as the dibromide is sensitive to heat and partially decomposes with the evolution of hydrogen bromide, even at temperatures less than 100°. In 14 runs, 53.4 kg. (93.2% average yield from diol) of the crude dibromide was obtained; distillation of 33.1 kg. of this product gave 14.1 kg. of purified dibromide (40% average yield). To eliminate losses inherent in the distillation, the remainder of the crude dibromide was used as such, since it was found to be essentially pure and its use gave rise to no undesirable by-products.

A small amount of this dibromide was prepared by the reaction of "2-methylpentadiene" (Shell Development Co.) with anhydrous hydrogen bromide. In a typical run about 200 ml. of the diene was placed in a 500-ml. 3-neck flask fitted with a stirrer, a gas inlet tube projecting beneath the liquid surface, and a gas outlet tube connected to a bubbler. When the flask and its contents had been cooled to about 0°, commercial hydrogen bromide gas was metered into the flask at such a rate that excess gas emerged occasionally at the exit bubbler. When the theoretical amount had been added, the dibromide was washed rapidly with ice-water to remove excess acid. The yields of the dibromide were practically quantitative and its physical properties checked closely with those of the same product prepared from the diol.

1,3-Dibromo-2,3-dimethylbutane.—Anhydrous hydrogen bromide was added to 2,3-dimethyl-1,3-butadiene by virtually the same procedure as described above. Two dibromides are produced by this reaction. One of the products, 2,3-dibromo-2,3-dimethylbutane (30% yield) is a solid melting at 160 to 164° and boiling at 78° (10 mm.). The other product, 1,3-dibromo-2,3-dimethylbutane (70% yield), is a liquid boiling at 76° (10 mm.). Thus it was easy to separate the desired product by chilling and removing most of the undesired 2,3-dibromide by filtration.

1,3-Dibromo-2,2-dimethylbutane.—The condensation product of acetaldehyde and isobutyraldehyde[12,13] was hydrogenated over Raney nickel at 70° and 1500 p.s.i. of hydrogen to produce 2,2-dimethyl-1,3-butanediol (b.p. 121° (20 mm.), $n^{20}\text{D}$ 1.4408); the yield was 13% based on isobutyraldehyde. The glycol was treated with phosphorus tribromide at 0°, and the mixture was then heated to 50° (to complete reaction with the primary hydroxyl group). The reaction mixture was poured onto crushed ice, and the heavy dibromide layer which separated was used without further purification.

1,1,2-Trimethylcyclopropane.—The 2,4-dibromo-2-methylpentane (5 moles) was caused to react with zinc dust in aqueous *n*-propanol at 0° by the procedure of Lankelma, *et al.*[3] All material boiling up to 70° was removed from the reaction mixture by distillation through a small Vigreux column. In 18 runs, a total of 5610 g. (67% average yield from dibromide) of crude (dried) hydrocarbon was obtained.

The small quantities of 1,3-dibromo-2,3-dimethylbutane and 1,3-dibromo-2,2-dimethylbutane were debrominated by essentially the same procedure.

Hydrogenolysis of 1,1,2-Trimethylcyclopropane.—The catalyst used was $^1/_8$ inch pellets of 20% nickel-on-kieselguhr (Universal Oil Products Co.); 20 g. of it was triturated under the hydrocarbon sample (140 g., 99 mole % pure), and the mixture was placed in a 300 ml. high-pressure, rocking autoclave (American Instrument Company). Reaction with hydrogen was effected as described earlier in this paper. The hydrogenate was fractionated at about 35-plate efficiency, the individual hydrocarbons being identified by comparison of their boiling points and refractive indices, as read from the distillation curves, with reliable literature values.

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[12] V. Grignard and P. Abelman, *Bull. soc. chim.*, [4] **7**, 645 (1910).

[13] E. Swoboda and W. Fossek, *Monatsh.*, **11**, 389 (1890).

COLUMBUS, OHIO RECEIVED JULY 2, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

The Synthesis, Purification and Properties of *t*-Amylbenzene[1]

BY MASAHIRO INATOME, KENNETH W. GREENLEE, JOHN M. DERFER AND CECIL E. BOORD

Much confusion exists in the literature concerning the physical properties of *t*-amylbenzene. In the present research several methods for preparing the hydrocarbon were investigated, and the reaction of *t*-amyl chloride with benzene, catalyzed with anhydrous ferric chloride, was found best from the standpoint of yield and purity of the product. Aluminum chloride, the commonly used catalyst, gave a product containing a major portion of isomeric amylbenzenes. Accurate physical properties for *t*-amylbenzene and for the derived *t*-amylcyclohexane are given for the first time.

Syntheses (mostly Friedel–Crafts type reactions[2]) and physical properties of *t*-amylbenzene have been reported in the literature on numerous occasions,[3] but the reported properties showed such a wide range of variation that it was impossible to judge which product, if any, was authentic and pure. The present work was undertaken to investigate and evaluate several methods for preparing *t*-amylbenzene and to obtain accurate physical properties for the hydrocarbon.

From previous work done in this Laboratory, it was known that the aluminum chloride catalyzed reaction between *t*-butyl chloride and benzene gave a 65% yield of 99.8 mole per cent. pure *t*-butylbenzene after a single distillation of the reaction product at about 20-plate efficiency. Consequently, the preparation of pure *t*-amylbenzene was first attempted by the aluminum chloride catalyzed reaction between *t*-amyl chloride and benzene. The reaction was carried out on the enlarged laboratory scale, and the reaction product showed itself to be a mixture on distillation at about 30-plate efficiency; the best fractions (3980 g., corresponding to a 52% yield) boiled at 190 to 191°, uncor., and had a refractive index range ($n^{20}\text{D}$) of 1.4930 to 1.4957. This product was then fractionated at better than 100-plate efficiency.[4] The observed boiling points described a curve (initial boiling point, 190.5°) which rose almost steadily throughout the first 74% of the distillation; the following 20% appeared on a plateau (b.p. 192.39 to 192.41°) (760 mm.); the residue, 6% of the charge, had

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[1] This paper was abstracted in part from a thesis submitted in 1949 by Masahiro Inatome to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degree Master of Science. The rest of the work described was carried out by the American Petroleum Institute Research Project 45 which is administered by The Ohio State University Research Foundation. This work was presented before the Organic Division of the A. C. S. at its 118th Meeting.

[2] For a review on this type of reaction see "Organic Reactions," Vol. III, by C. C. Price, John Wiley and Sons, Inc., N. Y., 1946, Chapter 1.

[3] A few of the key references to these works are: (a) G. F. Hennion and R. A. Kurtz, THIS JOURNAL, **65**, 1001 (1943); (b) V. N. Ipatieff and L. Schmerling, *ibid.*, **60**, 1476 (1938); (c) M. J. O'Conner and F. J. Sowa, *ibid.*, **60**, 125 (1938); (d) R. C. Huston, W. B. Fox and M. N. Binder, *J. Org. Chem.*, **3**, 251 (1938).

[4] This fractionation was performed at the National Bureau of Standards by the American Petroleum Institute Research Project 6, F. D. Rossini, Director.

properties similar to those of the plateau material. The refractive index curve roughly paralleled the boiling curve. As described later in this paper, the plateau material was shown to be relatively pure *t*-amylbenzene. Techniques used in attempting to identify the close-boiling impurities in the riser fractions included oxidation with alkaline permanganate, selective adsorption on silica gel, infrared absorption spectra, and physical property studies. Most of the evidence pointed toward isomeric amylbenzenes, especially 1-phenyl-2-methylbutane and 2-methyl-3-phenylbutane, but some of the oxidation evidence seemed inconsistent with these structures. The *t*-butyltoluenes were ruled out on the basis of their physical properties which are accurately known[5]; the properties of amylbenzenes reported in the literature are not sufficiently reliable to confirm or deny their presence in the mixture.[5a]

t-Amylbenzene was synthesized by two methods involving the Grignard reaction, methods which offered little likelihood of rearrangement and would give authentic *t*-amylbenzene.

The Grignard reagent from bromobenzene was condensed with an equimolar quantity of acetone; hydrolysis of the reaction product gave dimethylphenylcarbinol. Reaction of the crude carbinol with anhydrous hydrogen chloride at ice temperature converted it to the corresponding chloride, which was not purified but was condensed directly with ethyl Grignard reagent to produce *t*-amylbenzene. The products from the two runs were distilled separately at about 30-plate efficiency, and *t*-amylbenzene (b.p. 192.20 to 192.35°, n^{20}_{D} 1.4957 to 1.4958) was obtained in over-all yields of 9.9 and 17.4%, respectively. These products were bulked and refractionated at 30-plate efficiency; the physical properties of the best fractions (b.p. 192.36 to 192.39°, d^{20}_4 0.8747 to 0.8750, n^{20}_{D} 1.4958 to 1.4961) were considered reliable for *t*-amylbenzene. This product (as well as all other samples investigated in the present work) did not crystallize, but formed a viscous glass when cooled by liquid air; neither is any freezing or melting point for *t*-amylbenzene reported in the literature. An infrared absorption spectrogram of the product showed prominent bands in the several regions which characterize monoalkylbenzenes.[6]

The *t*-amylbenzene prepared by the reaction between phenylmagnesium bromide and *t*-amyl chloride boiled at 192.30° (760 mm.) and had a refractive index of 1.4953 to 1.4955, but the yield was only 1.5%, over-all.

The *t*-amylbenzene (plateau fractions) from the large scale aluminum chloride catalyzed reactions was shown to be virtually identical with that prepared by the two Grignard reactions on the basis of infrared spectra and physical properties.

Several experiments were run in which a mixture of isoamylenes (2-methyl-1- and 2-methyl-2-butene) was condensed with benzene in the presence of 96% sulfuric acid. Reaction time was varied from 1 to 3 hours and the temperature from 5 to 20°. The yield varied from 8 to 18% of a product of variable refractive index (1.4918 to 1.4951), after fractionation at about 10-plate efficiency. The product from six runs was bulked and refractionated at about 30-plate efficiency to obtain a sample (2% over-all yield) with the following physical properties: b.p. 192.33 to 192.43° (760 mm.), d^{20}_4 0.8727 to 0.8732, n^{20}_{D} 1.4947 to 1.4950. This product appeared to consist of *t*-amylbenzene, somewhat contaminated with olefinic or paraffinic material derived from amylene. The synthesis was judged unsuitable for production of *t*-amylbenzene in quantity and high purity.

The reaction between *t*-amyl alcohol and benzene in the presence of sulfuric acid gave apparently good *t*-amylbenzene (n^{20}_{D} 1.4957) in 5.4% yield.

The product of the reaction between *t*-amyl chloride and benzene in the presence of anhydrous $FeCl_3$ had physical properties (b.p. 192.36–192.38°, n^{20}_{D} 1.4956–1.4960, d^{20}_4 0.8747–0.8750) which corresponded closely to the values assumed correct for *t*-amylbenzene, and the yield was good[7] (60%, based on *t*-amyl chloride). An infrared spectrum of the best sample was, within experimental error, identical with that of the product made by the Grignard method. When ferric chloride with a nitromethane modifier[8] was used, the boiling point of the aromatic was slightly lower (192.29°), and the yield was reduced to 33% of the theoretical. When, however, the nitromethane modifier was added in the aluminum chloride catalyzed reaction of *t*-amyl chloride and benzene, *t*-amylbenzene (b.p. 192.35°, n^{20}_{D} 1.4956 to 1.4960) of good purity was obtained; the yields were 15 to 18% of the aromatic which, according to its infrared spectrum, was identical with that made by the Grignard method.

The reaction of *t*-amyl alcohol and benzene in the presence of aluminum chloride gave a mixture from which no *t*-amylbenzene could be isolated by distillation; the boiling point of the highest boiling fraction was 191.97° and the refractive index range was 1.4942 to 1.4952, both ranges being low.

To prove the structure of the *t*-amylbenzene, one of the best (plateau) fractions from the 100-plate distillation of the aluminum chloride catalyzed reaction between benzene and *t*-amyl chloride was hydrogenated to its hexahydro derivative, *t*-amylcyclohexane. To compare with this product, then, a sample was prepared by an independent method: technical *p*-*t*-amylphenol was hydrogenated; the resulting *p*-*t*-amylcyclohexanol was dehydrated; and the formed cycloölefin was hydrogenated to *t*-amylcyclohexane. In distillation analysis, it exhibited nearly constant properties (Table II) which were virtually identical with those of the hydrogenated *t*-amylbenzene. Neither sample would

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[5] K. T. Serijan, H. F. Hipsher and L. C. Gibbons, THIS JOURNAL, **71**, 873 (1949).

[5a] Work is underway in this Laboratory to synthesize high purity samples of these isomeric amylbenzenes and to determine their physical properties accurately.

[6] Communication from the Stamford Research Laboratories of the American Cyanamid Co.

[7] Using this method at a later date, the American Petroleum Institute Research Project 45 prepared over 2.2 gallons of tertiary amylbenzene with the following physical properties: b.p. 192.37 to 192.39° (760 mm.,) n^{20}_{D} 1.4957 to 1.4958, d^{20}_4 0.8749 to 0.8752.

[8] According to the suggestion of L. Schmerling, *Ind. Eng. Chem.*, **40**, 2072 (1948).

TABLE I

SYNTHESES OF *t*-AMYLBENZENE

Reactants	Catalyst	Reaction temp., °C.	*t*-Amylbenzene obtained	
			Yield, %	Quality
Benzene, *t*-amyl chloride	$AlCl_3$	25–30	52	Poor (isomers)
Benzene, *t*-amyl chloride	$AlCl_3$; CH_3NO_2	25–30	18	Good
Benzene, *t*-amyl chloride	$FeCl_3$	10–25	60	Good
Benzene, *t*-amyl chloride	$FeCl_3$; CH_3NO_2	10–25	33	Good
Benzene, *t*-amyl alcohol	$AlCl_3$	25–50	0	. . .
Benzene, *t*-amyl alcohol	H_2SO_4	60–65	5	Good
Benzene, *i*-amylenes	H_2SO_4	5–20	18	Poor (aliphatics)
2-Phenyl-2-chloropropane, ethylmagnesium bromide	. . .	35	17	Good
Phenylmagnesium bromide, *t*-amyl chloride	. . .	35	1.5	Good

TABLE II

PROPERTIES OF *t*-AMYLCYCLOHEXANE

	Prepared from *t*-amylbenzene	Prepared from *t*-amylphenol	Literature	
			a	*b*
B.p., °C. (760 mm.)	198.36–198.39	198.39–198.41	193.2–195.2	191–192
d^{20}_4	0.8287	0.8288	0.821 $\left(\frac{20}{20}\right)$	0.8226 $\left(\frac{16}{4}\right)$
n^{20}_D	1.4547–1.4549	1.4548	1.4510	1.4538 $\left(\frac{16}{D}\right)$

[a] F. K. Signaigo and P. L. Cramer, THIS JOURNAL, 55, 3326 (1933). [b] O. M. Halse, *J. prakt. Chem.*, 92, 40 (1915).

crystallize, but their infrared spectra were identical. It appears that the property data from the literature are unreliable.

Experimental

Aluminum Chloride Catalyzed Reaction.—*t*-Amyl chloride (25 moles) was added dropwise to a mixture of 100 moles of benzene and 100 g. of anhydrous aluminum chloride in a 3-neck flask, suitably equipped. Reaction proceeded with vigorous evolution of gas (hydrogen chloride), temperature remaining at 25 to 30°. Hydrolysis was carried out as soon as the last of the chloride had been added. Excess benzene was stripped from the product which was then separated from polyamylbenzenes by distillation under reduced pressure and was freed from halogen impurities by treatment with sodium in liquid ammonia to obtain a 52% over-all yield (average of 5 runs) of semi-pure *t*-amylbenzene.

Grignard Method 1.—Five gram atoms (121.5 g.) of magnesium turnings and 2 liters of absolute ether were placed in a 5-liter, 3-neck flask, suitably equipped. Five moles (784.5 g.) of bromobenzene (n^{20}_D 1.5232, Dow Chemical Company) diluted with an equal volume of ether was added dropwise into the flask with stirring.

After the addition of the bromobenzene was completed, 290 g. (5 moles) of acetone, dried over calcium chloride and mixed with 300 cc. of ether, was added dropwise at such a rate as to maintain a steady reflux of ether; hydrolysis was effected with water and dilute (1:1) hydrochloric acid. The crude product was stripped of ether, and then was treated exhaustively at 0° with anhydrous hydrogen chloride. The excess gas was removed by aspiration, and 3.9 moles (a 78% yield) of crude phenyldimethylcarbinyl chloride was obtained after drying over anhydrous sodium sulfate.

Ethylmagnesium bromide was prepared in the same manner as phenylmagnesium bromide, 3.9 moles each of ethyl bromide and magnesium and 1600 cc. of ether being used. Three and nine-tenths moles of crude phenyldimethylcarbinyl chloride in 500 cc. of ether was added dropwise to the ethylmagnesium bromide. The resulting mixture was refluxed for four days, and hydrolyzed as described previously.

The crude *t*-amylbenzene was dried by percolation through silica gel and treated with a sodium–liquid ammonia solution to remove chlorides. The product was steam distilled and dried to give 341 g. (a 46% over-all yield) of crude *t*-amylbenzene, which was subsequently distilled at atmospheric pressure on a thirty-plate column.

Grignard Method 2.—The apparatus used was the same as that of the previous Grignard reactions. Three moles of bromobenzene diluted with an equal volume of ether was added dropwise to 3 gram atoms of magnesium, which was covered with 700 cc. of ether. After the reaction was completed, 3 moles of *t*-amyl chloride was added to the Grignard product at such a rate as to maintain a steady reflux of ether. Then, the mixture was refluxed for 24 hours at 45°. After the mixture had been hydrolyzed with water and hydrochloric acid and the ether distilled off, the concentrate had a purple color. It was then treated with sodium in liquid ammonia, steam distilled and dried, 36 g. (an 8% yield) of crude *t*-amylbenzene resulting.

Sulfuric Acid-catalyzed Friedel–Crafts Reactions.—The method used was essentially that of Corson and Ipatieff.[9] Five moles (468 g.) of thiophene-free benzene (Mallinckrodt Chemical Works) and 92 g. of C.P. concentrated H_2SO_4 (sp. gr. 1.84) were placed in a 1-liter, 3-neck flask, suitably equipped. The mixture was cooled to 5° by an ice-bath, and 2 moles (140 g.) of isoamylene (b.p. 31–38°) was added dropwise with moderate stirring. The temperature could not always be maintained at 5° due to the heat of reaction. In all the runs (six), stirring was continued 10 minutes after the addition of the olefins was completed. The hydrocarbon layer was cooled to 0° and washed with four 50-cc. portions of cold concd. sulfuric acid, once with warm water (50°), twice with 3% KOH, again with distilled water, and then was dried over silica gel.

Sulfuric Acid-catalyzed Reaction of *t*-Amyl Alcohol and Benzene.[10]—Two moles of benzene and 5 moles of 80% H_2SO_4 were placed in a 1-liter, 3-neck flask, suitably equipped. Stirring was begun, and the contents heated to 60–65°. One mole (88 g.) of *t*-amyl alcohol was added dropwise, after which the reaction mixture was heated for a period of three and one-half hours. The hydrocarbon layer was washed with four 50-cc. portions of concentrated sulfuric acid, once with water, once with a dilute sodium carbonate solution, and then steam distilled. The product was dried over silica gel and distilled under reduced pressure.

Ferric Chloride-catalyzed Friedel–Crafts Reaction.—In a 500-cc., 3-neck flask, suitably equipped, were placed 1.35 moles (105 g.) of thiophene-free benzene and 0.07 mole of anhydrous ferric chloride (Coleman and Bell); partially deteriorated material (yellow to orange) was rejected, and only the black granular crystals were used. Stirring was begun, and the mixture was cooled to 10°, and then 0.27 mole of *t*-amyl chloride (b.p. 153° (750 mm.), n^{20}_D 1.4052) was added dropwise. After the addition was completed, the mixture was slowly warmed to 25°. When the evolution of hydrogen chloride gas ceased, the reaction mixture was poured into a hydrochloric acid–ice-water mixture. The hydrocarbon layer was washed with a sodium carbonate solution and steam distilled. Six such experiments were

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[9] B. B. Corson and V. N. Ipatieff, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 151.

[10] *Cf.* V. N. Ipatieff, H. Pines and L. Schmerling, *J. Org. Chem.*, **5**, 253 (1940).

carried out, and the crude hydrocarbons were combined for distillation.

Ferric Chloride-catalyzed Reaction Moderated with Nitromethane.—The method was the same as that employed previously except that 20 cc. of nitromethane was placed in the flask before the addition of *t*-amyl chloride.

Aluminum Chloride-catalyzed Reaction Moderated with Nitromethane.—To 0.037 mole (5 g.) of $AlCl_3$ and 2 moles (156 g.) of benzene was added 20 cc. of nitromethane, followed by the drop-wise addition of 1 mole (106.5 g.) of *t*-amyl chloride at room temperature; a rise in temperature was not noticed during the course of the experiment. The product was hydrolyzed in the usual manner.

The above experiment was repeated with 10 g. of $AlCl_3$ instead of 5 g., and the mixture was stirred vigorously during the addition of *t*-amyl chloride.

Aluminum Chloride-catalyzed Reaction between Benzene and *t*-Amyl Alcohol.[11]—One mole (88 g.) of *t*-amyl alcohol (n^{20}D 1.4052, b.p. 102° (750 mm.)) reacted at room temperature and high speed stirring with 4 moles (312 grams) of benzene, the reaction being catalyzed by one-half mole (66.7 g.) of $AlCl_3$; the reaction was exothermic, but no attempt was made to cool the mixture. After two-thirds of the alcohol had been added, the mixture separated into two layers, the bottom layer being very dense. Stirring was again started (with considerable difficulty), and the remainder of the alcohol was added with little evolution of HCl. The reaction mixture was poured into a hydrochloric acid–ice-water mixture and then washed with alkali and steam distilled.

Hydrogenation of *t*-Amylbenzene.—High purity *t*-amylbenzene (129 g.) was hydrogenated over nickel-on-kieselguhr catalyst at 200° and 1800 p.s.i. The hydrogenate (90 g.) was distilled at atmospheric pressure on a column rated at 20 theoretical plates. The observed boiling point was not constant, probably due to a little unchanged *t*-amylbenzene; therefore, the crude *t*-amylcyclohexane was percolated through silica gel, and redistilled before physical properties were measured.

***t*-Amylcyclohexane from *p*-*t*-Amylphenol.**—*p*-*t*-Amylphenol (800 g. or 4.9 moles), supplied by Sharples Chemicals Inc., was dissolved in 1000 cc. of ethylcyclohexane and hydrogenated over nickel-on-kieselguhr catalyst at 200° and 1800 p.s.i. Ethylcyclohexane was removed by distillation, and the hydrogenate was then distilled under vacuum to yield 643 g. (3.8 moles, a 78% yield) of *p*-*t*-amylcyclohexanol (b.p. 112° (9 mm.), n^{20}D 1.4763). Some fractions solidified in the receiver and the index of refraction was taken on the liquid portion only.

The alcohol, diluted with ethylcyclohexane, was dehydrated by passing it through a 2.5 × 100 cm. tube of 4–8 mesh alumina at 325° at a rate of one drop per 3 seconds. The dehydrated product (3.05 moles or 465 g.) distilled at 202° (747 mm.), had a refractive index range of 1.4641 to 1.4674, and amounted to a 91% yield.

Hydrogenation of 381 g. (2.50 moles) of the cycloölefin over nickel-on-kieselguhr at 150° gave 318 g. of crude *t*-amylcyclohexane almost all of which distilled at constant temperature. The yield was 83% on this step or 59% overall.

COLUMBUS, OHIO RECEIVED JULY 3, 1951

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[11] *Cf.* R. C. Huston and T. Y. Hsieh, THIS JOURNAL, **58**, 439 (1936).

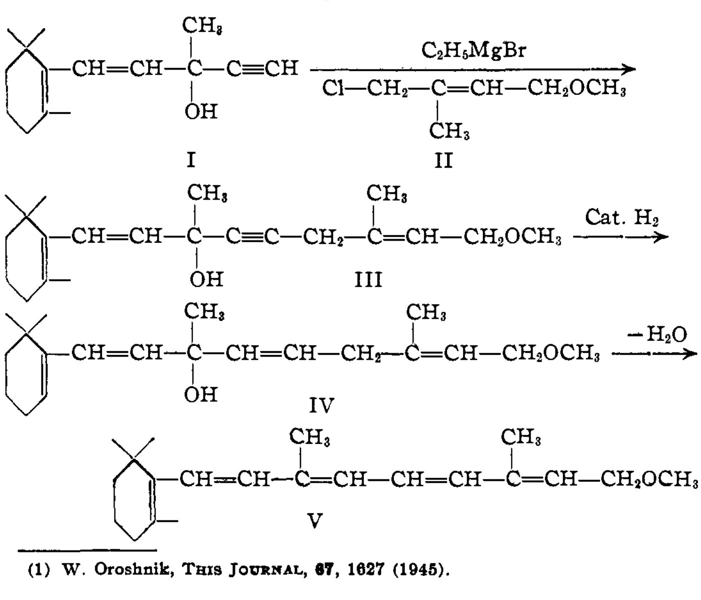
[CONTRIBUTION FROM THE DIVISION OF ORGANIC CHEMISTRY OF THE ORTHO RESEARCH FOUNDATION]

Synthesis of Polyenes. I. *Retro*vitamin A Methyl Ether. Spectral Relationships between the β-Ionylidene and *Retro*ionylidene Series

BY WILLIAM OROSHNIK, GEORGE KARMAS AND ALEXANDER D. MEBANE

A synthesis designed to give vitamin A methyl ether yielded this product in only minor quantity. Structural elucidation of the major product revealed a new series of polyenes isomeric with the β-ionylidene series in that the conjugated system is removed one carbon atom back into the ring. Members of this series may therefore be called *retro*ionylidene compounds. *Retro*vitamin A methyl ether was found to be biologically inactive. Its *cis* isomer represents an experimental contradiction to Pauling's rule. The absorption spectra of the triene, tetraene and pentaene members of this series have been correlated with their structures. On comparison with the spectra of other polyenes they appear normal while those of the β-ionylidene series are found to be hypsochromically displaced. The anomalous nature of the vitamin A spectrum, which has apparently not been generally recognized, is demonstrated.

In 1945, in a preliminary report,[1] a route for the synthesis of vitamin A methyl ether was presented which involved the following transformations



Although the desired product was obtained in only very small yields, we wish to report the details of this synthesis since it led to a new series of polyenes isomeric with the α- and β-ionylidene series.

The coupling of the Grignard reagent from ethynyl-β-ionol (I)[2] with methoxytiglyl chloride (II)[3] was accomplished in 75–85% yields with cupric chloride as catalyst.[4] The resulting acetylenic carbinol (III), originally reported as dehydrating upon distillation, was found to be distillable without decomposition if scrupulously freed of halides beforehand. Catalytic semihydrogenation of its acetylenic bond produced IV in almost quantitative

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[1] W. Oroshnik, THIS JOURNAL, **67**, 1627 (1945).

[2] W. Oroshnik and A. D. Mebane, *ibid.*, **71**, 2026 (1949).

[3] W. Oroshnik and R. A. Mallory, *ibid.*, **72**, 4608 (1950).

[4] J. P. Danehy, D. B. Killian and J. A. Nieuwland, *ibid.*, **58**, 611 (1936). These authors discovered the copper catalyzed condensation of simple alkylacetylenic Grignard reagents with allylic chlorides. The present work represents its first application to acetylenic carbinols and conjugated enynes.