

STUDIES ON THE OXIDATION OF HEXAMETHYLBENZENE, I;
OXIDATION OF HEXAMETHYLBENZENE WITH NITRIC ACID

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Translation of "Hekisamechirubenzen no shosan-sanka," Nippon Kagaku Kaishi, No.10, 1973, pp. 1959-1962

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16. Abstract The oxidative reaction of hexamethylbenzene (HMB) with nitric acid was studied, and the hitherto unknown polymethylbenzenepolycarboxylic acids were isolated: tetramethylphthalic anhydride, tetramethylisophthalic acid, 1,3,5-, 1,2,4- and 1,2,3-trimethylbenzenetricarboxylic acids. When HMB was warmed with 50% nitric acid at about 80°C, tetramethylphthalic anhydride and tetramethylisophthalic acid were initially produced. The continued reaction led to the production of trimethylbenzenetricarboxylic acids, but only slight amounts of dimethylbenzenetetracarboxylic acids were detected in the reaction mixture. Whereas tetramethylphthalic anhydride and tetramethylisophthalic acid were obtained, pentamethylbenzoic acid, a possible precursor of them, was scarcely produced. On the other hand, a yellow material extracted with ether from the initial reaction mixture contained bis-(nitromethyl)prehnitene (CH ₃) ₄ C ₆ (CH ₂ NO ₂) ₂ , which was easily converted into the phthalic anhydride.					
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STUDIES ON THE OXIDATION OF HEXAMETHYLBENZENE, I;
OXIDATION OF HEXAMETHYLBENZENE WITH NITRIC ACID

(received 17 March 1973)

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The oxidation reaction of hexamethylbenzene (HMB) with nitric acid was investigated, and previously unknown polymethylbenzene-polycarboxylic acids were separated: tetramethylphthalic anhydride, tetramethylisophthalic acid, and 1,3,5-, 1,2,4- and 1,2,3- trimethylbenzenetricarboxylic acids.

HMB was heated at approximately 80°C with 50% nitric acid, and first tetramethylbenzene dicarboxylic acids were produced, and as time passed trimethylbenzenetricarboxylic acids were produced, but almost no dimethylbenzenetetracarboxylic acids were produced. Furthermore, pentamethylbenzoic acid, thought to be the precursor of tetramethylbenzenedicarboxylic acid, was hardly detected at all, but bis-(nitromethyl)-prenitene was detected in the initial reaction mixture.

1 Introduction

Currently the use of aromatic hydrocarbons is focused on benzenes, toluenes and xylenes, and heavy aromatic hydrocarbons with C₉ and above are not sufficiently utilized.

The present research concerns the heavy aromatic hydrocarbon hexamethylbenzene (abbreviated to "HMB" in the following), and investigates the reactions products when this is oxidized by nitric acid. Up to now there have been practically no examples of oxidation of HMB with nitric acid, the only report has been of the tetramethylphthalic acid produced by Jacobsen²⁾ by heat-processing for two or three days in dilute nitric acid. However, repeated attempts by the authors have not established the repeatability of even the experimental results of Jacobsen²⁾.

1) This report is referenced as "Research on Oxidation of Hexamethylbenzene (Part 1)".

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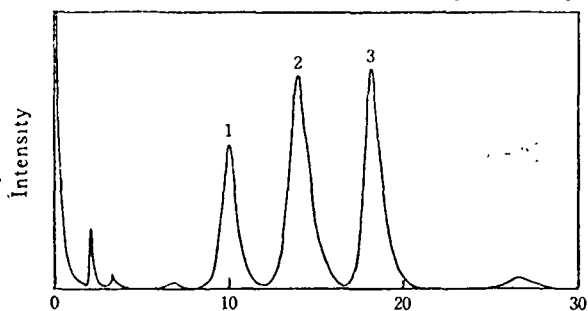
2) O. Jacobsen, Ber., 22, 1215 (1889).

The present report involves oxidation of HMB with 50% nitric acid, examination of the reaction products, and the separation of several polymethylbenzenepolycarboxylic acids as new substances, as well as several new observations.

2 The Experiment and Results

2.1 Raw Materials and Reagents

HMB was prepared using a method set forth in a separate report³⁾, and the substance synthesized by gas-phase contact reaction of phenol and methanol in the presence of an active alumina catalyst was dissolved in petroleum ether, then purified by passing through a column packed with active alumina. The solvent was removed, yielding crystals, and these were then recrystallized from methanol and used in the experiment (melting point 164-166^o C). Diazomethane was synthesized by the usual method from nitrosomethyl urea, dissolved in an ether solvent, and for the other reagents, high-quality commercial reagents were used. Bis-(nitromethyl)prenitene (CH_3)₃C(CH_2)₄C(CH_2)₆(CH_2)₂(NO_2)₂ was prepared as described in the literature⁴⁾ for use as a gas-chromatography identification sample, HMB and benzoilnitric acid were combined, and the resulting colorless crystals in the shape of long needles and a melting point of 138-139^o C had IR and NMR spectra which identify the structure. In the IR spectrum, absorption at the NO_2 frequencies of 1548 and 1373 cm^{-1} were noted, and in the NMR spectrum (δ ppm, CHCl_3), absorption of the CH_3 protons at 2.35 and 2.45, and absorption of the $-\text{CH}_2-$ proton at 5.95 were noted, and integration ratios of these were observed to be 3:3:2.



Retention time (min)
 Fig. 1 Gas chromatogram of esterified products (Me-esters)
 Column: Silicone DC 550 (20%) / Celite 545 (60~80 mesh)
 4 mm x 1 m, Temp: 215°C, Carrier gas: N₂ 40 ml/min,
 Detector: FID

3) Koji CHIBA, K. Endo, Japan Chem., 1973, 1152.

4) R. Willstaetter, H. Kubli, Ber., 42, 4151 (1909).

2.2 Laboratory Tests on Reaction Products

10.0 gm of HMB and 30 ml of 50% nitric acid were heated for 19 hours at approximately 80°C over a bath. After cooling, 0.6 gm of the colorless needle-shaped crystals (Precipitate 1) were brought to pH 4.2 by adding a 50% sodium hydroxide solution, then the yellow substance produced (Precipitate 2) was separated by filtering. The filtered liquid brought to pH 8, and 40.0 g of silver nitrate dissolved in a small amount of water was added and heated for 30 minutes at approximately 80°C. The precipitate produced was removed by filtering, then after vacuum-drying suspended in 100 ml of benzene, and this was circulated for 6 hours with 15 ml of methyl iodide, yielding 4.1 gm of oily methylester. The results of analyzing this by gas chromatography are shown in Fig.1, and the main peaks 1, 2 and 3 were found. This methylester mixture was cooled in icewater, then the crystals extracted were removed by filtering and recrystallized from methanol, yielding colorless plate-shaped crystals [1] with a melting point of 128-129°C. This substance matches Peak 3 of the preceding chromatogram. In the IR spectrum (cm^{-1}), absorption at the C=O frequency of 1732, and absorption at the C-O-C frequencies of 1218 and 1166 were noted. The results of elemental analysis agreed with the calculated values for trimethyl trimethylbenzenetricarboxylic acid.

Analytical values: C 61.83%, H 6.32%

Calculated values for $\text{C}_{15}\text{H}_{18}\text{O}_6$: C 61.22%, H 6.16%

Substance [1] was heat-processed for several hours over a bath with a solution of 2N sodium hydroxide, then oxidized with concentrated hydrochloric acid, and then vacuum-dried. This was mixed well with about the same quantity of calcium hydroxide, heated to 300-350°C in a circulating nitrogen, and the vapors produced were collected with ice-cooled ether. This results of analyzing this ether solution by gas chromatography (Hitachi Gaudet column: DDP-15 0.24 mm x 15m, column temperature: 60°C, carrier gas: 2 ml/min N_2) revealed a peak matching 1,2,3-trimethylbenzene. From the preceding facts, it was concluded that substance [1] was trimethyl 1,2,3-trimethylbenzenetricarboxylic acid. This is also supported by the fact that the NMR spectrum (δ ppm, C_6D_6) revealed the absorption of CH_3 proton

nucleus substitutions at 1.60 and 2.01, and absorption of $-OCH_3$ protons at 3.50 and 3.61 (integration ratios 1:2:1:2). After removal by filtering from the methylester mixture, a small quantity of ethanol was added to the mother liquor, and this was cooled by a cooling agent (ice, table salt), and by repeating recrystallization from methanol of the crystals extracted, colorless needle-shaped crystals with a melting point of 76-77°C were separated. This substance corresponds to Peak 2 of the gas chromatogram in Fig.1. In the IR spectrum (cm^{-1}), absorption was noted at the C=O frequency of 1726 and at the C-O-C frequencies of 1241 and 1157, and in the NMR spectrum (δ ppm, $CHCl_3$) exhibited clear triple lines with an integration of 1:1 at 2.2-2.4 (CH_3 proton nucleus substitution) and 3.9-4.0 ($-OCH_3$ proton), which indicates that [2] is trimethyl 1,2,4-trimethylbenzene-tricarboxylic acid. Peak 1 matches trimethyl 1,3,5-trimethylbenzene-tricarboxylic acid, which is reported in a subsequent report.⁵⁾ The previous Precipitate 1 was recrystallized from benzene, yielding a colorless needle-shaped crystal having a melting point of 238-239°C, of which the IR spectrum (cm^{-1}) exhibited absorption at the C=O frequencies of 1836, 1768, and absorption at the C-O frequencies of 1200, 910, suggesting the structure of an acid anhydride, and the results of elemental analysis agreed with the calculated value of tetramethyl-phthalate anhydride.

Analytical values: C 70.70%, H 5.81%

Calculated values for $C_{12}H_{12}O_3$: C 70.61%, H 5.93%

The NMR spectrum (δ ppm, $CHCl_3$) also exhibited absorption of CH_3 proton nucleus substitution at 2.30 and 2.62 (integration ratio 1:1), supporting the structure of a tetramethylphthalate anhydride. Precipitate 1 was dissolved in a hot alkaline solution, silver nitrate was added and the silver salts produced processed with methyl iodide yielding a methylester which had the IR and NMR spectra and melting point matching observations reported⁶⁾ for dimethyltetramethylphthalic acid. It is considered unusual for acid anhydrides to be produced in the presence of excess water, but the anhydrous ring of anhydrous tetramethylphthalate is extremely stable, and it has been confirmed that even when boiled with water for long periods it still does not release.

5) Koji CHIBA, Yoshiyuki MIZUNO, Japan Chem., 1973, No.11 Notices
 6) Koji CHIBA, Hideji SATA, Japan Chem., 1973, 1249

Next, 10.0 gm of HMB and 300 ml of 50% HMB were heated together for 15 minutes at approximately 80°C, and the liquid reaction mixture obtained was buffered with a 50% sodium hydroxide solution, after which an oily substance was ether-extracted. 30.0 gm of calcium chloride (CaCl₂ · 2H₂O) was added to the yellow aqueous solution and precipitation occurred. After washing with hydrated methanol, the excess was placed in a 10% sodium carbonate solution at 80°C for 30 minutes. The calcium carbonate produced as a white precipitate was removed by filtering, and the filtered liquid was oxidized with concentrated hydrochloric acid, yielding 0.1 gm of light-yellow precipitate. This was esterified with diazomethane, and then recrystallization from ether yielded needle-shaped crystals [3] with a melting point of 123-123°C. The IR spectrum (cm⁻¹) exhibited absorption at the C=O frequency of 1724 and absorption at the C-O-C frequencies of 1233 and 1162. The NMR spectrum (delta ppm, C₆D₆) exhibited absorption of the proton CH₃ nucleus substitution at 1.80, 2.02, and 2.15, and absorption of the -OCH₃ proton at 3.55 (integration ratio 1:2:1:2). The results of elemental analysis are as follows, matching the calculated values of dimethyl tetramethylisophthalic acid.

Analytical value: C 66.70%, H 7.04%

Calculated value for C₁₄H₁₈O₄: C 67.10%, H 7.25%

The preceding facts indicate that [3] is dimethyltetramethylisophthalic acid.

On the other hand, the ether extract (9.6 gm) obtained above was subjected to gas chromatography under the following conditions, and unreacted HMB (approximately 10% of the extract), anhydrous tetramethylphthalate (approximately 10%) and and bis-(nitromethyl)prenitene (approximately 40%) were identified, and several other peaks were noted, but it was not clear whether mononitro compounds were produced.

Column: Silicone SE-30 (10%)/Celite 545 (80-100 mesh) 4 mm x 1 m,
 Column temperature: 150°C, Carrier gas: 20 ml/min N₂.

2.3 Reaction Time and Reaction Products

2.0 gm of HMB and was dissolved in 30 ml of 50% nitric acid and heated to approximately 80 °C over a bath. After 1-2 hours the reaction mixture liquid had turned brown and produced bubbles, and a yellow oily substance was floating in it. After a specific reaction time, this was buffered with a 50% sodium hydroxide solution and ether-extraction was performed. 7.0 gm of silver nitrate dissolved in a small quantity of water was added to the water layer, and held at 80 °C for 30 minutes with occasional mixing. The precipitated silver chloride was removed by filtering, and after vacuum-drying, processed with methyl iodide and esterified. The methylesterified substance obtained in this way was subjected to gas chromatography in nearly the same conditions as described in the preceding paragraph, yielding the experimental results shown in Table 1. The amounts of each of the components was determined as the mixture ratios by weight from the peak area ratios, and it was ensured beforehand that the repeatability of the experimental results would be satisfactory. Reaction mixtures for which reaction times were greater than one hour were preceded by ether extaction, and the needle-shaped crystals floating in the liquid were removed by filtration and estimated as anhydrous ethylphthalic acid, and substances for which the reaction time was within 30 minutes were ether-extracted with approximately 10 ml, concentrated, cooled, and the extracted crystals were removed by filtering and became

Table 1 Reaction products
HMB 2.0 g, 50% HNO₃ 30 ml, Reaction temp · 80°C

React. time	Tetramethyl-		Trimethylbenzenetricarboxylic acid (mol%) ^{a)}			Extracts ^{b)} (g)
	phthalic anhydride	isophthalic acid	1,3,5-	1,2,4-	1,2,3-	
5(min)	—	0.4	—	0.1	0.1	1.8
10	6.0	3.1	0.2	0.6	0.3	1.8
15	9.9	8.3	0.3	0.5	0.3	1.9
30	—	10.5	0.6	0.8	0.1	1.8
1(hr)	9.6	9.0	1.3	1.2	0.6	1.5
2	—	6.2	2.8	4.2	2.7	0.7
5	7.9	3.3	4.0	4.8	3.6	0.5
9	—	1.9	4.4	6.3	4.1	0.3
16	—	0.8	3.9	5.8	4.2	0.3
19	2.4	1.0	1.9	6.5	6.2	—

a) mol% based on HMB added

b) The reaction mixture was neutralized with NaOH, and extracted with ether.

tetramethylphthalic anhydrides. These exhibited nearly a single peak in all gas chromatographs, and the retention time matched tetramethylphthalic anhydride.

When the reaction time was comparatively short, tetramethylisophthalic acid and tetramethylisophthalic anhydride were preferentially produced, and next trimethylbenzenetricarboxylic acids were produced. There was a slight difference among the production rates of isomers of trimethylbenzenetricarboxylic acid, and it was found that somewhat more of the two isomers other than 1,2,4-trimethylbenzenetricarboxylic acid were produced. However, even when the reaction continued for 19 hours, hardly any benzenetetracarboxylic acids were produced. Furthermore, pentamethylbenzoic acid, which is thought to be the precursor of tetramethylisophthalic acid and anhydrous tetramethylphthalic acid, was not detected at all. When the reaction continued for 1 or 2 hours and the methylesterified substances similarly obtained from the reaction mixture were subjected to gas chromatography, a very small amount of methylpentamethylbenzoic acid was detected and no more. Furthermore, since there is some doubt as to whether the pentamethylbenzoic acid was ether-extracted, a similar laboratory analysis was conducted using the ether-extracton for diazomethane, but methylpentamethylbenzoic acid was not detected.

3 Conclusions

HMB and 50% nitric acid wre heated over a bath, and trimethyl benzenetricarboxylic acids were produced with relative ease, while no dimethylbenzenetetracarboxylic acids were produced. There was a slight variation in the yield rates among the isomers of the trimethylbenzenetricarboxylic acids, and slightly more of the two isomers other than the 1,2,4-form were produced, and this may be because they have structures which are easily synthesized through either tetramethylisophthalic acid or tetramethylphthalic anhydride. As for tetramethylbenzenedicarboxylic acids, tetramethylisophthalic acid and tetramethylphthalic anhydride were detected, but pentamethylbenzoic acid, which is assumed to be its precursor, was hardly detected at all. On the other hand, after the inital reaction mixture liquid was buffered in alkali, the yellow substance obtained

by ether-extraction was found to contain unreacted HMB along with small quantities of bis-(nitromethyl)preinitene. It was already known that bis-(nitromethyl)preinitene readily produces tetramethylphthalic anhydride by hydrolysis⁶⁾. From the preceding it was clear that the preceding dicarboxylic acids were not produced by acidification of the pentamethylbenzoic acids, and they are thought to be synthesized through various compounds produced in the reaction between HMB and nitric acid, but this is not clear from the scope of the present report.

Finally, we wish to express our gratitude for the valuable advice of Prof. Shunroku KANNO, and Asst. Prof. Yoshio IMAI of our Macromolecular Chemistry Dept., and the support provided in elemental analysis by Haneyama Laboratories.

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