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

# Hydrogen Transfer. I. Reaction of *p*-Cymene with Olefinic Hydrocarbons in the Presence of Sulfuric Acid and Hydrogen Fluoride Catalysts[1,2]

BY V. N. IPATIEFF, HERMAN PINES AND R. C. OLBERG[2a]

In the course of the study of terpenic hydrocarbons which is being carried out in our laboratory, the reaction of *para*-cymene with dihydrolimonene (1-methyl-4-isopropylcyclohexene) in the presence of either sulfuric acid or hydrogen fluoride at 0° was included. It was noticed that this reaction proceeded abnormally[3] inasmuch as a 60% yield of 1-methyl-4-isopropylcyclohexane was obtained. This could not be attributed to a conjunct polymerization[4] of dihydrolimonene since the product obtained, including the high-boiling fractions, did not contain any olefinic hydrocarbons as determined by means of a potassium permanganate test.[5] It was also noticed that the high-boiling fraction resulting from this reaction had a much higher index of refraction than that expected from a cycloalkylation reaction. This material corresponded, according to elementary analysis, to a tricyclic hydrocarbon of the formula $C_{20}H_{24}$ (I). On the basis of these preliminary results, it was tentatively concluded that *p*-cymene acted as a hydrogen donor and dihydrolimonene as a hydrogen acceptor.

It was difficult to substantiate this conclusion as long as *p*-cymene and dihydrolimonene, having the same skeletal arrangement, were used as reactants. For this reason 3-methylcyclohexene was substituted for dihydrolimonene.

It was found in the reaction of *p*-cymene with 3-methylcyclohexene in the presence of either sulfuric acid or hydrogen fluoride, 62–80% of the methylcyclohexene was converted to methylcyclohexane. The yield of the expected methylcyclohexyl-*p*-cymene was very small, whereas a large amount of the tricyclic hydrocarbon, $C_{20}H_{24}$, was obtained which was identical with compound I. It was also found that for each mole of $C_{20}H_{24}$ produced there was one mole of methylcyclohexane formed.

If, however, *p*-cymene and a branched open chain olefin, such as trimethylethylene, were contacted in the presence of hydrogen fluoride, both an alkylation and a hydrogen transfer reaction occurred; the latter reaction was the predominant one. Isopentane and decanes were found among the reaction products. The presence of decanes is attributed to the dimerization of the trimethylethylene, which through a subsequent hydrogen transfer reaction yields decanes. The major part of *p*-cymene which underwent reaction yielded the hydrocarbon, $C_{20}H_{24}$, identical with the one described above.

In order to determine whether the hydrogen transfer reaction which involves *para*-cymene and an olefinic hydrocarbon is of a general nature, a series of experiments was made using various olefins.

It was found that cyclohexene[6] or straight chain olefin such as 1-octene, react with *p*-cymene in the usual manner yielding the corresponding mono- and disubstituted *p*-cymene; hydrogen transfer reaction did not occur.

**The Structure of the $C_{20}H_{24}$ Hydrocarbon (I).**—The facts described below and the postulated mechanism of hydrogen transfer reaction suggested that the $C_{20}H_{24}$ hydrocarbon corresponds to 1,3,3,6-tetramethyl-1-*p*-tolylindan (I). In order to establish conclusively the structure of compound (I) 1,3,3,6-tetramethyl-1-*p*-tolylindan was synthesized. The physical constants, nitro derivatives, and ultraviolet absorption spectra of the synthetic sample were compared with the tricyclic hydrocarbon obtained from the hydrogen transfer reaction; the two compounds were identical.[7]

Infrared absorption spectra of the synthetically prepared compound I and that obtained from the hydrogen transfer reaction were taken (Graph I and II). The 1,3,3,6-tetramethyl-1-*p*-tolylindan prepared from the latter reaction solidified on standing, so for that reason the infrared spectrum was taken in a carbon disulfide solution. The spectra of both compounds were found to be basically the same; the synthetic sample seems to be only about 95% pure. Due to the small amount of synthetic sample prepared, no attempt was made to purify it.

Compound I yielded on nitration a tetranitro derivative $C_{20}H_{20}N_4O_8$ melting at 252–253°. A disulfonamide of the hydrocarbon was obtained melting at 227–228°. The tricyclic hydrocarbon yielded on oxidation a dicarboxylic acid, $C_{20}H_{20}O_4$, melting at 294–295°.

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[1] This work was made possible through the financial assistance of Universal Oil Products Company.

[2] This paper was presented in part before the Organic Division of the American Chemical Society. September, 1946.

[2a] Present address: Paraffine Companies, Inc., Emeryville, Calif.

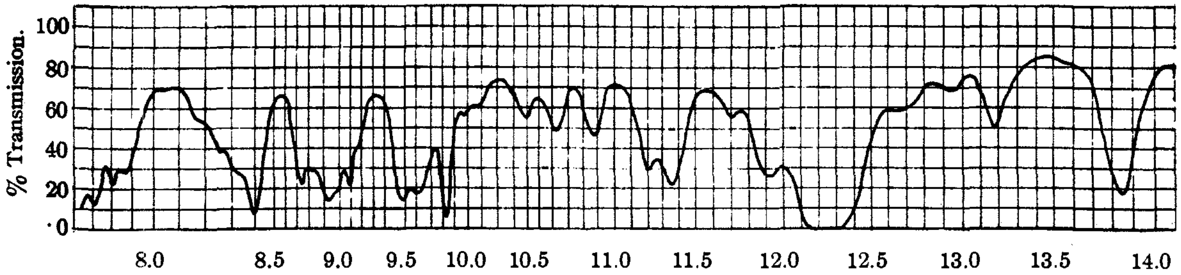
[3] For the literature references pertaining to the alkylation of aromatic hydrocarbons, see paper by V. N. Ipatieff, H. Pines and L. Schmerling, *J. Org. Chem.*, **5**, 253 (1940).

[4] V. N. Ipatieff and H. Pines, *J. Org. Chem.*, **1**, 464 (1936).

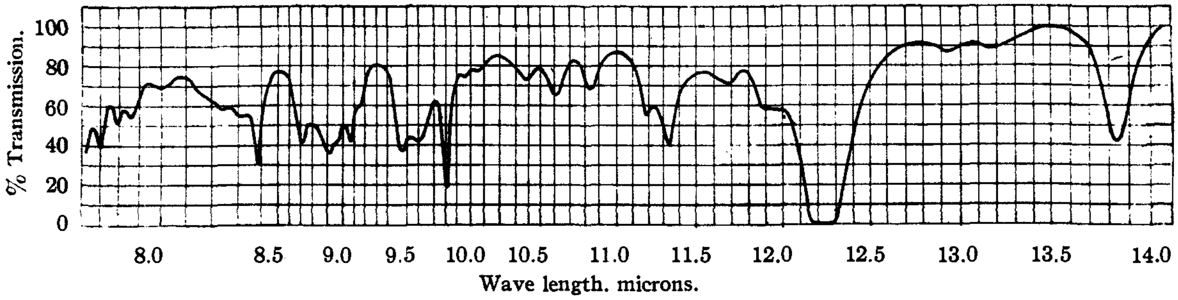
[5] V. N. Ipatieff, W. W. Thompson and H. Pines, THIS JOURNAL, **70**, 1658 (1948).

[6] H. Pines, A. Weizmann and V. N. Ipatieff, "Hydrogen Transfer II." Paper presented before the Organic Division of the American Chemical Society, New York, September 15–19, 1946.

[7] The same tricyclic hydrocarbon, $C_{20}H_{24}$, was reported by N. Puranen (*Ann. Acad. Sci. Fennicae*, **37A**, No. 10, 1–80 (1933); C. 1933 II, 856) to be formed by the treatment of *p*-cymene with nitrosylsulfuric acid in sulfuric acid. The melting point of the hydrocarbon and its nitro derivatives agrees with those obtained from the hydrogen transfer reaction. Puranen assigned to this compound the structure of 1,3,3,6-tetramethyl-1-*p*-tolylindan; he did not however prove the structure by either degradative or synthetic means.



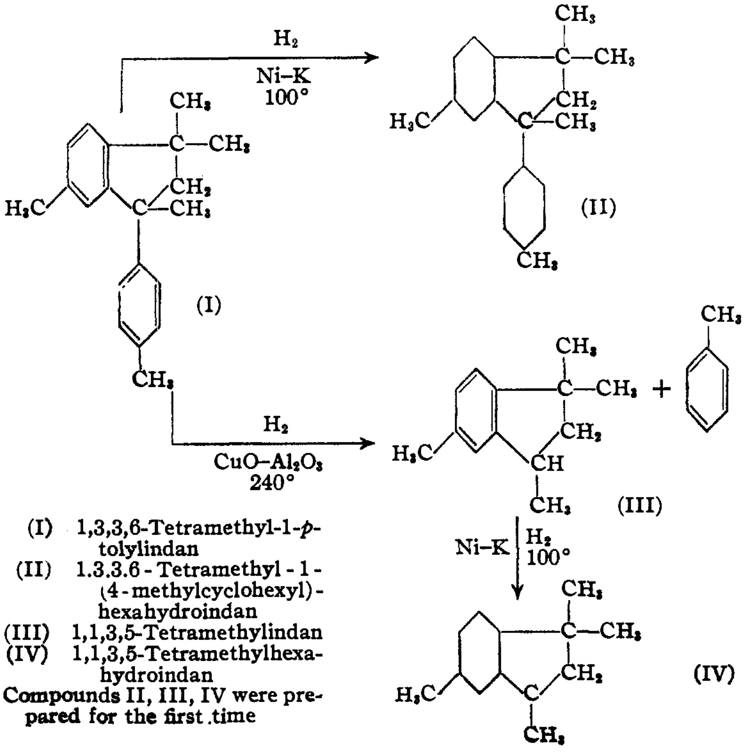
Graph I.—1.3.3.6-Tetramethyl-1-*p*-tolylindan: prepared by synthetic means.



Graph II.—1.3.3.6-Tetramethyl-1-*p*-tolylindan: obtained from a hydrogen transfer reaction.

The $C_{20}H_{24}$ hydrocarbon (I), on hydrogenation in the presence of a nickel-kieselguhr catalyst at 100° and under an initial hydrogen pressure of 100 atmospheres, absorbed six moles of hydrogen per mole of hydrocarbons to yield a compound corresponding to $C_{20}H_{36}$ (II).

The tricyclic hydrocarbon (I) on destructive hydrogenation at 240° under pressure in the presence of a copper oxide–alumina catalyst yielded toluene and a bicyclic aromatic hydrocarbon corresponding to $C_{13}H_{18}$ (III); some of the original tricyclic hydrocarbon was recovered.



(I) 1,3,3,6-Tetramethyl-1-*p*-tolylindan

(II) 1.3.3.6-Tetramethyl-1-(4-methylcyclohexyl)-hexahydroindan

(III) 1,1,3,5-Tetramethylindan

(IV) 1,1,3,5-Tetramethylhexahydroindan

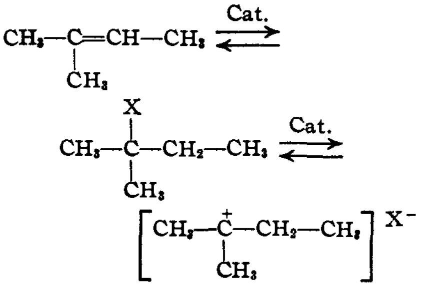
Compounds II, III, IV were prepared for the first time

The bicyclic hydrocarbon, $C_{13}H_{18}$ (III), obtained from the destructive hydrogenation, was further hydrogenated under pressure at 100° in the presence of a nickel–kieselguhr catalyst. A bicyclic hydrocarbon corresponding to $C_{13}H_{24}$ (IV) was obtained.

The tricyclic hydrocarbon $C_{20}H_{24}$ (I) did not undergo dehydrogenation when passed over platinized alumina at 300°.

**Mechanism of Reaction.**—The following mechanism is suggested to explain the hydrogen transfer reaction between trimethylethylene and *p*-cymene:

1. The olefinic hydrocarbons react with the catalyst; a carbonium ion is probably formed.



$$CH_3-\underset{CH_3}{\underset{|}{C}}=CH-CH_3 \xrightleftharpoons{\text{Cat.}}$$

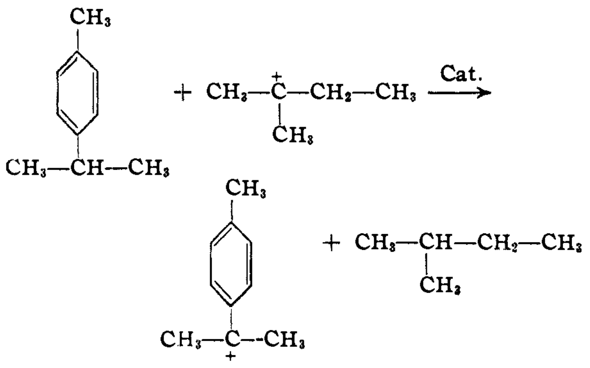
$$CH_3-\overset{X}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2-CH_3 \xrightleftharpoons{\text{Cat.}}$$

$$\left[CH_3-\overset{+}{\underset{CH_3}{C}}-CH_2-CH_3\right]X^-$$

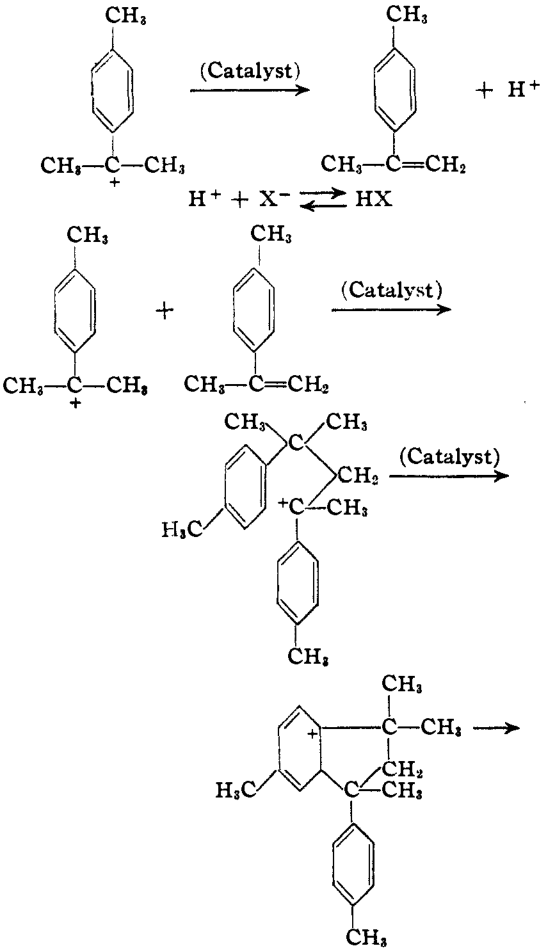
$X = HOSO_3$ or $H_{n-1}F_n$

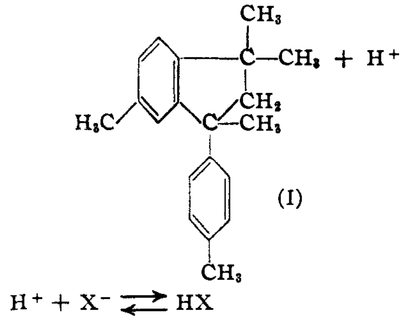
2. In the presence of an alkylating catalyst an exchange reaction

probably occurs similar to the type described by Bartlett, Condon and Schneider.[8]



3. Part of the dimethyl-*p*-tolyl carbonium ion formed may lose a proton to form 1-methyl-4-isopropenylbenzene; the latter on reaction with the dimethyl-*p*-tolylcarbonium ion forms probably 2,4-di-*p*-tolyl-4-methyl-2-pentylcarbonium ion. The latter through an internal addition to the benzene ring and a subsequent loss of a proton yields 1,3,3,6-tetramethyl-1-*p*-tolylindan (I).

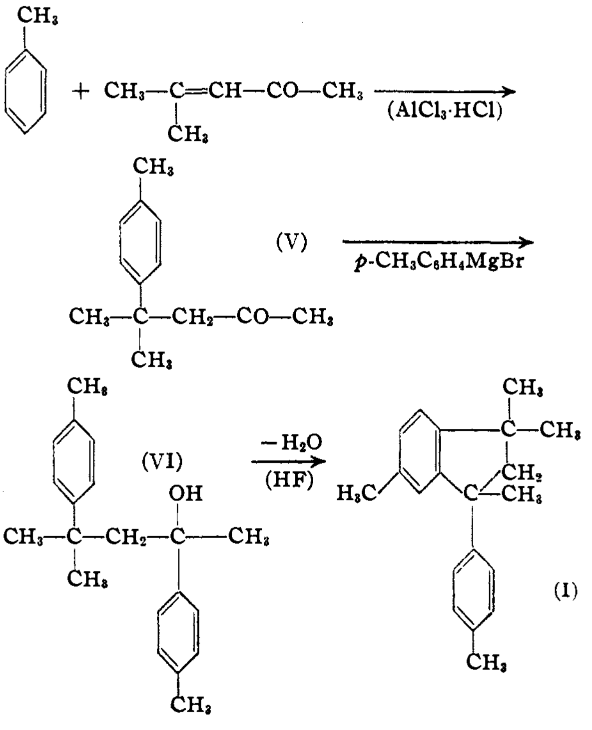




In order to prove that the formation of 1,3,3,6-tetramethyl-1-*p*-tolylindan (I) may proceed through the above indicated mechanism, 1-methyl-4-isopropenylbenzene was prepared and the compound treated with hydrogen fluoride under experimental conditions similar to those required for a hydrogen transfer reaction. The product of the reaction was 1,3,3,6-tetramethyl-1-*p*-tolylindane. This is in agreement with a similar result obtained by Bergmann, Taubadel and Weiss[9] who found that the dimerization of isopropenylbenzene in the presence of acid acting catalysts yields 1,3,3-trimethyl-1-phenylindan.

*p*-Cymene by itself does not undergo any changes when treated with either hydrogen fluoride or sulfuric acid under the experimental conditions used for the hydrogen transfer reaction.

1,3,3,6-Tetramethyl-1-*p*-tolylindan (I) was synthesized as follows.[9]



The para position of the substituents on the aro-

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[8] P. D. Bartlett, F. E. Condon and A. Schneider, This Journal, 66, 1531 (1944).

[9] The general scheme of the synthesis was similar to the method of E. Bergmann, H. Taubadel and H. Weiss, *Ber.*, 64, 1493 (1931).

TABLE I

| Experiment number | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Reagents used: | | | | | |
| *p*-Cymene, moles | 2.0 | 4.8 | 4.0 | 0.8 | 1.0 |
| Olefins. kind | Trimethylethylene | Methylcyclohexene | | Dihydrolimonene | Octene |
| Olefins, moles | 1.0 | 2.0 | 2.0 | 0.4 | 0.5 |
| Catalyst, kind | HF | $H_2SO_4$ | HF | HF | $H_2SO_4$ |
| Catalyst, moles | 8.4 | 2.4 | 6.6 | 3.3 | 0.6 |
| Results obtained: | | | | | |
| Hydrocarbon layer, grams | 318 | 800 | 696 | 154 | 175 |
| Hydrocarbon wt. % yield | 94 | 96 | 96 | 94 | 92 |
| Composition of hydrocarbon layer; based on total product recovered | | | | | |
| Saturated product formed, kind | Isopentane | Methylcyclohexane | | Paramenthane | Octane |
| Saturated product formed, moles | 0.33$^c$ | 1.31 | 1.69 | 0.17 | 0 |
| *p*-Cymene recovered, moles | 1.29 | 3.28 | 2.19 | .59 | 0.55 |
| Alkylated product,$^a$ grams | 51 | 42 | 39 | 5$^e$ | 88 |
| moles | 0.25 | 0.18 | 0.17 | 0.02 | 0.36 |
| 1,3,3,6-Tetramethyl-1-*p*-tolylindane, moles | .23 | .58 | .75 | .15 | 0 |
| Evaluation of yield: original aromatic hydrocarbon converted to$^b$ | | | | | |
| (1) Alkylated product,$^a$ mole % | 25$^f$ | 9 | 8.5 | 5.0 | 72$^g$ |
| (2) 1,3,3,6-Tetramethyl-1-*p*-tolylindan, mole % | 46 | 58 | 75 | 75 | 0 |
| Olefinic hydrocarbons converted to$^b$ | | | | | |
| (1) Saturated hydrocarbons, mole % | 43$^d$ | 65 | 84.5 | 42.5 | 0 |
| (2) Alkylated product,$^a$ mole % | 25$^f$ | 9 | 8.5 | 5.0 | 72$^g$ |

[a] Hydrocarbons corresponding to the interaction of a mole of olefins with a mole of aromatic hydrocarbons charged. [b] The yields were calculated on the basis of olefin reacted. [c] In addition to isopentane 0.05 mole of decanes was formed. [d] Includes decanes produced, which distilled at 145–155°, $n^{20}_D$ 1.4182. *Anal.* Calcd. for $C_{10}H_{22}$: C. 84.41: H, 15.59. Found: C, 84.64: H, 15.65. [e] Estimated from the index of refraction. [f] It distilled at 94–96° at 4 mm., $n^{20}_D$ 1.5021. *Anal.* Calcd. for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 88.74; H, 11.42. [g] It distilled at 126–129° at 4 mm., $n^{20}_D$ 1.4842. *Anal.* Calcd. for $C_{18}H_{30}$: C, 87.73: H, 12.27. Found: C, 88.11; H, 11.78.

matic ring was proved by means of oxidation of compound (V) to terephthalic acid.

## Experimental Part

The reactions of *p*-cymene with olefins in the presence of catalysts were carried out by the following procedure.

**Sulfuric Acid Catalyzed Reaction.**—The apparatus consisted of an appropriately sized three-neck flask equipped with a mercury sealed stirrer, reflux condenser and a water-cooled dropping funnel. The flask was surrounded by a cooling bath of ice and water. A thermometer was inserted into the reaction flask.

The sulfuric acid (96%) and one-half of the *p*-cymene were introduced into the flask and cooled at 0°. The olefinic hydrocarbon and the remainder of the *p*-cymene were mixed and added slowly with efficient stirring to the contents of the flask. The rate of addition was controlled so as to maintain the temperature inside the flask between 0° and 7°. After the addition was finished, the stirring was continued for a half hour.

The contents of the flask were poured into a separating funnel and allowed to stand for one to two hours in order to assure a complete separation of the acid and hydrocarbon layers.

The hydrocarbon layer was separated washed with water, with alkali, again with water, dried and distilled.

**Hydrogen Fluoride Catalyzed Reaction.**—The apparatus consisted of a copper flask provided with a copper stirrer and a dropping funnel. The flask was surrounded by a cooling bath of ice and water. The procedure was the same as that of sulfuric acid.

The contents of the flask were poured into a copper beaker containing ice precooled to about −30°. The hydrocarbon was separated and washed with dilute aqueous potassium hydroxide, followed by a water wash, then dried over calcium chloride and distilled.

The experimental results obtained are given in Table I. As an example of the methods used for the identification of the reaction product, Experiment 2 is described in detail.

**Experiment 2** (*p*-Cymene-methylcyclohexene–Sulfuric Acid).—Distillation of 700 g. of hydrocarbon mixture yielded the following fractions:

**Fraction 1**, b. p. 101°, $n^{20}_D$ 1.4220, 114 g., corresponds to methylcyclohexane, since on dehydrogenation over platinized alumina (Pt 7%) at 260°,[10] it yielded toluene. The latter was identified by means of its dinitro derivative, which melted at 70°.

**Fraction 3**, b. p. 172–174°, $n^{20}_D$ 1.4890, 378 g., consists of unreacted *p*-cymene, as determined by the ultraviolet absorption spectra.

**Fraction 6**, b. p. 124–126° at 4 mm., $n^{20}_D$ 1.5305, $d^{20}_4$ 0.9581, 28 g., corresponds to methylcyclohexyl-*p*-cymene.

*Anal.* Calcd. for $C_{17}H_{26}$: C, 88.63; H, 11.37. Found: C, 89.40; H, 10.68.

**Nitro Derivative.**—One ml. of the product was treated with 5 ml. of nitrating mixture composed of 1 vol. 72% nitric acid and 2 vol. 96% sulfuric acid. The nitro compound was crystallized from ethanol. It melted at 152–153°.

*Anal.* Calcd. for $C_{17}H_{24}N_2O_4$: C, 63.75; H, 7.50; N, 8.75. Calcd. for $C_{16}H_{22}N_2O_4$: C, 62.74; H, 7.19; N, 9.15. Found: C, 62.53; H, 6.91; N, 8.79.

According to elementary analysis, the nitro compound corresponds to isopropyl-(methylcyclohexyl)-dinitrobenzene; it seems that a methyl group in the benzenoid ring was replaced by a nitro group. Such replacement is quite common.[11]

**The sulfonamide** was prepared by the procedure of Huntress and Autenrieth[12] and crystallized twice from dilute alcohol and twice from benzene–pentane solution. It melted at 187–188°.

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[10] H. Pines and V. N. Ipatieff. THIS JOURNAL. **61**, 1076 (1939).

[11] D. Nightingale. *Chem. Rev.*. **40**, 117 (1947).

[12] E. H. Huntress and J. S. Autenrieth. THIS JOURNAL. **63**, 3446 (1941).

*Anal.* Calcd. for $C_{17}H_{27}NSO_2$: C, 66.02; H, 8.74; N, 4.53. Found: C, 66.22; H, 8.71; N, 4.65.

**Fraction 9**, b. p. 156° at 4 mm., $n^{20}_D$ 1.5580, 128 g., corresponds to 1,3,3,6-tetramethyl-1-*p*-tolylindan.

*Anal.* Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 91.31; H, 8.96.

The product crystallized out very slowly until it was seeded with (I). It melted at 37.5°.

**Nitration.**—One gram of the hydrocarbon $C_{20}H_{24}$ was dissolved in 5 ml. of chloroform, cooled to 0°, and to it was added 1.5 ml. of 96% sulfuric acid and 0.5 ml. of 72% nitric acid. A crystalline derivative was obtained, melting at 112–114°. After crystallization from ethanol it melted at 114–115°; it corresponded to 1,3,3,6-tetramethyl-5-nitro-1-(4-methyl-3-nitrophenyl)-indan.

*Anal.* Calcd. for $C_{20}H_{22}N_2O_4$: C, 67.80; H, 6.21; N, 7.90. Found: C, 68.12; H, 6.02; N, 7.89.

One-half ml. of the product was treated with 5 ml. of a nitrating mixture, composed of 1 vol. 72% nitric acid and 2 vol. 96% sulfuric acid, and heated for a few minutes to 70–80°. The product solidified while still hot; it was poured over ice, filtered and the solid crystallized from a hot ethanol–chloroform mixture. White glistening crystals were obtained, which melted at 251–252°. The nitro compound corresponds to 1,3,3,6-tetramethyl-5,7-dinitro-1-(4-methyl-3,5-dinitrophenyl)-indan. Mixed melting point with a synthetically prepared tetranitro derivative showed no depression.

*Anal.* Calcd. for $C_{20}H_{20}N_4O_8$: C, 54.05; H, 4.50; N, 12.61. Found: C, 54.20; H, 4.43; N, 12.84.

**The sulfonamide** crystallized from water–alcohol mixture; it melted at 227–228° and corresponded probably to 1,3,3,6-tetramethyl-1-(4-methyl-3-sulfonamido-phenyl)-5-sulfonamido-indan.

*Anal.* Calcd. for $C_{20}H_{28}O_4N_2S_2$: C, 56.87; H, 6.16; N, 6.63. Found: C, 57.57; H, 6.34; N, 6.34.

**Oxidation.**—One gram of the product was heated under reflux with a solution composed of 30 ml. of acetic acid, 30 ml. of water, 5 ml. of 96% sulfuric acid and 7 g. of chromic anhydride. The mixture was heated for six hours. The solution was cooled and diluted with water; a solid precipitated out, which was filtered and washed with water. The solid was dissolved in dilute aqueous sodium hydroxide and extracted with ether to remove any neutral material which might be present. The aqueous solution was then acidified with dilute hydrochloric acid. The organic acid which separated out melted at 294–295°; it corresponds to 1,3,3-trimethyl-1-(4-carboxyphenyl)-6-carboxyindan.

*Anal.* Calcd. for $C_{20}H_{20}O_4$ (mol. wt. 324): C, 74.08; H, 6.17. Found: C, 73.22; H, 6.78; neutral equivalent of the acid, 160.

**Hydrogenation.**—Fifteen grams of the hydrocarbon $C_{20}H_{24}$ was hydrogenated at 100° under an initial hydrogen pressure of 120 atmospheres and in the presence of 2.5 g. of a nickel–kieselguhr catalyst. From the pressure drop it was calculated that 6 moles of hydrogen were absorbed per mole of hydrocarbon.

The hydrogenated material distilled at 183° (13 mm., $n^{20}_D$ 1.4982, $d^{20}_4$ 0.9248. It corresponds to 1,3,3,6-tetramethyl-1-(4-methylcyclohexyl)-hexahydroindan (Compound II).

*Anal.* Calcd. for $C_{20}H_{36}$: C, 86.87; H, 13.13. Found: C, 86.70; H, 13.20.

**Destructive Hydrogenation.**—Twenty-seven grams of fraction 9 was submitted to destructive hydrogenation in the presence of 4 g. of a coprecipitated copper oxide–alumina catalyst (copper oxide 60% by wt.). The reaction was carried out in a 450 cc. capacity rotating autoclave at 270° and at an initial hydrogen pressure of 122 atm. measured at 28°. The time of heating was seven hours; the maximum pressure was 230 atm.; the final pressure measured at 28° was 106 atm.

The gases were collected and analyzed; they consisted of 99.4% of hydrogen. The liquid product was fractionally distilled and the following cuts were collected:

**Cut 1**, b. p. 108–110°, $n^{20}_D$ 1.4940, 3.5 g., consisted of toluene. A dinitrotoluene was prepared melting at 70°.

**Cut 3**, b. p. 210–212°, $n^{20}_D$ 1.5071, 6.5 g., corresponded to 1,1,3,5-tetramethylindan (Compound III).

*Anal.* Calcd. for $C_{13}H_{18}$: C, 89.66; H, 10.34. Found: C, 89.47; H, 10.50.

**Cut 4**, b. p. 158° at 4 mm., $n^{20}_D$ 1.5545, 12.5 g., corresponded to recovered compound I. It melted at 37.5° and yielded a tetranitro derivative melting at 250° and a sulfonamide melting at 123–124°.

*Anal.* Calcd. for $C_{13}H_{19}SO_2N$: N, 5.53. Found: N, 5.47.

A larger amount of 1,1,3,5-tetramethylindan was prepared and 17 g. of the hydrocarbon was hydrogenated in the presence of 3 g. of nickel–kieselguhr catalyst at 100° and under an initial hydrogen pressure of 100 atmospheres at 25°. From the drop in hydrogen pressure it was calculated that three moles of hydrogen was absorbed per mole of hydrocarbon. The hydrogenated product distilled at 213–215°, $n^{20}_D$ 1.4622. It corresponds to 1,1,3,5-tetramethylhexahydroindan (Compound IV).

*Anal.* Calcd. for $C_{13}H_{24}$: C, 86.25; H, 13.75. Found: C, 86.77; H, 13.40.

### Synthesis of 1,1,3,6-Tetramethyl-1-*p*-tolylindan (I)

**4-Methyl-4-*p*-tolyl-2-pentanone** (V).—The reaction vessel consisted of a 2-liter three-neck flask containing a mercury sealed stirrer, a dropping funnel and a reflux condenser. Toluene, 108 g. (2 *M*) and 200 g. of carbon disulfide were placed in the reaction flask which was surrounded with ice. To this solution was added 160 g. (1.2 moles) of aluminum chloride; on the addition of the catalyst the solution turned a deep red color. To the contents of the flask 98 g. (1 mole) of mesityl oxide was added over a period of two and one-half hours. After the addition was completed, the stirring was continued for an additional two hours. During all this time a slow stream of hydrogen chloride was bubbled into the liquid. The content of the flask was then poured onto ice. Two layers were formed: the upper (organic) layer was separated, washed with water, followed by sodium carbonate solution and again with water. The product was then steam distilled to remove the excess of toluene and carbon disulfide; the remaining material was separated from the water, dried and distilled under reduced pressure.

The 4-methyl-4-*p*-tolyl-2-pentanone (V) formed, distilled at 160° at 37 mm., $n^{20}_D$ 1.5082, $d^{20}_4$ 0.9594: yield, 40%.

*Anal.* Calcd. for $C_{13}H_{18}O$: C, 82.11; H, 9.47. Found: C, 82.15; H, 9.37.

**Semicarbazone**, after two crystallizations from 60% ethanol, melted at 190–191°.

*Anal.* Calcd. for $C_{14}H_{21}ON_3$: N, 17.00. Found: N, 17.40.

**Oxidation.**—One half gram of the ketone was treated under reflux for three hours with a solution consisting of 3.5 g. of chromic anhydride, 15 ml. of glacial acetic acid, 15 ml. of water and 4 ml. of 96% sulfuric acid. On dilution with water, a solid separated, which was filtered, washed with water and dried. It did not melt at 290°. The solid corresponded to terephthalic acid since the corresponding dimethyl ester melted at 141° and did not show a depression in melting point when mixed with a known sample of dimethyl terephthalate.

### 4-Methyl-2.4-di-*p*-tolyl-2-pentanol (VI)

*p*-Tolylmagnesium bromide prepared from 21 g. (0.12 mole) of *p*-bromotoluene and 2.9 g. (0.12 atom) of magnesium was condensed with 19 g. (0.1 mole) of (V). The carbinol VI, 18 g., distilled at 160° (3 mm.); $n^{20}_D$ 1.5520.

*Anal.* Calcd. for $C_{20}H_{26}O$: C, 85.11; H, 9.22. Found: C, 85.10; H, 9.17.

### 1,1,3,6-Tetramethyl-*p*-tolylindan (I)

Six grams of (VI) was dissolved in 15 g. of methylcyclohexane and the solution was added, with stirring, to 17 g. of anhydrous hydrogen fluoride at 0°. The content of the copper flask was then poured onto ice. The hydrocarbon layer was separated, washed with potassium hydroxide, water, dried over calcium chloride and distilled. Three grams of (I) was obtained, boiling at 161° (7.5 mm.), $n^{20}D$ 1.5579.

The infrared and ultraviolet absorption spectra were taken.

Two-tenths gram of (I) was nitrated with 5 ml. of nitrating mixture consisting of 2 vol. 96% sulfuric acid and 1 vol. of 72% nitric acid. The nitro compound obtained was crystallized from a solution of ethanol and chloroform. It melted at 251°, and did not depress the melting point of the tetranitro derivative of the $C_{20}H_{24}$ hydrocarbon.

### Dimerization of 1-Methyl-4-isopropenylbenzene

A. **Dimethyl-*p*-tolyl-carbinol.**—The carbinol was prepared from 256 g. (1.5 mole) of *p*-bromotoluene and 81 g. (1.4 mole) of acetone via a Grignard reaction according to the procedure of Sabatier and Marat.[13] The carbinol distilled at 73° (2.5 mm.), $n^{20}D$ 1.5168; yield 66%.

B. **1-Methyl-4-Isopropenylbenzene.**—Forty-three grams of the carbinol was passed at 350° during a period of one hour over 40 cc. of activated alumina of a 10–12 mesh size. The hydrocarbon distilled at 82° (21 mm.), $n^{20}D$ 1.5350: yield was over 80%.

C. **Polymerization of 1-Methyl-4-isopropenylbenzene.**—Eight grams of 1-methyl-4-isopropenylbenzene dissolved in 7 g. of methylcyclohexane was added with agitation to 10 ml. of anhydrous hydrogen fluoride placed in a copper beaker. The mixture was stirred for fifteen minutes and then poured onto 15 g. of ice precooled to −40°. The hydrocarbon layer was separated. diluted with ether, washed with aqueous potassium hydroxide, dried, and distilled. Three grams of a hydrocarbon boiling at 171° (5 mm.) was obtained; $n^{20}D$ 1.5545, melting point 33°. According to ultraviolet analysis it consisted of 1,3,3,6-tetramethyl-1-*p*-tolylindan (Compound I).

*Anal.* Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 91.03; H, 9.11.

On nitration with nitrating mixture consisting of 2 vols. of sulfuric acid and 1 vol. of nitric acid it formed a tetranitro derivative, which after two crystallizations from ethanol–chloroform solution melted at 248°, and did not depress the melting point of the tetranitro derivative prepared from a known sample of Compound I.

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## Summary

The reaction of *p*-cymene with trimethylethylene, methylcyclohexene, dihydrolimonene, 1-octene, and cyclohexene in the presence of either sulfuric acid or hydrogen fluoride was investigated.

Hydrogen transfer occurs when *p*-cymene reacts with the first three olefins; the products resulting from such reaction consist of isopentane, methylcyclohexane, and *p*-menthane, respectively, and 1,3,3,6-tetramethyl-1-*p*-tolylindan which is formed in each case.

1,3,3,6-Tetramethyl-1-*p*-tolylindan was synthesized.

A mechanism for the hydrogen transfer reaction is proposed:

The following new compounds and their derivatives were prepared: (a) 4-methyl-4-*p*-tolyl-2-pentanone, (b) 4-methyl-2,4-di-*p*-tolyl-2-pentanol, (c) 1,3,3,6-tetramethyl-1-(4-methylcyclohexyl)-hexahydroindan, (d) 1,1,3,5-tetramethylindan, and (e) 1,1,3,5-tetramethylhexahydroindan.

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[13] P. Sabatier and M. Murat, *Compt. rend.*, **156**, 184 (1913); *Ann. Chim.*, [9] **4**, 253 (1915).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, NORTHWESTERN UNIVERSITY MEDICAL SCHOOL]

# The Acid Hydrolysis of Egg Albumin. I. Kinetic Studies

BY HENRY B. BULL AND J. WILFRID HAHN

It becomes increasingly clear that a central problem of protein chemistry is the localization of the amino acid residues in the peptide chains, and it is possible that study of the hydrolysis of proteins might shed light on this problem. While the literature on protein hydrolysis is extensive, there are certain features of this reaction which have not been explored. The present paper reports the results of an investigation of the hydrolysis of purified hen's egg albumin at 30°, at 45° and at 60° by hydrochloric acid. The amino nitrogen, the free amino acids, the ammonia, the material insoluble in trichloroacetic acid as well as the heat coagulable material have been determined, and an interpretation of these results is suggested.

## Experimental

One volume of a solution of crystalline albumin prepared from fresh chicken eggs by the method of Kekwick and Cannan[1] was added to two volumes of concentrated hydrochloric acid. The flask containing the reaction mixture was securely stoppered and placed in a water-bath at the desired temperature and rotated occasionally. A single. clear, homogeneous phase resulted in a few minutes. At intervals, 20-cc. aliquots were removed and neutralized with powdered sodium bicarbonate, and the turbid solutions resulting made up to 50 cc. with water. Ammonia, free amino acids and amino nitrogen were determined on these dilutions.

Material precipitable by trichloroacetic acid was measured on 5-cc. aliquots of the reaction mixture which were diluted to 50 cc. without neutralization. Five cc. of this dilution was treated with 10 cc. of a 4% trichloroacetic acid solution, and after fifteen minutes filtered and the total nitrogen of the filtrate determined.

The heat coagulable material was determined by adjusting a 5-cc. aliquot of the hydrolyzate to about *p*H 4.5, heating on a boiling water-bath for five minutes. diluting to 50 cc. and filtering. Total nitrogen was run on the filtrate.

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[1] Kekwick and Cannan, *Biochem. J.*, **30**, 227 (1936).