The crude product was distilled, b. 97–110° (1 mm.). The viscous distillate was chilled and scratched, crystallizing readily. Recrystallization from a mixture of ether and ligroin afforded a white solid, m.p. 41–44°, in substantial agreement with the literature.[12]

The recrystallized diol (3.0 g.), Raney nickel[13] (*ca.* 12 g.) and absolute ethanol (50 ml.) were heated under reflux during six hours, whereupon the mixture was filtered and the cake rinsed with hot ethanol (100 ml.). The filtrate and washings were added to water (700 ml.), and the turbid mixture was extracted twice with ligroin. The extract was dried ($MgSO_4$) and the solvent was distilled through a small column. The residue was distilled through a semi-micro Claisen still, providing 1.2 g. of liquid, b.p. 95–134°. A small residue remained undistilled, whose infrared spectrum indicated it to be 2-phenyl-1-propanol. The distillate was redistilled and a fraction having b.p. 120–134° was collected. From this was prepared[14] a sample of 2,4-diacetylaminoethylbenzene, m.p. 224–226° (lit. 224°)[15] mixed m.p. with an authentic sample undepressed, whose infrared spectrum was identical in all respects with that of an authentic sample.

Experiments in Table I.—Each of the reactants listed in Table I was treated with Raney nickel in refluxing ethanol in the manner described above. The catalyst was filtered and washed with ethanol. The filtrate and washings were distilled approximately to dryness through a $^3/_8 \times 18''$ Stedman column. The residue was investigated for sparingly volatile materials with the aid of a vapor–liquid partition chromatographic column.[16] The distillate was treated with about a liter of water, and the mixture was continuously extracted with redistilled pentane until clear. The pentane extract was dried over phosphoric anhydride, after which the solvent was distilled through the Stedman column. The residue from this process was similarly investigated for volatile hydrocarbon components on the VLPC column.

The vapor–liquid partition column which was employed consisted of a thermostated $^1/_2 \times 48''$ glass tube with a Celite–silicone (2:1) packing. Helium at 5 p.s.i. pressure was used as a carrier gas, a tungsten lamp filament provided the detector,[17] and component efflux times were recorded on a Varian G-10 recorder. For characterization of each component two criteria were used: (1) component efflux times were compared with the efflux times under identical VLPC column conditions for authentic samples, and (2) each component from the VLPC column was isolated by chilling the exit gas stream in a Dry Ice–acetone-bath, then the infrared spectrum of the collected fraction was compared with that of an authentic sample. Rough estimates of the composition of each mixture placed on the VLPC column were obtained by comparing the recorded fraction peak-heights with the peak-heights obtained from similar mixtures of known composition.

The main products from these experiments are listed in Table I. In several reactions, notably 12–15, small amounts of additional by-products were isolated. These were characterized where possible by comparison of their efflux times on the VLPC column with those of authentic samples. Unfortunately these by-products were produced in such small quantities on the reaction scale employed that they could not be collected from the VLPC column for subsequent infrared examination. Thus in experiment 12 a trace of ethylbenzene resulted. In 13 a trace of toluene was found. In 14 the main product from the VLPC column appeared to be 3-cyclohexyl-1-propanol, $n^{20}{}_D$ 1.4761.

Anal. Calcd. for $C_9H_{18}O$: C, 75.99; H, 12.76. Found: C, 76.05, 76.07; H, 12.00, 11.96.

In addition smaller quantities of ethylbenzene, *n*-propylbenzene, toluene, ethylcyclohexane and methylcyclohexane were formed. The former two hydrocarbons were further characterized by comparison of their infrared spectra with authentic samples. In 15 very little reaction occurred, though five products were evident in too small quantity for isolation from the VLPC column. The efflux times of two of these products corresponded to the efflux times noted for methylcyclohexane and ethylcyclohexane.

---

[12] E. Eliel and J. Freeman, THIS JOURNAL, **74**, 923 (1952).

[13] R. Mozingo, *Org. Syntheses*, **21**, 15 (1941).

[14] N. Cheronis and J. Entrikin, "Semimicro Qualitative Organic Analysis," Thos. Y. Crowell Co., New York, N. Y., 1947, p. 314.

[15] G. Weisweiller, *Monatsh.*, **21**, 41 (1900).

[16] A. J. P. Martin and co-workers, *Biochem. J.*, **35**, 1358 (1941); **50**, 679 (1951).

[17] R. H. Eastman and H. S. Mosher, private communication.

STANFORD, CALIFORNIA

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Sodium-catalyzed Hydrogen Disproportionation of Phenylcyclohexene. Dehydrogenation and Condensation of Phenylcyclohexane[1]

BY HERMAN PINES AND MARJAN KOLOBIELSKI[2]

RECEIVED OCTOBER 26, 1956

1-Phenylcyclohexene on heating in the presence of sodium or sodium–benzylsodium catalyst at 200–220° undergoes a hydrogen transfer reaction resulting in the formation of two mole equivalents of phenylcyclohexane and one mole equivalent of biphenyl. When the temperature of the reaction was raised to 240°, hydrogen was evolved and the relative ratio of biphenyl to phenylcyclohexane steadily increased. The reaction also was accompanied by the formation of isomeric quaterphenyls obtained from the condensation of biphenyl with the liberation of hydrogen. 4,4′- and 3,4′-diphenylbiphenyl were isolated from the reaction product. Phenylcyclohexane underwent dehydrogenation to biphenyl when refluxed in the presence of a sodium–benzylsodium catalyst. The reaction was accompanied by the formation of quaterphenyls. 1-Cyclohexylcyclohexene under above conditions was converted to cyclohexylcyclohexane, phenylcyclohexane and biphenyl. The mechanism of hydrogen transfer and dehydrogenation reaction is discussed.

It was previously reported that both conjugated and non-conjugated monocyclic terpenes undergo double bond isomerization and dehydrogenation to *p*-cymene when refluxed in the presence of sodium and organosodium compound.[3,4] Under similar experimental conditions geminal akylcyclohexadienes, in which one of the carbon atoms on the ring has two alkyl groups attached to it, also undergo an aromatization reaction, but it is accompanied by a loss of one of the alkyl groups.[1]

Under similar condition *p*-methenes undergo only isomerization; dehydrogenation to *p*-cymene did not occur.[5] The difference in the behavior of *p*-menthadienes as compared with *p*-menthenes can be ascribed to an energy gain in passing from a cyclohexadiene to an aromatic hydrocarbon.

---

[1] Paper VIII of the series of Base-catalyzed Reactions. For VII see H. Pines and H. E. Eschinazi, THIS JOURNAL, **78**, 5950 (1956).

[2] Vladimir Ipatieff Postdoctoral Fellow, 1955–1956.

[3] H. Pines, J. A. Vesely and V. N. Ipatieff, THIS JOURNAL, **77**, 347 (1955).

[4] H. Pines and H. E. Eschinazi, *ibid.*, **77**, 6314 (1955).

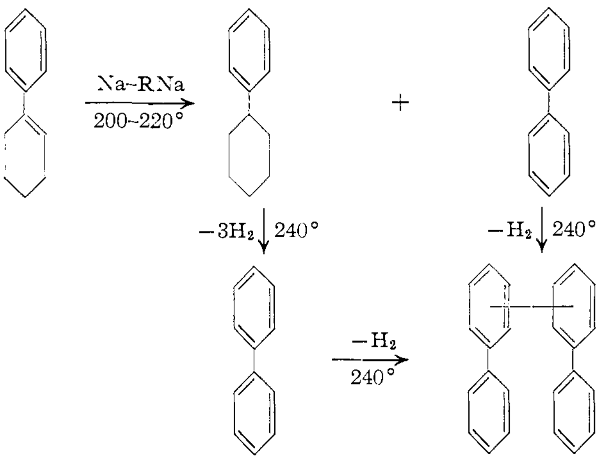
[5] H. Pines and H. E. Eschinazi, *ibid.*, **78**, 1178 (1956).

1,3-Cyclohexadiene is stabilized only by 2.8 kcal./mole of resonance energy while benzene is stabilized by 36.0 kcal./mole, as determined from the heats of hydrogenation of a number of olefinic hydrocarbons.[6]

The study of the effect of sodium–organosodium catalyst has now been extended to include phenylcyclohexene in which the double bond is in conjugation with the aromatic ring. It was found that this hydrocarbon on heating at 200–220° in the presence of sodium or sodium–benzylsodium catalyst undergoes an almost quantitative hydrogen disproportionation reaction resulting in the formation of 2 mole equivalents of phenylcyclohexane per mole equivalent of biphenyl; hydrogen was not evolved during the reaction.

When the temperature of the reaction was permitted to rise to 240°, a slow evolution of hydrogen was observed and the relative ratio of biphenyl to phenylcyclohexane steadily increased. The reaction was also accompanied by the formation of isomeric quaterphenyls, presumably from the condensation of biphenyl with the liberation of hydrogen.

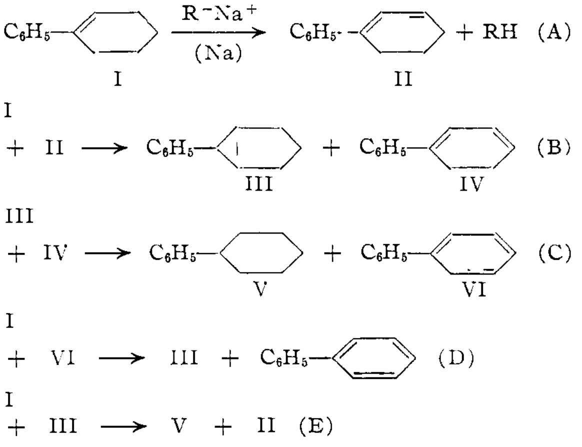
The following scheme illustrates the steps involved in the treatment of phenylcyclohexene with a sodium catalyst



A quaterphenyl, m.p. 164–165°, was separated which, according to the ultraviolet spectral analysis, λ_{max} 272 mμ (ε38,000), corresponded to 3,4′-diphenylbiphenyl. A smooth curve with only one maximum is in favor of this structure, while 2,4′-diphenylbiphenyl with a restricted free rotation about the internuclear bond, would show a fine structure in its absorption curve.[7] A solid, m.p. 295°, was also separated, the structure of which however was not further investigated. The rate of formation of the quaterphenyls was very slow.

Phenylcyclohexane was subjected to refluxing in the presence of sodium–benzylsodium catalyst at 240° in order to throw more light on the mechanism of the reaction. A slow evolution of hydrogen occurred with the corresponding formation of biphenyl and quaterphenyls. The latter were also formed when biphenyl was heated at 240° in the presence of the same catalyst; 4,4′-diphenylbiphenyl was separated from the reaction product.

The mechanism of the hydrogen disproportionation reactions can best be explained by means of carbanion chain reaction, which may proceed as



Benzylsodium added to the reaction flask was used to initiate the chain reaction. It was found, however, that in the case of phenylcyclohexene, owing to the conjugation of the double bond with the benzene ring, the carbanions necessary to cause the chain initiation reaction can be produced *in situ* presumably by the addition of the sodium to the olefinic double bond, as is the case with α-methylstyrene.[8]

The dehydrogenation of phenylcyclohexane to biphenyl can also be explained by a carbanion chain reaction which involves as the first step the removal of a proton from phenylcyclohexane. This requires more energy than the removal of a proton from phenylcyclohexene inasmuch as carbanion II is more stable than III. For that reason the reaction of phenylcyclohexane with the sodium catalyst proceeds at higher temperature than the reaction of phenylcyclohexene. Carbanion II may lose a proton to form compound I which may then undergo a hydrogen disproportionation reaction as indicated in steps A-D.

The formation of quaterphenyls is apparently the result of the addition of biphenylcarbanions to biphenyl followed by the loss of a hydride, according to a similar reaction, which was responsible for the formation of biphenyl from benzene.[9]

In order to determine the effect of phenyl group upon the hydrogen disproportionation of 1-phenylcyclohexene, an experiment was made in which 1-cyclohexylcyclohexene was refluxed in the presence of sodium–benzylsodium catalyst. It was found that after 48 hours of refluxing at 224° only 24% of the product reacted. The reacted material consisted of 65% phenylcyclohexane, 20% cyclohexylcyclohexane and 15% biphenyl. A corresponding amount of hydrogen also was produced. The greater resistance of cyclohexylcyclohexene toward a sodium-catalyzed reaction as compared with phenylcyclohexene is in agreement with the proposed mechanism. Owing to the contribution of

---

(6) G. B. Kistiakowsky and co-workers, THIS JOURNAL, **57**, 65, 876 (1935); **58**, 137, 146 (1935); **59**, 831 (1937).

(7) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," published by E. Arnold, London (England), 1955, p. 213.

(8) E. Bergmann, H. Taubadel and H. Weis, *Ber.*, **64**, 1493 (1931).

(9) H. Pines and V. Mark, THIS JOURNAL, **78**, 4316 (1956).

the resonance effect of the phenyl group, the formation of a carbanion from phenylcyclohexene is greatly facilitated. In a similar reaction reported previously it was observed that cyclohexene even at 280° undergoes but a slight conversion to benzene.[10]

Experimental Part

Materials.—1-Phenylcyclohexene, which was prepared by dehydration of 1-phenylcyclohexanol in refluxed toluene by means of potassium bisulfate, distilled at 116° at 10 mm., n_D^{20} 1.5720.

Phenylcyclohexane was prepared by treating cyclohexene with benzene in the presence of hydrogen fluoride, using the usual experimental conditions.[11] It distilled at 233–234°, n^{20}_D 1.5254.

Biphenyl was obtained commercially, m.p. 70°.

1-Cyclohexylcyclohexene, b.p. 127° at 8 mm., n^{20}_D 1.4944, was prepared by dehydration of 1-cyclohexylcyclohexanol obtained by the reaction of cyclohexanone with cyclohexylmagnesium bromide.

Apparatus and procedure were similar to those described previously.[4]

Catalyst.—The sodium–benzylsodium catalyst was prepared according to the previously described method.[5] Before carrying out the reactions the activity of the catalysts was tested by the addition of 15 ml. of *d*-limonene and recording the evolution of hydrogen during the refluxing of the limonene. After a few hours of reflux the hydrocarbons were removed under reduced pressure and to the catalyst was added the hydrocarbon under investigation.

Experiment 1. 1-Phenylcyclohexene, 220°.—The reaction was carried out in a 100-ml. three-neck flask.

1-Phenylcyclohexene, 19 g. (0.12 mole), was heated for 4 hours at 190° in the presence of a catalyst prepared from 2 g. of sodium and 1.5 g. of *o*-chlorotoluene. At this temperature the 1-phenylcyclohexene remained unchanged.

When 1-phenylcyclohexene was heated at 220° for 5 hours 315 ml. of gas was evolved. The product was removed from the catalyst by addition of benzene, decantation and filtration. The benzene was then distilled off, and the liquid hydrocarbon, 19 g., was analyzed. It contained 1.24 g. of *p*-cymene, which was produced from *d*-limonene used for testing of the catalyst. The remainder of the product was comprised of 64.5% phenylcyclohexane and 35.5% of biphenyl. A mixture of the two hydrocarbons prepared in the same ratio gave a superposable infrared spectrogram.

The phenylcyclohexane was separated from biphenyl by means of silica gel chromatography.[12]

The 315 ml. of hydrogen produced corresponded to the amount of *p*-cymene found in the reaction product.

Experiment 2. 1-Phenylcyclohexene, 242°.—The hydrocarbon, 25 g. (0.16 mole) was refluxed for 26 hours in the presence of a sodium catalyst prepared from the same quantity of material as indicated in expt. 1. The temperature of the reflux decreased progressively from 242 to 234°. A steady but a slow stream of hydrogen was evolved during the reaction; it amounted to 1520 ml. (0.068 mole) at S.T.P., after the deduction of the volume of hydrogen corresponding to the quantity of *p*-cymene found in the reaction product.

The recovered hydrocarbons were comprised of 0.73 g. of *p*-cymene and 22.5 g. of a mixture boiling at 230–240°. The latter consisted of 58% phenylcyclohexane and 42% biphenyl.

The residue of the distillation was treated with *n*-hexane and filtered. It yielded 0.5 g. of insoluble brown material and 1.7 g. of yellow oil, after the removal of the solvent. The solid was purified by sublimation in vacuum and crystallized from benzene–dioxane. It melted at 295° (block), $\lambda_{max}^{CHCl_3}$ 277 mμ (ϵ 43,100) and 288 mμ (ϵ 45,400).

Anal. Calcd. for $C_{24}H_{18}$: C, 94.08; H, 5.93. Found: C, 94.09; H, 5.78.

The yellow oil yielded a mixture of an oil and crystals (130 mg.). The latter on recrystallization from hexane–benzene formed colorless crystals, m.p. 164–165°, $\lambda_{max}^{CHCl_3}$ 272 mμ (ϵ 38,300).

Anal. Calcd. for $C_{24}H_{18}$: C, 94.08; H, 5.93; mol. wt., 306. Found: C, 93.98; H, 6.00; mol. wt. (determined by cryoscopic method in camphor), 300.

Experiment 3. 1-Phenylcyclohexene, 19 g. (0.12 mole) was heated for 5 hr. at 200° in the presence of 0.5 g. of sodium and under vigorous stirring. The product of reaction, n^{20}_D 1.5578, was composed of 35% of biphenyl and 65% phenylcyclohexane.

Experiment 4. Phenylcyclohexane, 45 g. (0.28 mole), was refluxed for 30 hours in the presence of a catalyst prepared from 5 g. of sodium and 5 g. of *o*-chlorotoluene in 35 ml. of toluene. During refluxing the temperature rose progressively from 240 to 250°. The volume of hydrogen produced during the reaction was 11,500 ml. (0.515 mole) at S.T.P.

The reaction product separated in the manner described in expt. 1 and 2, yielded a mixture of hydrocarbons, 30.5 g., which distilled at 125–130° at 27 mm. It was composed of 59% of the starting phenylcyclohexane and 41% of biphenyl. The residue from the distillation yielded 1 g. of a solid, m.p. 200–210°, and 6 g. of a yellow oil. The latter yielded on sublimation 0.5 g. of crystals melting at 159–161°. On recrystallization from hexane–benzene colorless crystals were obtained, m.p. 164–165°.

Experiment 5. Biphenyl, 9.8 g. (0.064 mole), was refluxed for 23 hours in the presence of a catalyst prepared from 2 g. of sodium and 1.2 g. of *o*-chlorotoluene. The reflux temperature increased progressively from 236–280°. The volume of evolved hydrogen amounted to 1720 ml. (0.077 mole).

After the reaction the contents of the flask were extracted with benzene. A solid product, 7 g., was separated which on treatment with ether yielded 1.0 g. of insoluble brown product, m.p. 245–250°, and 6.0 g. of biphenyl (63% based on the starting material).

The high melting product, after sublimation in vacuum, yielded 0.1 g. of yellow crystals which, after recrystallization from benzene–dioxane, produced colorless crystals, m.p. 303° (block). It corresponded to 4,4′-diphenylbiphenyl, $\lambda_{max}^{CHCl_3}$ 298 mμ (ϵ 40,800).

Anal. Calcd. for $C_{24}H_{18}$: C, 94.08; H, 5.93. Found: C, 93.86; H, 5.93.

Experiment 6. 1-Cyclohexylcyclohexene, 17 g. (0.104 mole), was refluxed at 224° for 48 hours in the presence of a catalyst prepared from 2.0 g. of sodium and 1.5 g. of *o*-chlorotoluene in 13 ml. of toluene. During the reaction 1,200 ml. (0.054 mole) of hydrogen was liberated.

After the reaction, the contents of the flask were extracted with benzene, filtered and the solvent and the small amount of *p*-cymene present were removed by distillation. The residue was flash distilled at 220–223°, n^{20}_D 1.5012, 16.5 g.

Five grams of the mixture was dissolved in *n*-pentane and chromatographed over silica gel. The following fractions were separated: (a) 0.14 g., pure bicyclohexyl; (b) 0.25 g., comprised of 35% bicyclohexyl and 65% of the starting material; (c) 3.13 g., starting material; (d) 1.48 g. consisting of 36.7% starting material, 50.8% phenylcyclohexane and 12.5% biphenyl.

From the above analysis it was calculated that the recovered reaction product consisted of 76.5% starting material, 15.3% phenylcyclohexane, 4.6% bicyclohexyl and 3.7% biphenyl.

In order to verify the above results 5.7 g., of the distillate, n_D^{20} 1.5012, was dissolved in 10 ml. of ethanol and hydrogenated in the presence of 1.2 g. of platinum oxide. The product absorbed 913 ml. of hydrogen at 26° and 754 mm. of pressure, which corresponded to 75% olefins present in the mixture. After filtration and elimination of the solvent, 3.3 g. of the mixture was chromatographed over silica gel. The following fractions were separated: (a) 2.57 g., bicyclohexyl; (b) 0.64 g. composed of 83% phenylcyclohexane and 17% biphenyl.

On the basis of the above analysis the selectively hydrogenated product consisted of 80% bicyclohexyl, 16.5% phenylcyclohexane and 3.5% biphenyl. A synthetic mixture of the same concentration gave a superimposable infrared spectrogram.

EVANSTON, ILLINOIS

---

(10) V. Mark and H. Pines, THIS JOURNAL, **78**, 5946 (1956).

(11) H. Pines, A. Edeleanu and V. N. Ipatieff, *ibid.*, **67**, 2193 (1945).

(12) B. J. Mair, *J. Research Natl. Bur. Standards*, **34**, 435 (1945).