absorbed to the extent of 41–42% by concentrated sulfuric acid.

When care was taken to prepare very finely divided lithium, the use of magnesium to induce formation of the organolithium compound became unnecessary in ether, although still no reaction could be induced in benzene. The evolution of gas during the formation of the lithium compound at the same time became insignificant.

Carbonation of the organolithium compound from 3.5 g. of lithium yielded 3 cc. of trimethylacetic acid and 4 cc. of a colorless camphoraceous-smelling liquid boiling at 153° and solidifying only partially from 10° down to dry-ice temperature. It consumed one mole of methylmagnesium iodide per 74.5 g. in the Grignard machine and gave no gas. These would be the properties of impure *t*-butyl trimethylacetate.

The reaction of *t*-butyllithium with hexamethylacetone copiously evolved isobutylene and yielded a product from which was isolated 66% di-*t*-butyl carbinol, m. p. 48–50°, 10% impure starting material, and 15% of a solid, m. p. 119–121°, identical with a dimolecular reduction product of hexamethylacetone previously prepared by T. R. Steadman in this Laboratory, to be described in a future paper. Therefore no detectable reaction other than reduction had taken place.

Experimental

Preparation of Lithium Sand.—Mineral oil was purified by shaking with sulfuric acid followed by water. It was then clarified with charcoal, heated to 250° with sodium for twenty-four hours, and reclarified. This specially purified oil was then placed in a three-necked flask containing a dropping funnel, reflux condenser and Hershberg wire stirrer,[4] and swept continuously by a current of dry, purified nitrogen. Pieces of lithium, cut under oil and scraped clean, were introduced into the flask, the oil was heated to 250° and the stirrer was started, whipping the lithium into very fine shining particles. When the desired fineness had been attained the motor was stopped and the oil allowed to cool. The oil was then displaced by distilling in absolute ether and flushing through a stopcock in the bottom of the flask. The particles obtained in this way retain their luster for several hours under nitrogen.

***t*-Butyllithium.**—In a typical experiment, 3.5 g. of lithium sand was covered with 150 cc. of anhydrous ether and 27 cc. of *t*-butyl chloride was added gradually with active stirring over a period of six hours. Only a slight amount of lithium remained unconsumed and only 25 cc. of gas was evolved.

Reaction between *t*-Butyllithium and Hexamethylacetone.—To the stirred reagent prepared from 3 g. of lithium and 23 cc. of *t*-butyl chloride, a solution of 30 g. of hexamethylacetone and 30 cc. of anhydrous ether was added during two hours. Heat was evolved and the ether boiled vigorously. In the intermediate stages the reaction mixture assumed a reddish-brown tint, but was colorless or faint yellow at the end. During the reaction a gas was constantly evolved which was inflammable and decolorized bromine solution. After decomposition with iced ammonium chloride solution the ethereal solution was dried and distilled. After distillation through a one-foot, partial take-off Vigreux column the fractions were as follows: I, 157–165°, 1.5 g., mainly hexamethylacetone; II, 165–168°, 1.0 g., mixture of hexamethylacetone and di-*t*-butylcarbinol; III, 168.0–168.4°, 16.5 g., di-*t*-butylcarbinol, m. p. 48–50°; IV, residue—6 g. Fractions III and IV solidified. On recrystallization of the latter from aqueous methanol 3.8 g. of material was obtained, melting at 119–121° and showing no depression with the dimolecular reduction product of hexamethylacetone obtainable from the action of sodium or lithium on this ketone.[5]

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[4] Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 313 (1936).

[5] This work will be reported in a later communication.

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The Vapor Phase Nitration of Toluene

BY J. L. BULLOCK AND E. T. MITCHELL

Holleman[1] in 1914 investigated the proportions of ortho, meta and para isomers formed in the nitration of toluene. In the reaction carried out at 30°, using nitric acid (sp. gr. 1.475), he established the proportion as being 58.8% ortho, 4.4% meta and 36.8% para. Later investigations by Ingold and co-workers[2] using nitric acid (sp. gr. 1.52) showed the same ratio of isomers. Under the usual conditions of nitration, using a nitric-sulfuric acid mixture, a slightly different ratio has been reported,[3] 62% ± 1 ortho, 4.2–4.5% meta and 32–33.5% para.

The present investigation treats the nitration of toluene in the vapor phase using nitric acid of varying concentrations. The proportions of ortho, meta and para isomers are recorded in Table I. Holleman found that an increase in temperature of nitration (from −30 to 60°) resulted in a decrease in the para isomer and an increase in the meta and the ortho isomer. It is rather surprising therefore to note a larger amount of para at a temperature of 150° than that recorded for nitration at room temperature. On increasing the temperature to 250° the change in ratio appears to be in the same direction as that noted by Holle-

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[1] Holleman, *Rec. trav. chim.*, **33**, 1–34 (1914).

[2] Ingold, Lapworth, Rothstein and Ward, *J. Chem. Soc.*, 1959 (1931).

[3] Gibson, Duckham and Fairbairn, *ibid.*, **121**, 270–283 (1922).

man. The magnitude of the change, however, is too small to allow any conclusions to be drawn as to the general change in the ratio with change in temperature.

Orton[4] studied the reaction at room temperature, using a ratio of 3.5 moles of nitric acid to 1 mole of toluene. He indicated only the yield of mononitrotoluene and did not mention the proportion of isomers that might be present. He found that on keeping the ratio of nitric acid to water above 3.5 moles of acid to 1 mole of water he obtained 17–18% mononitrotoluene. In the present work a ratio of 1.7 moles of nitric acid to 1 mole of toluene was used.

TABLE I

Temp., °C.	HNO_3–H_2O ratio (moles)	Total yield,[a] %	Percentage ortho	meta	para	Freezing point, °C. initial	final
30 (Orton)	1.7:1	None	..	...	..		
30 (Orton)	3.5:1	17–18	..	...	..		
150	0.7:1	37	55.7	5.0	39.3	7.6	−18.27
150	1.2:1	62	55.3	4.7	40.0	8.3	−18.10
150	0.7:1	30	55.9	5.0	39.1	7.25	−18.25

[a] Based on toluene employed.

In the described runs the amount of oxidation product averaged approximately 1.0–2.0%, based on the amount of toluene employed. In order to note any possible change in the isomer ratio brought about by oxidation, synthetic mixtures of 1.0 mole of nitrotoluene, consisting of 55.0% ortho, 5.0% meta and 40% para, and 1.0 mole of nitric acid (70%) were allowed to flow through the apparatus at 150° and also at 250°. At the end of the run the isomer ratio was determined. The results of three such runs carried out at 150° are: Run 1, 54.9% ortho, 5.0% meta and 40.1% para; Run 2, 54.9% ortho, 5.1% meta and 40.0% para; Run 3, 55.0% ortho, 5.0% meta and 40.0% para.

At 250°, the largest variation in isomer ratio was found to be still only about 0.1%. The amount of oxidation product obtained under the above conditions varied from 1.5–2.5%.

Experimental

Nitric acid used was prepared by the distillation of a mixture of 1 part of commercial nitric acid (sp. gr. 1.42) with 2–3 parts of sulfuric acid. The nitric acid thus obtained was redistilled with 1 part of sulfuric acid. To rid the acid of nitrogen dioxide fumes it was warmed to 50° and dry air bubbled through while the acid was cooling to room temperature.

The toluene used had a boiling point range of 111–112°. It was sulfur free.

The apparatus was designed to allow nitric acid and toluene, flowing from burets at controlled individual rates, to vaporize separately in a preheater, to mix and to pass through the reaction chamber, which was kept at a fixed temperature constant to within ±2°, and finally to provide for the condensation and collection of the products. The reaction chamber was a Pyrex glass tube approximately 1 inch (2.5 cm.) in diameter and 40 inches (100 cm.) in length. This was set into a long electrically heated furnace. The temperature was measured with a chromel-alumel thermocouple which was inserted into a thin-walled internal glass well.

In each run 40 cc. of toluene was used. The rate of flow was 1 cc. per minute.

The products from each reaction, which amounted to approximately 75 cc., were neutralized with 2 *N* sodium hydroxide, extracted three times with ether and the ether extracts washed once with 0.1 *N* sodium hydroxide and then with water. They were dried over anhydrous sodium sulfate and the ether and toluene distilled off very slowly through a Widmer column. Finally the mixture of nitrotoluenes was distilled, at 122–128° (33 mm.), to a constant density. They were analyzed by the freezing point method according to Gibson, Duckham and Fairbairn.[3]

In order to be certain that the distillation process which the mixture was finally subjected to produced no change in the ratio of isomers, a synthetic mixture of 20 ml. of nitrotoluene and 20 ml. of toluene was distilled as above. The nitrotoluene mixture employed consisted of 55.0% ortho, 5.0% meta and 40.0% para. The isomer ratio determined at the end of two such distillations showed 55.0% ortho, 5.0% meta and 40.0% para in one case and 55.1% ortho, 5.0% meta and 39.9% para in the other.

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(4) Orton, *Ber.*, **40**, 370–376 (1908).

The Absorption Spectrum of Biphenylene

BY EMMA P. CARR, LUCY W. PICKETT AND DOROTHY VORIS

In a recent article Lothrop[1] reported the synthesis of biphenylene, an interesting hydrocarbon whose structure, on the basis of the chemical evidence, indicated a polynuclear aromatic hydrocarbon in which the benzene rings are condensed with a four membered ring. The absorption spectrum of such a compound is of particular interest and Dr. Lothrop has kindly furnished the material for this study. The hydrocarbon was examined in hexane solution with a Hilger quartz prism spectrograph and the absorption curve is shown in the accompanying figure with the log of ε, the molecular extinction coefficient, plotted against wave number. There is a group of well-defined bands from 25,000 to 32,000 cm.$^{-1}$ which is thought to include two band systems, one of low intensity with the first observed band at

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(1) W. C. Lothrop, THIS JOURNAL, **63**, 1187 (1941).