Detection of Palladium.—All four of the reagents may be used for the detection of palladous chloride or nitrate, although p-nitrosoaniline is less sensitive than the others. The sensitivities determined on the spot-plate under different conditions are recorded in Table II. The tests were made by adding a drop of the reagent solution to 0.05 ml. of the palladous salt of the designated concentration. Results obtained for the diethyl reagent are similar to those for the dimethyl. The sensitivities for palladous nitrate are approximately the same as for the chloride.

TABLE II

Medium	Dimethyl	Diphenyl
Water	1:8,000,000	1:10,000,000
Buffer (pH 4.7)	1:8,000,000	1: 8,000,000
Buffer (pH 1.4)	1:5,000,000	1: 5,000,000

Summary

The reactions of p-nitrosodiphenylamine, p-nitrosoaniline, p-nitrosodimethylaniline and p-nitrosodiethylaniline, compounds containing the p-nitrosophenylamino group, p-$\mathrm{NOC_6H_4N}<$, with palladous chloride and palladous nitrate, are described. The highly colored complexes are useful for the detection or colorimetric determination of small amounts of palladium. In the case of the chloride, the complexes have been isolated and found to have the general composition, $\mathrm{Pd[NOC_6H_4N<]_2Cl_2}$.

p-Nitrosodimethylaniline and p-nitrosodiethylaniline possess the following advantages over p-nitrosodiphenylamine as colorimetric reagents for palladous chloride: (1) faster reaction rate, (2) greater stability, (3) smaller temperature effect, (4) more suitable for spectrophotometric studies.

Relative absorption curves are given for solutions of the reagents and for those of their complexes.

Solutions of the p-nitrosodimethylaniline–palladous chloride complex were found to follow the Lambert–Beer law for concentrations of palladium up to 1 : 5,000,000.

A procedure is presented for the colorimetric determination of palladium in the presence of silver.

UNIVERSITY, VIRGINIA RECEIVED JULY 19, 1941

NOTES

t-Butyllithium

BY PAUL D. BARTLETT, C. GARDNER SWAIN AND ROBERT B. WOODWARD

In a number of cases organolithium compounds are found to be much less subject to hindrance in reactions involving addition to the carbonyl group than are the corresponding Grignard reagents.[1,2] The inaccessibility and theoretical interest of tri-t-butylcarbinol prompted us to investigate t-butyllithium, which had not been reported at the time of this work, and to compare it with t-butylmagnesium chloride in its reaction with hexamethylacetone.[3] We find that, like the Grignard reagent, t-butyllithium produces with hexamethylacetone only reduction and no addition.

Unsuccessful attempts were made to prepare t-butyllithium by the reaction of small pieces of lithium or of lithium globules (made by shaking molten lithium under mineral oil at 250° and cooling) with t-butyl chloride in ether or benzene or with t-butylmagnesium chloride. Metathesis between phenyllithium and t-butylmagnesium chloride was also tried unsuccessfully. However, a vigorous reaction between t-butyl chloride and lithium globules could be induced in dry ether under nitrogen by the addition of a little magnesium metal ($^1/_{35}$ of the weight of the lithium) and priming with a little t-butylmagnesium chloride. This suggests that a free-radical intermediate in the formation of the Grignard reagent may react with the lithium. A trace of magnesium would suffice for such a process, since it would be constantly regenerated from its chloride by lithium. There was no evidence of appreciable formation of lithium nitride. In a series of runs, the coarser the lithium used the more gas was given off in the formation of the t-butyllithium. This gas was

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(1) Wittig, *Ber.*, **68**, 924 (1935).

(2) Ziegler, *Angew. Chem.*, **49**, 455 (1936).

(3) Conant and Blatt, THIS JOURNAL, **51**, 1227 (1929). References to t-butyllithium have since appeared in papers by Gilman and coworkers, *ibid.*, **62**, 2813, 3206 (1940).

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).