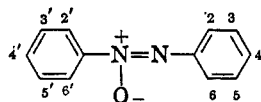


ucts) by sulfuric acid.¹ Shemyakin, Maimind, and Vaichunaite² rearranged azoxybenzene with N¹⁵ as a label and reported that the oxygen had appeared at the erstwhile 4 and 4' positions on the hydroxyazobenzenes and observed that the 4 position was slightly favored. It was felt by us that employment of ring labeling



would provide a firmer basis for considering a possible mechanism for the rearrangement, since the use of N¹⁵ assumes that each nitrogen remains attached to its ring throughout the rearrangement, certainly a reasonable hypothesis but one violated to some extent with diazonium ions.³ Therefore, azoxybenzene-1-C¹⁴ of known structure was prepared⁴ by vigorous oxidation of 2-(phenyl-1-C¹⁴)-3-cyanoindazole 1-oxide, followed by decarboxylation of the resultant azoxybenzene-2'-carboxylic acid-1-C¹⁴. The indazole was synthesized by condensing *o*-nitrobenzaldehyde and aniline-1-C¹⁴, followed by converting the anil thus formed to the cyano compound, and closing the ring with elimination of water.

The azoxybenzene-1-C¹⁴ was rearranged to hydroxyazobenzene by heating with concentrated sulfuric acid. The location of the tracer carbon atom was determined by reductive cleavage to aniline and *p*-aminophenol. Radioactive assays of the azoxybenzene, *p*-aminophenol, and acetanilide, to which the aniline had been converted, showed that the oxygen had appeared at the erstwhile 4 and 4' positions on the hydroxyazobenzenes, with the 4' position slightly favored.

Our results are therefore in essential agreement with those previously reported² though the slight excess of the 4' vs. 4 substitution, the opposite of that previously reported, remains unexplained. At any rate, a symmetrical intermediate appears to play an important part.^{5,6}

Experimental Section

2-(Phenyl-1-C¹⁴)-3-cyanoindazole Oxide.—A 30.2-g portion of *o*-nitrobenzaldehyde was condensed with 18.6 g of aniline-1-C¹⁴ and the resulting anil was converted to 2-(phenyl-1-C¹⁴)-3-cyanoindazole 1-oxide, mp 194–195°, by the method of Behr.⁴ The yield was 15.0 g (70% over-all).

Azoxybenzene-1-C¹⁴-2'-carboxylic Acid.⁴—2(Phenyl-1-C¹⁴)-3-cyanoindazole 1-oxide (12.0 g) was heated under reflux for 2 hr with chromic anhydride and acetic acid, allowed to cool, and poured into water. Successive extractions with ether and 10% aqueous sodium hydroxide, followed by acidification with 10% phosphoric acid, precipitated a sticky substance which later solidified. The solid was air dried and recrystallized from benzene-hexane as small, orange crystals, mp 102–103°, yield 8.0 g (64%).

Azoxybenzene-1-C¹⁴.—Azoxybenzene-1-C¹⁴-2'-carboxylic acid (8.0 g) was heated under reflux with copper powder and a trace of cupric acetate in pyridine for 18 hr. After the flask had cooled, the contents were filtered and the insoluble material was washed with ether. The combined filtrate was poured into 500 ml of ether and the ether solution was washed successively

with 10% hydrochloric acid, water, 5% aqueous sodium hydroxide, and again with water. The solution was dried and the ether was evaporated. The crude azoxybenzene (6.0 g), mp 32–34°, was separated from impurities by chromatography on an alumina column with hexane the mobile solvent. The yield was 4.5 g (68%) of azoxybenzene-1-C¹⁴, mp 35–36°.

The Wallach Transformation.—A solution of 4.0 g of azoxybenzene-1-C¹⁴ in 40 ml of 83% sulfuric acid was heated at 90° for 30 min and the products were separated and purified according to the procedure of Gore and Hughes.⁷ Crude *p*-hydroxyazobenzene in an amount of 2.2 g was obtained. Recrystallization from benzene gave 2.0 g (50%) of the phenol, mp 152–153°.

Reductive Cleavage of *p*-Hydroxyazobenzene-C¹⁴.—*p*-Hydroxyazobenzene⁸ (1.72 g) was reductively cleaved in the manner described in the literature to give *p*-aminophenol and aniline.

The *p*-aminophenol was recrystallized from 95% ethanol and weighed 0.474 g (50%), mp 193–194°. The aniline was converted to acetanilide which, after two crystallizations from water, weighed 0.603 g (51% over-all), mp 114°.

Radioactivity Assays.—The samples were assayed in duplicate with an error of about ±2%, or less, which is approximately that to be expected for samples of this level of radioactivity. The results are given in the Table I.

TABLE I

RADIOACTIVITY OF C ¹⁴	
Compd	μcurie/mmole
Azoxybenzene	0.3550
Acetanilide	0.1730
<i>p</i> -Aminophenol	0.1627

Acknowledgment.—The authors are indebted to Dr. C. J. Collins for the radioactivity assays.

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1,1,4,6,7-Pentamethylindan

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Isoprene combines with 1,2,4-trimethylbenzene (pseudocumene) in the presence of concentrated sulfuric acid to give a crystalline hydrocarbon, mp 74–76°, in 70% yield. 1,1,4,6,7-Pentamethylindan (1) was suggested² as the most likely structure for this new hydrocarbon. The most convincing argument for this assignment is the known course of electrophilic substitution of 1,2,4-trimethylbenzene in comparable reactions and comparison with products obtained from other cyclalkylation reactions. The nmr, mass, and infrared spectra of the new hydrocarbon clearly showed it to be a pentamethylindan. However, these data failed to eliminate conclusively structure 2 as a possibility. It is recognized that an appropriate catalog of nmr spectra

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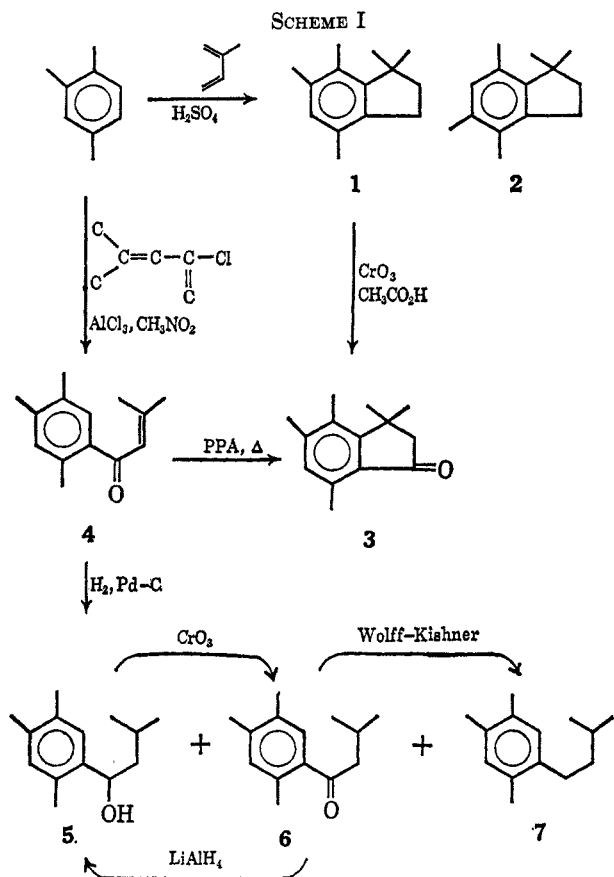
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would have readily clarified this point; however, the spectra of the model compounds were not available.

A convincing structure assignment for the unknown pentamethylindan became essential because this hydrocarbon has been prepared in quantity and purified as a reference hydrocarbon for the Standard Samples Program of the American Petroleum Institute.³

A structure proof for the isoprene cyclialkylation product from 1,2,4-trimethylbenzene was carried out, as shown in Scheme I, by chromic acid oxidation of 1



to 3,3,4,5,7-pentamethyl-1-indanone (3) which was directly compared with a sample of 3 obtained by independent synthesis from 1,2,4-trimethylbenzene *via* the ketone 4. The structure of 4 was obtained by conversion to 5, 6, and 7, and establishing the structure of these. The hydrogenation of the α,β -unsaturated ketone 4 in the presence of Pd-C in acetic acid solution gave 5, 6, and 7 in the ratio of 6:2:1. We attribute this extensive hydrogenation and hydrogenolysis of 4 to the unsaturation on both sides of the carbonyl function. A similar result was observed in the reduction of mesityl oxide to 4-methyl-2-pentanol.⁴

The separation of 5 and 6 was facilitated by oxidizing the mixture of 5, 6, and 7 with chromic acid to a mixture of 6 and 7 which effectively removed 5 as a contaminant. In a like manner, 6 was removed from the mixture by lithium aluminum hydride reduction of 6 to 5. The purification of 5 and 6 was considerably simplified by these interconversions.

(3) Correspondence regarding samples of 1 should be directed to A. J. Streiff, American Petroleum Institute Samples Office, Petroleum Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

(4) E. Bretner, E. Roginski, and P. N. Rylander, *J. Org. Chem.*, **24**, 1855 (1959).

The number of products obtained from these oxidation and reduction reactions, along with the coincidence of their peak gas chromatography retention times with those of individual components of the original mixture, strongly supports the functional group assignments to 5 and 6 and suggests that 7 is a hydrocarbon, since the retention time of the latter on the gas chromatogram remained unchanged by these reactions.

The structure of the key reaction product 7 was rigorously established through its infrared, mass, and nmr spectra. These data and corresponding studies for 4, 5, and 6 establish 4, 5, 6, and 7 to be 1,2,4,5-tetra-substituted benzenes. The unsaturated ketone 4 was cyclized to 3,3,4,5,7-pentamethyl-1-indanone (3), and this latter ketone was shown to be identical with 3 prepared from 1 by comparison of their infrared, mass, and nmr spectra. A mixture of 3 from the two sources showed no depression in melting point.

Experimental Section

1,1,4,6,7-Pentamethylindan (1).⁵—Into a 22-l. flask equipped with an XP Lightnin stirrer and dropping funnel were placed 5 l. of pseudocumene and 700 ml of 93% sulfuric acid. The flask and contents were cooled to 0° with an ice-salt bath, and a mixture of 1008 ml of isoprene (10.2 moles) and 1.6 l. of pseudocumene was added over a period of 2 hr. The reaction mixture was stirred for 15 min more. During the course of addition, the temperature varied from -5 to 2°. After crude product was poured into a 12-l. separatory funnel, the acid layer was drained and 500 ml of water was added to hydrolyze the remaining organic layer. The mixture was neutralized with aqueous sodium carbonate, dried over magnesium sulfate, and filtered. Distillation gave 4030 g of recovered pseudocumene and 1342 g (70.0%) of the colorless, crystalline indan melting at 74–75°. The residue weighed 186 g. The crude indan was recrystallized from ethanol-benzene, Skelly solvent B, and again from ethanol-benzene. The melting range of the purified indan was 74–76° and this product was shown by gas chromatography analysis (10 ft \times 1/4 in., 20% LAC-886 at 180°) to be one compound. The infrared spectrum showed ν_{max}^{KB} 860 cm^{-1} and 1310 cm^{-1} , indicative of an indan and pentaalkylbenzene structure.^{2,6} A parent ion peak at m/e 188 was observed in the mass spectrum⁶ of 1. The nmr spectrum showed absorption signals relative to tetramethylsilane⁷ due to a pair of geminal methyl groups at 1.33 ppm (6 H, singlet), a methylene group centered at 1.85 ppm (2 H, triplet), three methyl groups attached to an aromatic ring at 2.12, 2.17, and 2.18 ppm (9 H, 3 singlets), a methylene group centered at 2.64 ppm (2 H, triplet), and one proton attached to an aromatic ring at 6.64 ppm (1 H, singlet).

2',3,4',5'-Tetramethylcrotonophenone (4).⁸—A 72-g (0.6 mole) sample of 1,2,4-trimethylbenzene was acylated with 66 g (0.55 mole) of 2,2-dimethylacryloyl chloride⁹ in 250 ml of nitromethane by adding 80 g (0.6 mole) of aluminum chloride over 1 hr at -10°. The product was distilled at 137–141° (6 mm) [lit.⁸ bp 131–131.5° (6 mm)] to give, after a small forerun, 92 g (76% yield) of 4. Gas chromatography analysis at 200° on a 1/4 in. \times 10 ft column of 80–100 mesh, acid-washed Chromosorb W coated with 25% Carbowax 20M showed a major peak at 43-min retention time and a small peak at 31 min. The infrared spectrum of 4 showed absorption at 1655 cm^{-1} and 855 cm^{-1} (neat) and the ultraviolet spectrum showed λ_{max}^{EtOH} 260 $m\mu$ ($\log \epsilon$ 5.92). The mass spectrum showed a parent ion peak at m/e 202.⁸

(5) Taken in part from the M.S. thesis of J. R. M., Oklahoma State University, May 1965.

(6) We are indebted to Mr. Mynard C. Hamming and Dr. R. D. Grigsby of the Continental Oil Co., Ponca City, Okla., for mass spectra and Dr. M. Evens for infrared determinations.

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(9) 2,2-Dimethylacryloyl chloride was prepared from 2,2-dimethylacrylic acid by reaction with thionyl chloride.

The nmr spectrum of **4** showed absorption signals due to two protons attached to an aromatic ring at 6.86 and 7.18 ppm (2 H, 2 singlets), an olefinic proton at 6.35 ppm (1 H, multiplet), three methyl groups attached to an aromatic ring at 2.36, 2.20, and 2.20 ppm (9 H, 3 singlets), and two methyl groups attached to a double-bond carbon at 2.14 and 1.93 ppm (6 H, 2 doublets).

The orange 2,4-dinitrophenylhydrazone of **4** melted at 211–213°.

Anal. Calcd for $C_{20}H_{22}N_4O_4$: C, 62.81; H, 5.80; N, 14.65. Found: C, 62.48; H, 6.09; N, 14.68.

3,3,4,5,7-Pentamethyl-1-indanone (3) from 4.—A 20-g sample of **4** was cyclized by heating in the presence of 200 g of polyphosphoric acid from an initial temperature of 80° to a final temperature of 110° during 15 min. The reaction mixture was cooled to 60°, poured over crushed ice, and extracted with ether, and the ether layer was dried and distilled to give 19.8 g (98% yield) of yellow oil. The oil, after distillation at 100–105° (3 mm), was crystallized from ether to give colorless 3,3,4,5,7-pentamethyl-1-indanone (**3**) which melted at 52–53° (lit.⁸ mp 54–55.5°).

The red 2,4-dinitrophenylhydrazone melted at 263–265°.

Anal. Calcd for $C_{20}H_{22}N_4O_4$: C, 62.81; H, 5.80; N, 14.65. Found: C, 62.92; H, 5.96; N, 14.81.

3,3,4,5,7-Pentamethyl-1-indanone (3) from 1.—1,1,4,6,7-Pentamethylindan (**1**) (94 g, 0.5 mole), 150 ml of methylene chloride, and 150 ml of acetic acid were placed in a 2-l., three-necked flask equipped with a mechanical stirrer, a condenser, and a thermometer. To this cooled solution, 75 g (0.75 mole) of chromium trioxide dissolved in 50 ml of water and 350 ml of acetic acid were added over a period of 40 min, and the reaction mixture was stirred at room temperature for 10 days. The course of the reaction was followed by sampling at intervals and analyzing the samples by gas chromatography on the Carbowax 20M column at 200°. During this period, an additional 40 g of chromium trioxide and 350 ml of acetic acid were added. The reaction mixture was poured onto ice and was then extracted with ether. The ether layer was washed with sodium bicarbonate solution, dried, and concentrated to give a dark green oil. Gas chromatographic analysis of this crude material on the Carbowax column showed 6% starting material, which was removed by steam distillation. The steam-distillation residue was extracted with ether, and the ether extract was dried and concentrated to give 82 g of oil which was distilled at 100–105° (3 mm). The product crystallized on standing, and, after crystallization from ether, gave colorless material, mp 51.5–52.5°. Gas chromatographic analysis on the Carbowax 20M column showed a single compound with the same retention time as the indanone prepared from **4**. The melting point of a mixture of **3** from **1** and **4** showed no depression. The 2,4-dinitrophenylhydrazone of **3**, mp 263–265°, was prepared. An admixture of this derivative with the 2,4-dinitrophenylhydrazone of **3** prepared from **4** showed no depression in melting point. The nmr spectra of the two ketones in CCl_4 were identical and showed absorption peaks due to geminal methyl groups at 1.55 ppm (6 H, singlet), three methyl groups attached to an aromatic ring at 2.51, 2.35, and 2.30 ppm (9 H, 3 singlets), a methylene group at 2.46 ppm (2 H, singlet), and a proton attached to an aromatic ring at 6.83 ppm (1 H, singlet). The mass spectrum shows a parent ion peak at m/e 202.

Hydrogenation of 2',3,4',5'-Tetramethylcrotonophenone (4).—The ketone **4** (15 g), dissolved in 25 ml of acetic acid, was shaken in the presence of 500 mg of 10% Pd-C in the presence of catalyst at 40 psi of hydrogen for 24 hr. The excess was vented and the catalyst filtered out of the suspension. The filtrate was diluted with water and extracted with ether, and the ether extract washed with saturated sodium bicarbonate solution, dried, and concentrated to give 14.8 g of colorless oil. The infrared spectrum of this oil showed ν_{max}^{neat} 3367 and 1696 cm^{-1} , indicative of hydroxyl and ketone carbonyl functions.⁹ Gas chromatographic analysis on the Carbowax 20M column showed three peaks in the ratio 6:2:1. These were subsequently shown to be **5**, **6**, and **7**, respectively.

Lithium Aluminum Hydride Reduction of the Crude Mixture of 5, 6, and 7.—The crude mixture of **5**, **6**, and **7** (1 g) was reduced by 100 mg of lithium aluminum hydride dissolved in 100 ml of refluxing anhydrous ether. The product was isolated as an oil which showed two gas chromatography peaks on the Carbowax column corresponding to **5** and **7**. An absorption band, ν_{max}^{neat} 3367 cm^{-1} , indicative of the presence of alcohol **5**, was observed.⁶ There was no absorption due to ketone carbonyl.

Lithium Aluminum Hydride Reduction of Purified 2',3,4',5'-Tetramethylbutyrophenone (6) to 3-Methyl-1-(2,4,5-trimethylphenyl)-1-butanol (5).—A 2.04-g sample of **6**, purified by preparative-scale gas chromatography on a Carbowax 20M column, was reduced with lithium aluminum hydride as described above to give 3-methyl-1-(2,4,5-trimethylphenyl)-1-butanol (**5**) as white needles, mp 47–48°, which showed ν_{max}^{KBr} 3340 and 870 cm^{-1} in the infrared and the following nmr absorption: two protons attached to an aromatic ring at 7.04 and 6.72 ppm (2 H, 2 singlets), the proton on the carbon-bearing hydroxyl at 4.72 ppm (1 H, 2 doublets), three methyl groups attached to an aromatic ring at 2.16, 2.16, and 2.14 ppm (9 H, 3 singlets), the hydroxyl proton at 1.80 ppm (1 H, singlet), three aliphatic protons from 1.8 to 1.0 ppm (3 H, multiplet), and two geminal methyl groups centered at 0.91 ppm (6 H, 2 doublets).

Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.82; H, 10.81.

Chromic Acid Oxidation of the Crude Mixture of 5, 6, and 7.—The crude mixture of **5**, **6**, and **7** (30.5 g) from the hydrogenation of **4** was dissolved in 250 ml of distilled acetone and oxidized with 40 ml of a solution of chromic acid, sulfuric acid, and water.¹⁰ 2',3,4',5'-Tetramethylbutyrophenone (**6**)¹¹ (26 g) was isolated from the reaction mixture and purified by preparative gas chromatography on a Carbowax column to remove **7**. A sample of **6** was analyzed.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.10; H, 9.77.

The orange 2,4-dinitrophenylhydrazone of **6** on recrystallization from isopropyl alcohol melted at 133–134°.

Anal. Calcd for $C_{20}H_{24}N_4O_4$: C, 62.48; H, 6.29; N, 14.58. Found: C, 62.36; H, 6.27; N, 14.38.

The infrared spectrum of purified **6** showed ν_{max}^{neat} 1696 cm^{-1} and 865 cm^{-1} , indicative of the presence of a ketone function and tetraalkylbenzene ring.

The nmr spectrum of **6** showed absorption due to an isopropyl group centered at 0.935 ppm (6 H, doublet), two methyl groups on aromatic ring at 2.17 ppm (6 H, singlet), a methyl group on aromatic ring at 2.39 ppm (3 H, singlet), one methylene group centered at 2.65 (2 H, doublet), and two protons on an aromatic ring at 6.84 and 7.28 ppm.

Wolff-Kishner Reduction of 2',3,4',5'-Tetramethylbutyrophenone (6) to 1-Isopentyl-2,4,5-trimethylbenzene (7).—The ketone **6** (10.2 g) was dissolved in 150 ml of diethylene glycol and heated at 70–80° with 7 ml of 85% hydrazine hydrate and 12 g of potassium hydroxide for 2 hr. The temperature was slowly increased and the hydrocarbon **7** was steam distilled from the reaction flask as it formed. The distillate was extracted with ether, and washed with 10% hydrochloric acid, then with water. The ethereal extract was dried and distilled under reduced pressure to give 1-isopentyl-2,4,5-trimethylbenzene (**7**), bp 72–74° (0.4 mm). Gas chromatography analysis of **7** on the Carbowax 20M column at 200° showed a single peak.

Anal. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.55; H, 11.68.

The infrared spectrum of **7** showed ν_{max}^{neat} 870 cm^{-1} , characteristic of a 1,2,4,5-tetrasubstituted benzene.⁶ The mass spectrum showed the expected parent ion peak at m/e 190.⁶ The nmr spectrum of **7** showed absorption due to an isopropyl group centered at 0.941 ppm (6 H, doublet), the angular proton of the isopropyl group, as well as the adjacent methylene group, centered at 1.39 ppm (4 H, multiplet), two methyl groups attached to an aromatic ring at 2.11 ppm (6 H, singlet), a methyl group attached to an aromatic ring at 2.15 ppm (3 H, singlet), a methylene group centered at 2.44 ppm (2 H, multiplet), and two protons on an aromatic ring at 6.73 ppm (2 H, singlet).

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