcd.)

[a] Sample numbers of Nashida and Hashima.[3] [b] MGM = Synthetic 12-mannosido-*epi*-β-gentiobiose hendecaacetate.

The synthetic compound and these fractions were all insoluble in ethyl ether. The properties given by Nashida and Hashima[3] for what they thought was the best fraction of their trisaccharide acetate were as follows: m. p. 95–110°, $[\alpha]^{20}$D in chloroform +18° and in benzene +6°. The molecular weight and acetic acid content of this particular fraction were not given but other fractions were listed which were found to have similar specific rotations. In every case the acetic acid content given was higher than the values in Table I and the molecular weights were lower, indicating that these latter fractions may have contained a larger percentage of a disaccharide octaacetate. In addition most of these fractions were ether soluble. Also it is of interest to point out that β-D-mannosido-β-D-glucose octaacetate[2] is ether soluble and its $[\alpha]^{19}$D +38.9° ($CHCl_3$).

On the basis of the above-mentioned observa-

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[1] Abstracted from a thesis presented by Eugene A. Talley to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] E. A. Talley, D. D. Reynolds and W. L. Evans, THIS JOURNAL, **65**, 575 (1943).

[3] Kitsuji Nishida and Hideo Hashima, *J. Dept. Agr. Kyushu Imp. Univ.*, **2**, 277–360 (1930).

[4] To be published.