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			Freezing point, °C.	
			ortho	meta	para	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.

DEPARTMENT OF CHEMISTRY
CLARK UNIVERSITY
WORCESTER, MASS.

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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).

25,530 cm.$^{-1}$ and an overlapping one of high intensity with the first strong band at 27,910 cm.$^{-1}$. Analogous separations of about 800, 1200 and 1600 cm.$^{-1}$ are evident in the members of each of the two groups. Farther in the ultraviolet is a very intense band with maximum at 40,250 cm.$^{-1}$.

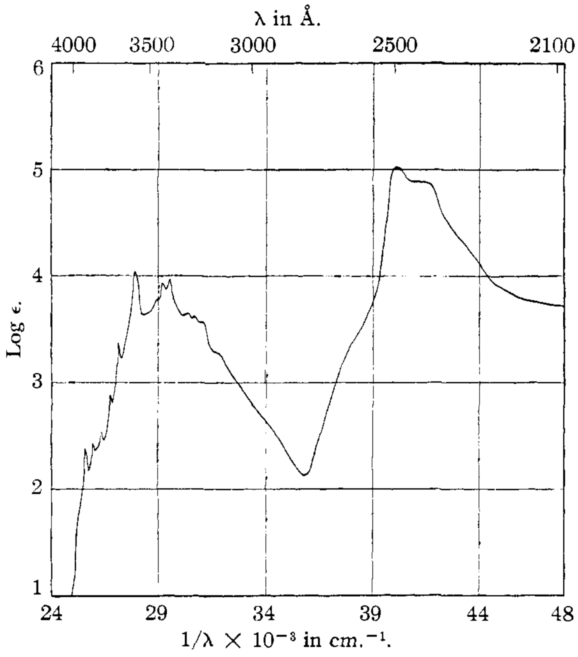

Fig. 1.

The spectrum has certain similarities to those of condensed ring compounds such as naphthalene and fluorene and this relationship would give further evidence in support of the structure of the compound as given by Lothrop.

Department of Chemistry
Mount Holyoke College
South Hadley, Mass.
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Purification of Anthracene

By O. C. Dermer and Jack King

The observations of Clar[1] and Bachmann and Kloetzel[2] on the ease of formation and dissociation of maleic anhydride adducts of anthracenes led us to investigate the purification of anthracene itself by way of the Diels–Alder reaction. This has been discussed recently by Polyakova,[3] but his procedure is complicated by his desire to recover maleic anhydride.

Thirty-five grams of technical anthracene (purity about 80%) and 62 g. of maleic anhydride (200% excess) were added to 700 ml. of benzene and the solution refluxed for ninety minutes. The solid anthracene-9,10-*endo*-α,β-succinic anhydride that separated from the cooled mixture was recrystallized twice from aqueous acetone; yield, 29 g. (67%).

Pyrolysis of this compound by itself proved unsatisfactory, but when it was ground with 40 g. of soda lime and heated strongly in a porcelain dish covered with an inverted funnel and a receiver, anthracene having a slight yellow tinge sublimed out. This was collected and recrystallized twice from toluene. Fifteen grams (80% for this step only) of colorless, highly fluorescent anthracene, m. p. 217° (cor.), was obtained.

Department of Chemistry
Oklahoma Agricultural and Mechanical College
Stillwater, Oklahoma
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[1] Clar, *Ber.*, **64**, 2194 (1931).

[2] Bachmann and Kloetzel, This Journal, **60**, 481 (1938).

[3] Polyakova, *Org. Chem. Ind.* (U. S. S. R.), **7**, 305 (1940); *Chemical Abstracts*, **35**, 4008 (1941).

The Dissociation of Tetraphenylhydrazine and its Derivatives

By Gilbert N. Lewis and David Lipkin

In a recent study by Cain and Wiselogle[1] of the rate of reaction between tetraphenylhydrazine and nitric oxide, it was shown that the rate-determining step is the dissociation of the hydrazine into two diphenylnitrogen radicals. For this process they obtain 30 kcal. as the heat of activation.

In contrast with this high energy of activation for the dissociation process, they point out that, by the ordinary method of calculating bond energies from thermochemical data, the heat of dissociation of hydrazine itself is only 20 kcal.[2] They agree with Wieland[3] that the substitution of phenyl groups would greatly reduce this figure. A large heat of activation for the dissociation and a small heat of dissociation would imply a high activation energy also for the reverse process: the formation of tetraphenylhydrazine from two molecules of diphenylnitrogen.[4] In the analogous reaction by which a molecule of hexaphenylethane is formed from two molecules of triphenylmethyl, activation is required amounting to 6–8 kcal.[5] The existence of such a heat of activation for the recombination of nitrogen free radicals would be of much interest in connection with the theories recently set forth by Lewis and Seaborg.[6]

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[1] Cain and Wiselogle, This Journal, **62**, 1163 (1940).

[2] Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 2nd ed., 1940.

[3] Wieland, "Die Hydrazine," Ferdinand Enke, Stuttgart, 1913.

[4] See also a discussion of this question, *Chem. Soc. London Ann. Repts.*, **37**, 268 (1940).

[5] Ziegler, Orth and Weber, *Ann.*, **504**, 131 (1933).

[6] Lewis and Seaborg, This Journal, **61**, 1886 (1939).