[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

# The Rearrangement of Allyl Groups in Three-carbon Systems. IV. Hydrocarbons

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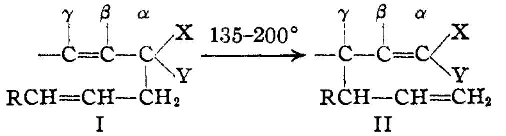
The following thermal rearrangement has been observed to occur in enough instances to establish the reaction as fairly general when X and Y are CN or $COOC_2H_5$[1]



$$\begin{array}{c}\overset{\gamma}{-C}=\overset{\beta}{C}-\overset{\alpha}{C}{<}^{X}_{Y}\\ RCH=CH-CH_2\end{array}\xrightarrow{135-200^\circ}\begin{array}{c}\overset{\gamma}{-C}-\overset{\beta}{C}=\overset{\alpha}{C}{<}^{X}_{Y}\\ RCH-CH=CH_2\end{array}$$

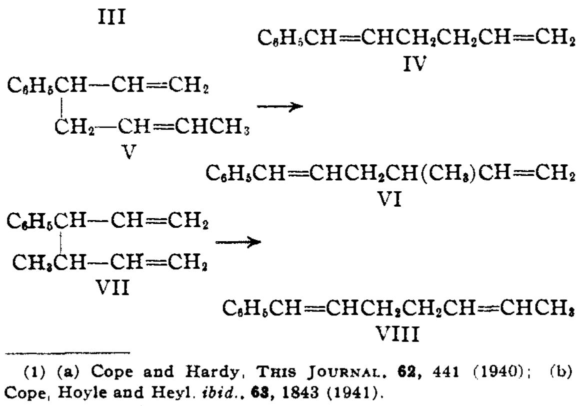
I II

(R = H or $CH_3$)

The allyl-type group has been shown to undergo inversion in two such cases, as indicated in the equation.[2] This fact, together with first-order reaction kinetics and the observation that no interchange of migrating groups occurs when a mixture of two such compounds is heated, indicates that the rearrangement proceeds by an intramolecular cyclic mechanism.

The influence of the groups, X and Y, is presumed to be derived from electron attraction, which enables the allyl group to release the electron pair binding it to the $\alpha$-carbon atom. A conjugated double bond is formed in the $\alpha,\beta$-position while, at the same time, the allyl group becomes attached in the $\gamma$-position. Less strongly activated systems, in which the negative groups, X and Y, are phenyl and nitrile groups or in which a single nitrile or carboxyl group is attached to the $\alpha$-carbon atom, also undergo the rearrangement.[3] The work now being reported was undertaken to find the least activation which would permit occurrence of the rearrangement.

The hydrocarbons III, V and VII have been synthesized and their behavior on heating has been determined. They rearranged at 165–185° in the manner shown in the following equations.



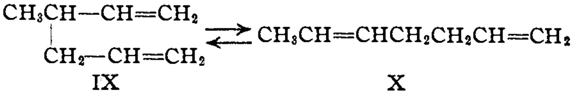
$$\begin{array}{l}C_6H_5CH-CH=CH_2\\ \quad CH_2-CH=CH_2\\ \quad\text{III}\end{array}\longrightarrow C_6H_5CH=CHCH_2CH_2CH=CH_2\ \text{IV}$$

$$\begin{array}{l}C_6H_5CH-CH=CH_2\\ \quad CH_2-CH=CHCH_3\\ \quad\text{V}\end{array}\longrightarrow C_6H_5CH=CHCH_2CH(CH_3)CH=CH_2\ \text{VI}$$

$$\begin{array}{l}C_6H_5CH-CH=CH_2\\ \ CH_3CH-CH=CH_2\\ \quad\text{VII}\end{array}\longrightarrow C_6H_5CH=CHCH_2CH_2CH=CHCH_3\ \text{VIII}$$

Evidently, a single phenyl group provides sufficient activation for the rearrangements. Proof of the structures of the pairs, V → VI and VII → VIII, shows that in these rearrangements the allyl group undergoes inversion.

The aliphatic diolefin, IX, also rearranged, although incompletely, giving X when heated at 300°. The reverse rearrangement proceeded to a limited extent at the same temperature.



$$\begin{array}{l}CH_3CH-CH=CH_2\\ CH_2-CH=CH_2\\ \quad\text{IX}\end{array}\rightleftarrows CH_3CH=CHCH_2CH_2CH=CH_2\ \text{X}$$

This isomerization establishes the surprising fact that no negative group must be present to weaken the bond between the allyl group and the $\alpha$-carbon atom and to form a conjugated system in the rearrangement. It also proves that the rearrangement may be reversible when the stabilities of the two isomers are similar. The high temperature required for this reaction and the fact that it does not go to completion substantiate the ideas previously expressed concerning the function of negative groups in labilizing such systems to rearrangement.

Synthesis, rearrangement, and proof of structure of the hydrocarbons were accomplished in the following manner. Allylbenzene was converted into a sodium salt with sodamide and alkylated in liquid ammonia solution with allyl bromide, crotyl chloride, and methylvinylcarbinyl chloride to yield III, V and VII, respectively. Since rearrangements might occur in this synthesis, it was necessary to prove the structure of each of the products. III was hydrogenated quantitatively to 3-phenylhexane and converted into 3-(2,4-diacetamino)-phenylhexane, which was identical with a known sample. V and VII were degraded by ozonization, followed by cleavage of the ozonides with hydrogen peroxide, to known succinic acid derivatives. V yielded phenylsuccinic acid, which was converted into phenylsuccinanilic acid, and VII gave $\alpha$-phenyl-$\beta$-methylsuccinic acid, further identified as the imide.

III rearranged, without decomposition or polymerization on heating at 176–178° in a nitrogen atmosphere for twenty-six hours, to IV, which was isolated in 72% yield. The structure of IV was established by quantitative catalytic hydrogenation to 1-phenylhexane, which was converted into 1-(2,4-diacetamino)-phenylhexane. In addition, succinic acid, benzoic acid and formaldehyde (as the methone derivative) were isolated as cleavage products from the ozonization of IV. V was converted into VI in 72% yield by heating under nitrogen for sixty-five hours at 165–185°. Ozonization of VI led to benzoic acid and methyl-

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(1) (a) Cope and Hardy, THIS JOURNAL, **62**, 441 (1940); (b) Cope, Hoyle and Heyl, *ibid.*, **63**, 1843 (1941).

(2) Cope, Hofmann and Hardy, *ibid.*, **63**, 1852 (1941).

(3) Whyte and Cope, *ibid.*, **65**, 1999 (1943).

succinic acid. VII rearranged to VIII in 90% yield on heating at 170–185° for thirty-one hours under nitrogen. The structure of VIII also was proved by ozonization, from which benzoic and succinic acids were obtained.

The diolefin, X, has been prepared previously from allylmagnesium bromide and crotyl bromide,[4] and both IX and X have been prepared by reaction of a mixture of the crotyl chlorides and allyl chloride with magnesium.[5] In this work, it was found more convenient to prepare IX by reaction of allyl bromide with the Grignard reagent prepared from methylvinylcarbinyl bromide (yield 50–54%) and X by reaction of primary crotyl chloride with allylmagnesium bromide (yield 53%). Boiling points and refractive indices of IX and X checked values reported previously[4,5] very closely. Their structures were verified by ozonization; IX yielded methylsuccinic acid and X, succinic acid.

When IX was heated at 300° for twenty-four hours under nitrogen in a sealed tube, pure X was isolated from the product by fractional distillation in yields of 14 and 20% in duplicate runs. The lower boiling fractions appeared to be mixtures of IX and X. The identity of X produced by this rearrangement was established by its boiling point and refractive index and by ozonization, which yielded succinic acid. On identical treatment of X, 21–33% was recovered unchanged and lower boiling fractions were obtained from which the small amount of IX present could not be isolated in a completely pure state. Its presence in the fraction of approximately correct boiling point was proved by ozonization, which produced methylsuccinic acid together with succinic acid derived from the unchanged X which was present. Henne and Turk[6] have observed the partial isomerization of X to IX under more drastic conditions, *i. e.*, when the hydrocarbon was passed over activated alumina in the gas phase at 365°.

The preparation of III was first attempted from the acetylene derivative, $C_6H_5CH(C_3H_5)$-$C{\equiv}CH$ (XI), which was obtained from 3-chloro-3-phenylpropyne and allylmagnesium bromide. Reduction of XI with sodium and liquid ammonia under various conditions did not lead to a pure product, because the double bond formed in the reduction migrated either partly or completely into conjugation with the ring. The rate of reduction of XI in the presence of Raney nickel did not change after the absorption of one mole of hydrogen.

Preliminary work has been done on the synthesis of the octatriene, $CH_2{=}CHCH(C_3H_5)$-$CH{=}CH_2$ (XII). 1,4-Pentadiene was converted into a sodium salt[7] with sodamide in liquid ammonia and alkylated with allyl bromide. The product is believed to be XII from its analysis, method of synthesis, and normal molecular refraction. Insufficient material was available for a complete proof of structure and study of its rearrangement.

## Experimental[8]

**3-Phenyl-1,5-hexadiene (III).**—Allylbenzene was prepared from phenylmagnesium bromide and allyl bromide[9]; yield 86–88%, b. p. 40–40.5° (8 mm.), $n^{25}D$ 1.5082. Sodium (4.0 g., 0.174 atom) was converted into sodamide in 300 ml. of liquid ammonia in a 500-ml. three-necked flask[10] marked with approximate volume graduations. Allylbenzene (20.7 g., 0.174 mole) was added under slight nitrogen pressure, with stirring and without external cooling during ten minutes. It formed a soluble, dark red sodium salt. Stirring was continued for ten minutes. In the meantime, liquid ammonia (200 ml.) was placed in a second 500-ml. three-necked flask, fitted with a mercury-sealed stirrer, reflux condenser protected by a soda-lime tube, and a graduated dropping funnel containing 21.4 g. (0.177 mole) of allyl bromide. The flask containing the sodium salt was then connected to an ammonia cylinder and a soda-lime tube connected to a gas absorption trap. A tube reaching to the bottom of this flask was attached to a neck of the second flask. Allyl bromide and the solution of the sodium salt were then added simultaneously to the second flask during about twenty minutes, with stirring and without external cooling. The allyl bromide was added at such a rate that it was always in slight excess, judged by the volumes of liquid in the graduated funnel and flask and the fact that the red color of the sodium salt was discharged immediately on reaction with allyl bromide. The sodium salt was forced into the second flask by ammonia pressure created by pinching the rubber connection to the gas trap. The allyl bromide was also forced in under slight nitrogen pressure. The transfer of the sodium salt was completed by rinsing with liquid ammonia. After the addition was complete, dry ether (50 ml.) was added and stirring was continued until the ammonia had vaporized. The mixture was then refluxed for fifteen minutes. It was cooled and added to a mixture of ice and water containing 1 ml. of concd. sulfuric acid. The ether layer was separated and the aqueous layer was extracted with ether. The combined ether solutions were washed successively with water, saturated sodium bicarbonate, and water. After drying over sodium sulfate, the product was distilled through a 15-cm. Widmer column, yielding 15.8 g. (57%) of III, b. p. 78° (8 mm.); $n^{25}D$ 1.5141; $d^{25}_4$ 0.8911; *M*D calcd. 53.09, found 53.47.

*Anal.* Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.30; H, 8.87.

A similar preparation using 0.9 mole quantities gave 53% of III.

**3-Phenyl-1,5-heptadiene (V).**—V was prepared, by the method described above, from 41.4 g. of allylbenzene, the sodamide from 8.0 g. of sodium, and 33.0 g. of pure primary crotyl chloride.[11] This procedure yielded 39.4 g. (65%) of V. On redistillation through a Widmer column, V had b. p. 64–65° (1.0 mm.); $n^{25}D$ 1.5135; $d^{25}_4$ 0.8893; *M*D calcd. 57.71, found 58.27.

*Anal.* Calcd. for $C_{13}H_{16}$: C, 90.60; H, 9.40. Found: C, 90.57; H, 9.46.

**3-Methyl-4-phenyl-1,5-hexadiene (VII).**—The preparation of VII was identical with that of V, except that an equal amount of 3-chloro-1-butene (methylvinylcarbinyl chloride)[11] was used. The yield of pure VII was 39.3 g. (65%), which on redistillation through a Widmer column had b. p. 103–103.5° (18 mm.); $n^{25}D$ 1.5122; $d^{25}_4$ 0.8899; *M*D calcd. 57.71, found 58.11.

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[4] Slotterbeck, Ph.D. Dissertation, Ohio State University, 1936.

[5] Henne, Chanan and Turk, THIS JOURNAL, **63**, 3474 (1941).

[6] Henne and Turk, *ibid.*, **64**, 826 (1942).

[7] This sodium derivative has been prepared and carbonated by Taylor and Connor, *J. Org. Chem.*, **6**, 696 (1941).

[8] Melting points are corrected and boiling points are uncorrected.

[9] Hershberg, *Helv. Chim. Acta*, **17**, 351 (1934).

[10] See THIS JOURNAL, **60**, 2644 (1938) for the general procedure.

[11] Roberts, Young and Winstein, *ibid.*, **64**, 2163 (1942).

*Anal.* Calcd. for $C_{13}H_{16}$: C, 90.60; H, 9.40. Found: C, 90.88; H, 9.40.

**Structure of III.**—In a quantitative hydrogenation, 0.398 g. of III absorbed 109 ml. of hydrogen (97% of two molar equivalents) in alcohol solution in the presence of 0.5 g. of palladinized charcoal.[12] Reduction of 10.3 g. of III in the same manner gave 8.8 g. (84%) of 3-phenylhexane, b. p. 84° (12 mm.); $n^{25}$D 1.4843; $d^{25}_4$ 0.8563; *M*D calcd. 54.03, found 54.25. These physical constants agree with values reported previously.[13] This sample of 3-phenylhexane was converted into 3-(2,4-diacetamino)-phenylhexane by the general procedure of Ipatieff and Schmerling[14] in 70% yield; m. p. 207–208° after recrystallization from 25% ethanol.[15]

*Anal.* Calcd. for $C_{16}H_{24}N_2O_2$: C, 69.52; H, 8.75. Found: C, 69.57; H, 8.77.

A known sample of 3-phenylhexane was prepared by treating propiophenone with propylmagnesium iodide, dehydrating the resulting carbinol by refluxing with iodine in benzene solution, and hydrogenating the mixture of olefins produced, in the presence of palladinized charcoal. The yield of 3-phenylhexane prepared in this manner was 72%, based on the carbinol; b. p. 80° (10 mm.); $n^{25}$D 1.4843; $d^{25}_4$ 0.8566; *M*D calcd. 54.03, found 54.25. The m. p. of the diacetamino derivative and its mixed m. p. with the sample described above was 207–208°.

**Rearrangement of III.**—The isomerization of III proceeded very slowly at 150° but readily at 176–178°. III (25 g.) was heated at 176–178° under an atmosphere of nitrogen for a total of twenty-six hours.[16] Distillation through a Widmer column yielded 18 g. (72%) of practically pure IV, which on redistillation had b. p. 102.5–103.5° (8 mm.); $n^{25}$D 1.5421; $d^{25}_4$ 0.9005; *M*D calcd. 53.09, found 55.28 (exaltation 2.19).

*Anal.* Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.23; H, 8.97.

**Structure of 1-Phenyl-1,5-hexadiene (IV).**—IV (4.704 g.) absorbed 1335 ml. of hydrogen (100.3% of two molar equivalents) in alcohol solution in the presence of 1 g. of palladinized charcoal. Distillation yielded 4.4 g. (91%) of 1-phenylhexane, b. p. 92° (7.5 mm.); $n^{25}$D 1.4840; $d^{25}_4$ 0.8549; *M*D calcd. 54.03, found 54.29.[17]

1-(2,4-Diacetamino)-phenylhexane was prepared from this sample in 63% yield, m. p. 205–206° after recrystallization from 40% ethanol.[18] Mixed m. p. with the corresponding derivative of 3-phenylhexane was depressed to 171.5–173.5°.

*Anal.* Calcd. for $C_{16}H_{24}N_2O_2$: C, 69.52; H, 8.75. Found: C, 69.45; H, 8.60.

A sample of 1-phenylhexane prepared by the hydrogenation of caprophenone[17c] in the presence of palladinized charcoal had b. p. 90° (7 mm.), $n^{25}$D 1.4839, and gave a diacetamino derivative identical with the one obtained from the reduction product of IV.

IV (2.06 g.) in 40 ml. of dry ethyl acetate was ozonized at −25° until a test portion no longer absorbed bromine. After removal of the solvent, the residue was refluxed with 30 ml. of water and 17 ml. of 30% hydrogen peroxide for fourteen hours. After decolorization with Norite and cooling, 0.58 g. of benzoic acid crystallized. Succinic acid (0.88 g.) was obtained by extracting the filtrate with a small volume of ether and concentrating the aqueous solution. Both were identified by mixed m. p.

The ozonide from a similar procedure was decomposed by hydrogenation at 0°[19] in the presence of palladinized charcoal. Treatment with methone gave the formaldehyde derivative, m. p. and mixed m. p. 192–192.5°.

**Structure of V.**—V (2.2 g.) was ozonized at about −45° in ethyl acetate solution. The solvent was removed *in vacuo* and the residue heated with 60 ml. of glacial acetic acid and 17 ml. of 30% hydrogen peroxide for three hours on the steam-bath. Concentration *in vacuo* left a sirup which was dissolved in ether, washed with water and acidified 2% ferrous sulfate.[20] Acids were extracted with sodium bicarbonate and re-extracted into ether after acidification. A combination of crystallization from benzene and sublimation of the residue from the mother liquor gave 0.4 g. of slightly impure phenylsuccinic acid. The m. p. of this acid after recrystallization from water was 169.5°, in agreement with recorded values.[21] The acid was converted into phenylsuccinanilic acid by the procedure of Hann and Lapworth[21b]; m. p. 171–171.5°.[21b,22]

**Rearrangement of V.**—V (12.3 g.) was heated for a total of sixty-five hours at 165–185°. Distillation through a Widmer column gave 8.9 g. (72%) of VI, which on redistillation had b. p. 66.5–69° (0.21 mm.); $n^{25}$D 1.5336; $d^{25}_4$ 0.8916; *M*D calcd. 57.71, found 60.02 (exaltation 2.31).

*Anal.* Calcd. for $C_{13}H_{16}$: C, 90.60; H, 9.40. Found: C, 90.90; H, 9.36.

**Structure of 4-Methyl-1-phenyl-1,5-hexadiene (VI).**—VI (1.1 g.) was ozonized in the same manner as V. After removal of the acetic acid and hydrogen peroxide, water was added to the residue and the solution reconcentrated. Then, re-addition of water and filtration yielded 0.17 g. of benzoic acid. After extraction of the filtrate with a small volume of chloroform, the water was removed and the residue crystallized from benzene, yielding 0.37 g. of methylsuccinic acid, m. p. 109.5–110° after recrystallization. This m. p. was not depressed on mixture with a known sample (m. p. 110–111°) prepared from ethyl crotonate and potassium cyanide.[23]

**Structure of VII.**—VII (2.7 g.) was ozonized in the same manner as V. Crystallization from benzene and sublimation of the residue from the mother liquor gave 0.26 g. of α-phenyl-β-methylsuccinic acid, m. p. 174–176° after recrystallization from benzene.[24] The acid was converted into the corresponding imide by distilling its ammonium salt.[24] The imide after recrystallization from ether and pentane had m. p. 107–107.5°, which was not depressed on mixture with a known sample kindly furnished to us by Dr. McRae.

**Rearrangement of VII.**—VII (15.5 g.) was rearranged to VIII by heating at 170–185° in a nitrogen atmosphere for thirty-one hours. The yield of VIII was 13.9 g. (90%). On redistillation through a Widmer column, it had b. p. 77–78° (0.6 mm.); $n^{25}$D 1.5407; $d^{25}_4$ 0.9012; *M*D calcd. 57.71, found 60.04 (exaltation 2.33).

*Anal.* Calcd. for $C_{13}H_{16}$: C, 90.60; H, 9.40. Found: C, 90.40; H, 9.45.

**Structure of 1-Phenyl-1,5-heptadiene (VIII).**—VIII (1.9 g.) was ozonized in the same manner as V. Benzoic acid (0.85 g.) was isolated by crystallization from water, and succinic acid (1.31 g.), by washing the filtrate with a small volume of ether and concentrating the aqueous layer. Both were identified by mixed m. p.

**3-Methyl-1,5-hexadiene (IX).**—3-Bromo-1-butene[25] (141 g., 1.04 moles) in 775 ml. of dry ether was added to 150 g. (6 atoms) of magnesium turnings under 500 ml. of

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[12] Hartung, THIS JOURNAL, **50**, 3372 (1928).

[13] Spiegler and Tinker, *ibid.*, **61**, 1002 (1939).

[14] Ipatieff and Schmerling, *ibid.*, **59**, 1056 (1937).

[15] Gilman and Meals, *J. Org. Chem.*, **8**, 126 (1943), report m. p. 199–201°.

[16] See ref. 1b for the procedure followed to insure complete rearrangement.

[17] These physical constants are in fair agreement with values reported by (a) Schmidt, Hopp and Schoeller, *Ber.*, **72B**, 1893 (1939); (b) Simon, *Bull. soc. chim. Belg.*, **38**, 47 (1929); (c) Ju, Shen and Wood, *J. Inst. Petroleum*, **26**, 514 (1940).

[18] Ref. 15 reports m. p. 200–202°.

[19] Fischer, Düll and Ertel, *Ber.*, **65**, 1467 (1932).

[20] Modeled after a procedure described by Smith and Rouault, THIS JOURNAL, **65**, 745 (1943).

[21] (a) Higson and Thorpe, *J. Chem. Soc.*, **89**, 1472 (1906); (b) Hann and Lapworth, *ibid.*, **85**, 1365 (1904).

[22] Anschütz, *Ann.*, **354**, 136 (1907).

[23] Higginbotham and Lapworth, *J. Chem. Soc.*, **121**, 49 (1922).

[24] McRae and McGinnis, *Can. J. Research*, **18B**, 90 (1940), report m. p. 173–174°.

[25] Winstein and Young, THIS JOURNAL, **58**, 104 (1936).

dry ether in a 2-l. three-necked flask over a period of seventeen hours, with efficient stirring and in a nitrogen atmosphere.[26] The reaction mixture was refluxed for fifteen minutes, cooled and filtered through glass wool by nitrogen pressure into another three-necked flask. Titration, using phenolphthalein as the indicator,[27] showed that the yield of Grignard reagent was 72%.[28] Allyl bromide (86.5 g., 0.72 mole) was added during one and one-half hours, with sufficient cooling to keep the reaction mixture at room temperature. The mixture was stirred for one and one-half hours, refluxed for one hour, cooled in ice, and added slowly with stirring to ice and dilute sulfuric acid. The ether solution was washed with cold water and saturated sodium bicarbonate and dried over sodium sulfate. Distillation through an adiabatic, total reflux, variable take-off column with a 70 × 1.2 cm. section packed with glass helices yielded 34.6 g. (50%) of IX, b. p. 80–81°, $n^{20}_{\mathrm{D}}$ 1.4099. The fractions boiling between 82 and 100° were too small (8.4 g.) for the isolation of X from the preparation.

**1,5-Heptadiene (X).**—Allylmagnesium bromide was prepared from 150 g. of allyl bromide in 730 ml. of dry ether and 90 g. of magnesium turnings under 370 ml. of dry ether during ten hours in a nitrogen atmosphere.[29] The ether solution was filtered through glass wool under nitrogen pressure, 1-Chloro-2-butene[11] (110 g.) was added during three hours, allowing the solution to reflux, and the preparation and purification were completed as described for IX. The yield of X was 62.6 g. (53.5%), b. p. 94.0–94.5°, $n^{20}_{\mathrm{D}}$ 1.4199.

The reaction of 3-chloro-1-butene and allylmagnesium bromide under the conditions outlined above resulted in 14–17% yields of slightly impure IX and 29–38% of pure X. In all of these preparations, the Grignard reagents were used in slight excess to minimize the presence of the halogen compounds in the products.

**Structure of IX.**—Physical constants previously reported[5] for IX (b. p. 80°, $n^{20}_{\mathrm{D}}$ 1.4116) correspond closely to the constants noted above. Its structure was confirmed by ozonization of a 1.0-g. sample at −65° followed by decomposition of the ozonide with hydrogen peroxide as described for V. Methylsuccinic acid (0.85 g.) was isolated and identified by mixed m. p. with a known sample.

**Structure of X.**—Physical constants previously reported for X (b. p. 94–94.4°; 93.7°; $n^{20}_{\mathrm{D}}$ 1.4196; 1.4200)[4,5] are in excellent agreement with the properties of X prepared in this work. Confirmation of its structure was obtained by ozonization of a 1.0-g. sample, as outlined for IX, which yielded 1.05 g. of succinic acid, identified by m. p. and mixed m. p. with a known sample.

**Rearrangement of IX.**—IX (21.5 g.) was heated in a sealed tube under nitrogen at 300–305° for twenty-four hours. The product was distilled through an adiabatic, total reflux, variable take-off column with a 30 × 1.1 cm. section packed with glass helices. Fractions obtained were: (a) 6.2 g. of a mixture of IX and X b. p. 86–94°, $n^{20}_{\mathrm{D}}$ 1.4149–1.4192; (b) 4.2 g. (20%) of X, b. p. 94–95°, $n^{20}_{\mathrm{D}}$ 1.4210. Distillation of the residue through a smaller column gave: (c) 2.0 g. of X, b. p. 94–95°, $n^{20}_{\mathrm{D}}$ 1.4220; (d) 6.1 g. of distillation residue (partly holdup, partly higher boiling material).

Ozonization of 1.0 g. of fraction (b) gave 0.97 g. of slightly impure succinic acid, identified by m. p. and mixed m. p. after recrystallization.

**Rearrangement of X.**—X was recovered unchanged after refluxing or after heating in sealed tubes at 200 and 225°, all for twenty-four hours under nitrogen.

A sample heated at 330–340° was almost completely polymerized, as was one at 300–305°. Some rearrangement and relatively little polymerization occurred at 300–305° in the remaining cases, as in the following example.

A 49-g. sample was heated at 300–305° for twenty-four hours and then separated by distillation without fractionation into 34.8 g., b. p. 90–100°, and 13.6 g. of higher boiling material. Redistillation of the distillate through the column with a 30 × 1.1 cm. packed section gave: (a) 11.0 g. of a mixture of IX and X, b. p. 87.5–94°, $n^{20}_{\mathrm{D}}$ 1.4141–1.4193; (b) 16.4 g. (33%) of X, b. p. 94–96°, $n^{20}_{\mathrm{D}}$ 1.4198–1.4211; (c) 4.0 g. hold-up.

A 1.0-g. sample of fraction (a), b. p. 87.5–89°, $n^{20}_{\mathrm{D}}$ 1.4141, on ozonization gave a mixture of acids which was separated by fractional crystallization from benzene into 0.38 g. of succinic acid and 0.07 g. of methylsuccinic acid. Both were identified by m. p. and mixed m. p.

**3-Phenylhexen-5-yne-1 (XI).**—Phenylethynylcarbinol was prepared from benzaldehyde and sodium acetylide. Yields were 63–68% when acetylene was passed through the reaction mixture while the benzaldehyde was added.[30]

Redistilled phosphorus trichloride (77 g.) was added with stirring during two hours to a mixture of 203 g. of phenylethynylcarbinol, 31 g. of dry pyridine and 320 ml. of dry ether at −2 to +2°. Stirring was continued while the mixture came to room temperature (one hour) and remained at room temperature for six hours. It was poured into ice and water, and the ether layer was washed with water, saturated sodium bicarbonate, and water, all at 5°. The ether solution was dried over sodium sulfate and distilled through a Widmer column *in vacuo* under nitrogen and with a trace of hydroquinone, yielding 156 g. (67%) of 3-chloro-3-phenylpropyne, b. p. 58.5–60° (1 mm.); $n^{25}_{\mathrm{D}}$ 1.5508; $d^{25}_{4}$ 1.1004; $M_{\mathrm{D}}$ calcd. 43.03, found 43.65.

*Anal.* Calcd. for $C_9H_7Cl$: C, 71.77; H, 4.69. Found: C, 71.64; H, 4.79.

The chloro compound is a lachrymator and skin irritant. The corresponding bromide could not be distilled without decomposition, even at $1 \times 10^{-4}$ mm.

Allylmagnesium bromide was prepared by adding 121 g. of allyl bromide in 580 ml. of dry ether to 73 g. of magnesium turnings under 200 ml. of dry ether during seven and one-half hours.[29] The Grignard reagent was filtered through glass wool under nitrogen pressure; yield by titration, 83%. 3-Chloro-3-phenylpropyne (48.6 g.) in 125 ml. of dry ether was added during one and one-half hours. After being stirred for one hour and allowed to stand overnight, the mixture was added slowly to ice and water and acidified with cold 20% hydrochloric acid. The ether solution was washed successively with water, saturated sodium bicarbonate solution and water, and dried over sodium sulfate. Distillation through a Vigreux column gave 38 g. of crude XI, and redistillation through a Widmer column gave 16.8 g. (34%) of pure XI, b. p. 60.5–61° (1.6 mm.); $n^{25}_{\mathrm{D}}$ 1.5228; $d^{25}_{4}$ 0.9214; $M_{\mathrm{D}}$ calcd. 51.56, found 51.77.

*Anal.* Calcd. for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92.53; H, 7.82.

The presence of an acetylenic hydrogen in XI was established by the fact that it formed a mercury derivative.[31]

Reduction of XI with sodium and liquid ammonia[32] gave a product which had a correct analysis for III, did not form a mercury derivative,[31] and absorbed two moles of hydrogen in a quantitative reduction. The product had an exaltation in molecular refraction, however, which indicated that the double bond had migrated into conjugation with the ring. When ammonium sulfate was present during the addition of the sodium,[33] the product had a boiling point and a refractive index in approximate agreement

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(26) Young, *et al.*, THIS JOURNAL, **55**, 4908 (1933).

(27) Gilman, Wilkinson, Fishel and Meyers, *ibid.*, **45**, 150 (1923).

(28) Young, Winstein and Prater, *ibid.*, **58**, 289 (1936); Young, Kaufman, Loshokoff and Pressman, *ibid.*, **60**, 900 (1938); Young, Ballou and Nozaki, *ibid.*, **61**, 12 (1939), and Young and Pokras, *J. Org. Chem.*, **7**, 233 (1942), have presented evidence indicating that this reagent consists of 56% of methylvinylcarbinylmagnesium bromide and 44%, crotylmagnesium bromide. IX and X have been prepared by this method by Wax, M. A. Dissertation, University of California, Los Angeles, 1940.

(29) Gilman and McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928).

(30) Campbell, Campbell and Eby, THIS JOURNAL, **60**, 2882 (1938). Jones and McCombie, *J. Chem. Soc.*, 733 (1942), have increased the yield to 82.5% by continuing the passage of acetylene for three hours.

(31) Johnson and McEwen, THIS JOURNAL, **48**, 469 (1926).

(32) Campbell and Eby, *ibid.*, **63**, 216, 2683 (1941).

(33) Henne and Greenlee, *ibid.*, **65**, 2020 (1943).

with the constants for III. Its purification was not attempted since the preparation outlined above for III is simpler and leads to a purer product.

**3-Vinyl-1,5-hexadiene (XII).**—1,4-Pentadiene was prepared by the Boord synthesis.[34] XII was prepared by alkylating the sodium salt, prepared from 23.4 g. of 1,4-pentadiene and the sodamide obtained from 7.94 g. of sodium with 41.8 g. of allyl bromide. The procedure described for III was followed, except that a dry-ice condenser was used to condense the low-boiling hydrocarbons in the preparation of the sodium salt and in the alkylation. Distillation through the column with a 30 × 1.1 cm. packed section gave 7.7 g. (21%) of crude XII, b. p. 101–106°. After repetition of the alkylation, the combined products were redistilled, yielding XII with b. p. 103–103.5°; $n^{25}\text{D}$ 1.4301; $d^{25}_4$ 0.7410; $M\text{D}$ calcd. 37.75, found 37.73.

*Anal.* Calcd. for $C_8H_{12}$: C, 88.80; H, 11.20. Found: C, 88.97; H, 11.23.

We are indebted to Miss Frances Marx, Miss Lois E. May, and Mr. Saul Gottlieb for all the microanalyses reported in this work.

## Summary

3-Phenyl-1,5-diolefins (III, V and VII) have been prepared by the alkylation of the sodium salt of allylbenzene with allyl bromide, crotyl chloride and methylvinylcarbinyl chloride in liquid ammonia solution. These hydrocarbons rearrange on heating at 165–185°, yielding 1-phenyl-1,5-diolefins. Inversion of the two butenyl groups occurs during the rearrangement of V and VII. 3-Methyl-1,5-hexadiene has been shown to rearrange partially to 1,5-heptadiene on heating at 300°. The reverse rearrangement occurs to a limited extent at the same temperature.

These observations extend the scope of three-carbon systems in which allyl groups are known to rearrange and establish the reversibility of the rearrangement for a case in which the two isomers have similar stabilities.

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(34) Shoemaker and Boord, This Journal, **53**, 1505 (1931); Kistiakowsky, Ruhoff, Smith and Vaughan, *ibid.*, **58**, 146 (1936).

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[Contribution from the Laboratory of Organic Chemistry of the University of Wisconsin]

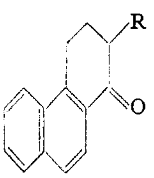
# 16-Equilenone and 16,17-Substituted Equilenane Derivatives

By A. L Wilds and Lloyd W. Beck

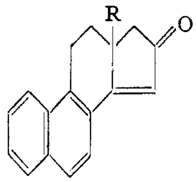
Recently[1] a method was described for the synthesis of partially hydrogenated 1,2-cyclopentenophenanthrene derivatives related to the female sex hormones. The ketone IIIa was prepared by cyclization of the substituted diketo ester (or the related 1,4-diketone) which resulted from the reaction of 2-bromo-1-ketotetrahydrophenanthrene (I) with acetoacetic ester. Since the sex hormones carry a methyl group between the C and D rings, the extension of this method to the homolog of IIIa containing the angular methyl group (III) was of especial interest.

Such an extension of the method would involve the alkylation of acetoacetic ester with a tertiary halide, the 2-methyl-2-bromo ketone corresponding to I, a type of reaction which usually results in dehydrohalogenation rather than the desired alkylation. A test of this step was made, however, using sodiomalonic ester since any alkylation product could be isolated easily, subsequent to hydrolysis and decarboxylation. An improved method was developed for the preparation of 1-keto-2-methyltetrahydrophenanthrene (II) from which the necessary bromo ketone was obtained in excellent yield by bromination.

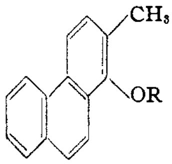
By condensation of the bromo ketone with sodiomalonic ester, it was possible to obtain the acid V in 24% yield. Although the yield was much higher than anticipated, it was still too low to make this a practical synthetic approach. The acid was accompanied by a phenolic fraction from which was isolated 2-methyl-1-phenanthrol (IV) in 18 to 30% yield. This phenanthrol, which has not been described previously, could be prepared in excellent yield by the action of boiling 2,4,6-trimethylpyridine on the bromo ketone to eliminate hydrogen bromide. Upon methylation the phenanthrol gave a methyl ether IVa which agreed in melting point with the compound prepared by Hill and Short[2] in low yield from 3-methyl-2-methoxyphenylacetic acid through the Pschorr synthesis.



I R = Br
II R = $CH_3$



III R = $CH_3$
IIIa R = H



IV R = H
IVa R = $CH_3$

As a more satisfactory method of preparing the desired intermediate compounds for the synthesis of III, we investigated the direct alkylation of the ketone II through reaction of its sodium enolate with an appropriate bromo compound. The enolate, prepared by means of sodium amide, reacted readily with methyl bromoacetate to give

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(1) Wilds, This Journal, **64**, 1421 (1942).

(2) Hill and Short, *J. Chem. Soc.*, 260 (1937).