[Contribution from the School of Chemistry of the University of Minnesota]

Polyalkylbenzenes. XXXI.[1] Preparation and Physical Properties of 1,2,3-Trimethylbenzene (Hemimellithene)

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Hemimellithene (1,2,3-trimethylbenzene) is not formed when xylenes are methylated by methyl chloride and aluminum chloride,[3] nor can it be obtained from the other trimethylbenzenes by a Jacobsen rearrangement, for none of the trialkylbenzenes so far studied undergo any rearrangement when their sulfonic acids are kept in contact with sulfuric acid.[4] In previous papers[3b,4a,5,6] efficient methods have been described whereby seven of the eight polymethylbenzenes (three or more methyl groups) may be prepared in quantity from the methylation product of xylene, and certain physical properties of these seven hydrocarbons have been reported.[3a,7] In order to complete the series of preparative methods for the polymethylbenzenes, the work reported in this paper was undertaken.

Hemimellithene was first prepared by Jacobsen[8] and, shortly afterward, Jacobsen and Diecke[9] prepared the hydrocarbon by a very laborious method from *m*-xylene. Much later, v. Auwers[10] prepared the substance by means of a Wurtz–Fittig reaction from 3-iodo-*o*-xylene, but the yields were poor and the starting material was itself difficult to obtain. v. Braun and Nelles[11] prepared a mixture of hemimellithene and pseudocumene by reduction of the product obtained by chloromethylation of *o*-xylene, but they made no attempt to separate the two hydrocarbons.

In 1934, Tawney[12] carried out a synthesis of 2,3-dimethylbenzyl alcohol, starting with benzylmagnesium chloride and taking advantage of the Tiffeneau rearrangement which the Grignard reagent undergoes when it reacts with formaldehyde.[13] The first product, *o*-methylbenzyl alcohol, was converted to the Grignard reagent and then to 2,3-dimethylbenzyl alcohol by reaction with formaldehyde. Agre[14] converted this alcohol into hemimellithene via the Grignard reagent; he also prepared the hydrocarbon from 3-bromo-*o*-xylene by methylation of the Grignard reagent with methyl sulfate. Meanwhile, Reichstein, Cohen, Ruth and Meldahl[15] extended the Tiffeneau reaction one step further and used it as a method for preparation of 2,3,4-trimethylbenzyl alcohol. In the last step they obtained some hemimellithene as a by-product. Mair and Schicktanz[16] found that hemimellithene occurred to an extent of 0.6% in certain crude petroleums; they made a very careful study of the physical properties of the hydrocarbon obtained from this source.

Although Agre had obtained an over-all yield of only 11% of hemimellithene from benzyl chloride, the Tawney–Agre method appeared to be the only one capable of development into an efficient laboratory method for preparation of the hydrocarbon in quantity. A detailed study of the various steps in the synthesis has made it possible to increase the over-all yield of hydrocarbon from benzyl chloride to 26%, and several hundred grams of the substances have been prepared using this method.

The chief losses in the synthesis occurred in the formation of the Grignard reagents from the chlorides, and in the Tiffeneau rearrangement when formaldehyde reacted with the benzylmagnesium chlorides. All of the previous workers[12,14,15] reported low boiling and high boiling by-products, and noted the formation of the ethanes which resulted from the coupling of two benzyl groups during the reaction.

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[1] Paper XXX, This Journal, **62**, 2635 (1940).

[2] Abstracted from a thesis by L. J. Spillane, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment for the M.S. degree, January, 1940.

[3] (a) Smith and Lund, This Journal, **52**, 4144 (1930); (b) Smith and Cass, *ibid.*, **54**, 1604 (1932).

[4] (a) Smith and Cass, *ibid.*, **54**, 1614 (1932); (b) Smith and Moyle, *J. Org. Chem.*, **2**, 112 (1937); (c) This Journal, **58**, 1 (1936); (d) Smith and Guss, *ibid.*, **62**, 2631 (1940).

[5] Smith and Cass, *ibid.*, **54**, 1609 (1932).

[6] Smith and Lux, *ibid.*, **51**, 2994 (1929).

[7] (a) Smith and MacDougall, *ibid.*, **51**, 3001 (1929); (b) MacDougall and Smith, *ibid.*, **52**, 1998 (1930).

[8] (a) Jacobsen, *Ber.*, **15**, 1855 (1882); (b) **19**, 1214 (1886).

[9] Jacobsen and Diecke, *ibid.*, **20**, 904 (1887).

[10] Von Auwers, *Ann.*, **419**, 116 (1919).

[11] Von Braun and Nelles, *Ber.*, **67**, 1094 (1934).

[12] P. O. Tawney, M.S. Thesis, University of Minnesota, 1934, pp. 35–42.

[13] (a) Tiffeneau and Delange, *Compt. rend.*, **137**, 573 (1903); (b) Schmidlin and Garcia-Banùs, *Ber.*, **45**, 3193 (1912); (c) Carre, *Bull. soc. chim.*, [4] **5**, 486 (1909); (d) Carre, *ibid.*, **7**, 841 (1910); (e) Austin and Johnson, This Journal, **54**, 647 (1932); (f) Gilman and Kirby, *ibid.*, **51**, 3475 (1929); *ibid.*, **54**, 345 (1932).

[14] C. L. Agre, Ph.D. Thesis, University of Minnesota, 1936, pp. 53–61.

[15] Reichstein, Cohen, Ruth and Meldahl, *Helv. Chim. Acta.*, **19**, 412 (1936).

[16] Mair and Schicktanz, *Bur. Standards, J. Research*, **11**, 665 (1933).

In the present work, the low boiling products were found to be hydrocarbons, toluene in the first cycle, and *o*-xylene in the second. No ethanes were isolated, although they may have been present. The high boiling material, often formed in relatively large amounts, gave a blood red color with sulfuric acid[17] and was found to contain large amounts of the formals resulting from the action of excess formaldehyde upon the alcohols in the presence of the acid hydrolyzing agents.[18] These high boiling residues from the Grignard reaction were heated for several hours with ethanol and a trace of hydrochloric acid[18]; *o*-methylbenzyl alcohol was obtained in sufficient amounts to raise the total yield from about 60 to 73% based on the benzyl chloride used. Although quite analogous, treatment of the high boiling material for formal failed to increase the yield of 2,3-dimethylbenzyl alcohol in the next cycle. This alcohol was always accompanied by a product boiling from eight to ten degrees lower: while not investigated in detail, this substance was most likely β-(*o*-tolyl)-ethanol, the "normal" reaction product of *o*-methylbenzylmagnesium chloride and formaldehyde.

Preparation of the chlorides from the alcohols was in every case a smooth reaction. The action of dry hydrogen chloride upon the alcohols in petroleum ether gave excellent yields (83–91%).

Conversion of 2,3-dimethylbenzyl alcohol to hemimellithene was accomplished by high pressure hydrogenation over copper–chromium oxide catalyst at 225°. Hemimellithene resulted in 92% yield, with practically no by-products. Agre[14] obtained only a 66% yield of the hydrocarbon by converting the chloride to the Grignard reagent and hydrolyzing the latter; the method of v. Braun and Nelles,[11] reduction of benzyl chlorides by zinc and alkali, merely resulted in hydrolysis of 2,3-dimethylbenzyl chloride to the alcohol. Likewise reduction of 2,3-dimethylbenzyl alcohol by the method of Clemmensen failed; practically all of the alcohol was recovered even after prolonged boiling with the reagents.

Experimental Part

***o*-Methylbenzyl Alcohol.**—Paraformaldehyde (165 g., dried *in vacuo* over phosphorus pentoxide for several days) was added to a filtered solution of benzylmagnesium chloride (prepared from 430 cc., 3.4 moles of benzyl chloride)[18a] and the mixture was heated and stirred for eighteen hours. The magnesium compounds were decomposed by pouring the mixture over ice (800 g.) and adding dilute sulfuric acid. The ether layer was separated, washed successively with water, sodium carbonate (5%) and again with water. The aqueous layer and first washings were extracted thoroughly with ether and these extracts washed as before. All the ethereal solutions were combined, dried over sodium sulfate, and the solvent was removed by distillation through a packed column. The residue (about 400 cc.), when fractionated through the same column, gave *o*-methylbenzyl alcohol (248–263 g., 59–63%) boiling at 106–109° under 12 mm., 118–123° under 24 mm., 123–127° under 27 mm.[19] The conditions described above gave the best yields; the effect of variations in procedure may be summarized as follows: (a) excess metal appeared to be quite necessary; (b) no solvent gave as good yields as ethyl ether alone. When butyl ether alone was used, no carbinol resulted; when a mixture of ethyl ether and butyl ether was used, the yield of carbinol was less than 50%; when ethyl ether and toluene were used, the yield of carbinol was less than 20%. (c) Whether trioxymethylene or gaseous formaldehyde was used made little difference in the yield of carbinol, but on a large scale external depolymerization of paraformaldehyde was very inconvenient.

Decomposition of the Formal.—The high boiling residue (117.6 g.) (from a single experiment in which the yield of carbinol was 60%) was refluxed with ethanol (57 cc.) and hydrochloric acid (2.3 cc.) for five hours. The alcohol was removed by distillation and the residue was poured into water and extracted thoroughly with ether. After drying the solution over sodium sulfate, the ether was removed. From the residue there was obtained by fractionation 40.6 g. of *o*-methylbenzylcarbinol (10% based upon 3.4 moles of benzyl chloride originally used) boiling at 122–127° under 28 mm. The amount of carbinol recovered from the formal varied greatly in different experiments; in one experiment only 7 g. was recovered from 36.5 g. of the high boiling residue; in another experiment, 9.5 g. was recovered from 13.6 g. of material boiling at 194–218° under 24 mm.; in a third experiment, 64 g. of carbinol resulted from 148 g. of the residue. It appeared that the more high boiling by-product there was obtained, the greater the percentage of it that could be converted into the carbinol, but the yield of carbinol from the main reaction also decreased as the amount of high boiling residue increased. The amount of this residue was always less when gaseous formaldehyde was used and much greater when paraformaldehyde was depolymerized in the reaction mixture.

***o*-Methylbenzyl Chloride.**—The alcohol (247.7 g.) was dissolved in a liter of purified petroleum ether (b. p. 40–70°; shaken with sulfuric acid repeatedly, then washed and distilled) and a rapid current of dry hydrogen chloride was passed into the cooled (0°) solution for three hours. The cooling bath was removed, and a somewhat slower stream of the gas was passed into the solution at room temperature (intermittently over three days) for nine hours longer. The water layer was removed, and the solution was washed

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[17] Descude, *Ber.*, **29**, 49 (1896).

[18] For a similar example of formal formation in a Grignard reaction involving formaldehyde, see "Organic Syntheses," Coll. Vol. I, John Wiley and Son, Inc., New York, N. Y., 1932, p. 184.

[18a] "Organic Syntheses," Coll. Vol. I, John Wiley and Son, Inc., New York, N. Y., p. 458.

[19] Reichstein, *et al.*, ref. 15, give the b. p. as 115–120° under 14 mm.

successively with water, sodium carbonate (5%) and again with water. After drying the solution over sodium sulfate, the solvent was removed by distillation and the residue was fractionated. Practically all of it boiled at 98–100° under 28 mm.; the yield was 258 g. (91%).[20]

2,3-Dimethylbenzyl Alcohol.—Freshly distilled 2-methylbenzyl chloride (255 g.) and magnesium (130 g.) were converted to the Grignard reagent by exactly the same procedure described above, except that this amount of chloride was dissolved in a liter (8.5 moles) of ether. The amount of dried paraformaldehyde was 100 g. The reaction mixture was processed as above; the crude product was distilled through a 6″ (15-cm.) jacketed column packed with 1/8″ (3-mm.) glass helices. The fraction boiling at 126–133° under 23 mm. (119 g., 48%) was collected. The distillate solidified on cooling, but it was contaminated with an impurity (the β-tolylethanol ?) which could not be removed by fractionation. The substance was purified by crystallizing it from petroleum ether (b. p. 30–60° or 40–77°). Considerable amounts of the alcohol were retained by the mother liquor; it was recovered by distilling off some of the solvent and chilling the residue, or by distilling off all the solvent and crystallizing the residue from a small amount of solvent. When thus purified, the alcohol melted at 65–66.5°.[21] Five experiments were carried out using the above procedure; the yields were 41–48%. In one experiment, the ether was replaced by benzene before the paraformaldehyde was added. The yield in this case was only 5.5 g. (from 46.2 g. of chloride); the product was very impure, and a large amount (18.3 g.) of high boiling residue resulted. In the preparation of this carbinol larger amounts of low boiling products were formed than in the preparation of *o*-methylbenzyl alcohol. These substances accounted for 20–30% of the reaction product; they were probably formed by reduction during formation of the Grignard reagent, since the reaction with formaldehyde was complete as shown by the color test with Michler ketone,[22] and no unchanged chloride was recovered from any of the reaction products. Allowing the mixture to stand after reaction with formaldehyde resulted in a very considerable decrease in the yield of the alcohol.

Decomposition of the Formal.—The high boiling residue (86.5 g.) from this preparation, when subjected to the treatment described above, gave only 3 g. of the carbinol, b. p., 133–137° under 37 mm., together with a residue of 73 g.

2,3-Dimethylbenzyl Chloride.—This was prepared from the alcohol by the procedure described above. The yields in two experiments were 82 and 87% of a product which boiled at 97–102° under 14 mm.[23]

Hemimellithene.—2,3-Dimethylbenzyl alcohol (61.5 g., recrystallized, m. p. 65–66.5°) was dissolved in ethanol (70 cc.), copper chromium oxide catalyst containing barium oxide (3 g.)[24] was added and the mixture was reduced in a bomb at 220–235° for eight and one-half hours. The initial hydrogen pressure at 28° was 1500 lb. (100 atm.), the maximum pressure reached during the reaction was 2900 lb. (190 atm.). The catalyst was filtered off, the filtrate was diluted with water (600 cc.) and extracted thoroughly with ether. After drying the solution over sodium sulfate, the solvent was removed and the residue was distilled through a short column packed with glass helices. The fraction boiling at 172–173° (50 g., 92%) was collected. There was no high boiling residue. In order to obtain a pure product such as the one above, it was necessary to use purified starting material. In one experiment, 23.2 g. of impure alcohol, boiling at 124–126° under 24 mm., and non-crystallizable, and 65 g. of the purified material (b. p. 127°, under 17 mm.) were dissolved in ethanol (80 cc.) and reduced as above in the presence of 2 g. of the same catalyst. The product was fractionated twice through a Fenske column, giving: A, 25 g., b. p., 152–162°; B, 34 g., b. p. 169–174.5°; C, 17.5 g., b. p. 128–136° under 32 mm. B was hemimellithene; C was recovered starting material. A was refractionated twice through a Fenske column and separated into two fractions: A′, 11 g., b. p. 142–143°; A″, 8 g., b. p., 150–154°. A′ was probably *o*-xylene, although it was not characterized except for its boiling point.[25] A″ was probably *o*-ethyltoluene[26] which was formed by reduction of β-(*o*-methylphenyl)-ethanol present in the crude starting material. It followed, therefore, that in the reaction between *o*-methylbenzylmagnesium chloride and formaldehyde, some of the "normal" reaction product was formed and that this was the persistent impurity, boiling from 8–10° lower, which always accompanied the main product.

When the reduction of the alcohol (17.5 g.) was carried out using a copper chromium oxide catalyst free from barium, only 6 g. of hemimellithene resulted; the remainder of the product was unchanged alcohol. Reduction of the alcohol (10.3 g.) by the Clemmensen method, using the modified procedure of Martin[27] gave only 3–4 cc. of liquid boiling at 125–142° under 25 mm.; the remainder of the product was a very viscous material. Reduction of the *chloride* (20.5 g.) in ethanol (20 cc.) for three hours by hydrogen (42 lb.) in the presence of a platinum oxide catalyst was unsuccessful; 17.0 g. of the chloride was recovered, and no hemimellithene was formed. Reduction of the chloride (43 g.) by zinc and sodium hydroxide[11] was not only unsuccessful, but the procedure was accompanied by great losses of material. Only 6 g. of hemimellithene together with 17 g. of the alcohol were obtained. No chloride was recovered.

Physical Properties

For determination of physical properties, hemimellithene (250 cc.) was refluxed for five and one-half hours over metallic sodium, cooled, filtered from the sodium and the filtrate was distilled twice through a Fenske column 26″ × 3/4″ packed with 1/4″ single turn helices. Two cuts were made first: A, b. p. 170–171.9° (about a third of the material) and B, b. p. 171.9–172.4° (uncor.) under 741.4 mm. Fraction B was redistilled and three cuts taken: C, b. p. 172.2–172.35°; $n^{31.5}\mathrm{D}$ 1.5085; D, b. p. 172.2–172.3°;

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[20] Reichstein, *et al.*, ref. 15, obtained 85–92% yields and give the b. p. as 76–80° under 14 mm.

[21] Reichstein, *et al.*, ref. 15, report the m. p. as 64°.

[22] Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

[23] Reichstein, *et al.*, ref. 15, give the b. p. as 99° under 12 mm.

[24] Adkins, "Reaction of Hydrogen with Organic Compounds," University of Wisconsin Press, Madison, Wis., 1937, p. 13.

[25] Zelinsky and Dworshantschik, *J. Russ. Phys.-Chem. Soc.*, **35**, 563 (1903), report the b. p. of 1,2,3-trimethylcyclohexane as 141° under 736 mm.

[26] Klages and Keil, *Ber.*, **36**, 1637 (1903), give the b. p. of this substance as 162.5° (cor.) under 760 mm.

[27] Martin, THIS JOURNAL, **58**, 1438 (1936).

$n^{31.5}_D$ 1.5085; E, b. p. 172.5°; $n^{31.5}_D$ 1.5087. The data showed all three of the final fractions to be the same; they were therefore combined and used as pure hemimellithene.

Density.—The pycnometer had a capacity of about 10 cc., and was constructed so that the liquid contained in it did not touch the ground glass surfaces of the stopper. Hemimellithene evaporated so rapidly when it wetted ground glass surfaces that a pycnometer in which this happened was useless. The data are given in Table I.

TABLE I

DENSITY OF 1,2,3-TRIMETHYLBENZENE[28]

t, °C	0	20	25	30
$d^{t°}_{4°}$	0.9101	0.8944	0.8906	0.8866
S.G.$^{t°}_{t°}$	.9103	.8960	.8932	.8904

Refractive Index.—An Abbe refractometer was used; the values below 15° were somewhat difficult to check because water frequently condensed as a mist on the prisms during the very hot, humid weather.

TABLE II

REFRACTIVE INDICES OF 1,2,3-TRIMETHYLBENZENE[29]

Temp., °C.	n^t_D	dn/dt	M.R. Obsd. (Calcd., 40.161)	E
5	1.5209			
10	1.5185	0.00048		
15	1.5160	.00050		
20	1.5130	.0006	40.325	+0.165
25	1.5110	.0004	40.397	+ .236
30	1.5090	.0004	40.447	+ .286

Vapor Pressure.—The boiling point of the hydrocarbon was determined under a series of pressures in the apparatus described by MacDougall and Smith.[7b] The manometer was of the closed tube type. It had a range of one atmosphere and could be read to ±0.5 mm. The thermometers were calibrated by the Bureau of Standards or by the Reichsanstalt, and were immersed completely in the vapors. The data are given in Table III. The boiling point of the hydrocarbon at 760 mm., obtained by graphical extrapolation, is 176.2 ± 0.1°.[30] The equation $\log_{10} p = 5.6063 - 0.3938/T - 0.3735/T^2$ fits the data approximately, the average deviation being ±3.8 mm. and the maximum deviation being +16.6 mm. The latent heat of vaporization at 760 mm. and 176.2°, calculated from this equation using the modified Clapeyron-Clausius relationship $L = 2.303\ RT^2\ (\mathrm{d} \log_{10} P_s)/\mathrm{d}T$ is 9410 cal. per mole.

Freezing Point.—The method used was that described by Smith and MacDougall.[7a] The cooling bath was composed of carbon tetrachloride and chloroform, and a differential in temperature of about 10° was maintained by adding pieces of dry-ice from time to time. The thermometer, made by Rascher and Betzold, number 14165, had a range of +3 to −50°, reading to 0.1° directly. While not calibrated, this thermometer was certified as within the limits of accuracy for calibration by the Bureau of Standards.[31] Readings were taken each minute during the determination. Plotted, the "plateau" occurred at −24.78°. When this value was corrected for total immersion, the value for the freezing point became −25.41° (±0.05°). The only value for this constant in the literature is that of Mair and Schicktanz,[16] who give −25.47°.

TABLE III

VAPOR PRESSURE–TEMPERATURE RELATIONSHIPS OF 1,2,3-TRIMETHYLBENZENE

P, mm.	°C.	P, mm.	°C.
1.75	34.9	80.0	102.10
2.25	40.8	106.0	109.3
3.25	41.8	123.0	113.0
4.0	45.25	140.5	117.14
5.0	47.8	166.5	122.3
6.0	50.3	196.5	127.76
6.75	51.8	243.0	133.3
9.25	56.25	307.5	141.3
10.5	58.2	405.5	151.06
16.5	65.7	481.5	157.24
22.0	71.75	546.0	162.2
31.5	77.6	591.5	165.66
47.5	86.25	639.0	168.21
56.25	92.8	676.5	170.46

Summary

1. A four-step synthesis of 1,2,3-trimethylbenzene, starting with benzyl chloride and based upon the Tiffeneau rearrangement, has been described in which the over-all yields are about 26%. The steps in this synthesis (and the yield in each step) are: (a) benzyl chloride to o-methylbenzyl alcohol (70 %), (b) o-methylbenzyl chloride (91%), (c) 2,3-dimethylbenzyl alcohol (45%), (d) hemimellithene (92%).

2. The physical properties of a carefully purified specimen of synthetic hemimellithene were determined. These included density, refractive index, vapor pressure curve, and freezing point. The values obtained are in remarkable agreement with those given by Mair and Schicktanz,[16] who obtained their hydrocarbon from petroleum.

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[28] Von Auwers, ref. 10, gives 0.895 at 20°; Mair and Schicktanz, ref. 16, give 0.8951 at 20°.

[29] Von Auwers, ref. 10, gives 1.51335 at 19.55° and 1.5132 at 20°; Mair and Schicktanz, ref. 16, give 1.5116 at 25°.

[30] Jacobsen, *Ber.*, **19**, 2517 (1886) gives 175–175.5°; v. Auwers, ref. 10, gives 175.5° under 744 mm.; Mair and Schicktanz, ref. 16, give 176.10° under 760 mm.

[31] The authors are greatly indebted to Dr. Matthew Kiess of the Department of Chemistry, St. John's College, for the loan of this thermometer.