

The gas, which was absorbed and then evolved, corresponded to 30 to 40% of that calculated for addition and could not be increased by long extended treatment of the olefin at -30° or by the use of catalysts, such as ferric chloride.

In order to establish whether the hydrogen chloride is actually added to form a tertiary chloride stable at low temperatures, kinetic studies were made. Phenylidimethylcarbinyl chloride was prepared by addition of hydrogen chloride to α -methylstyrene. After removal of dissolved hydrogen chloride by pumping at -80° , the product was dropped into 100 ml. of 95% ethanol at -80° . After 10 min., to permit solution of the solid chloride, a 5-ml. aliquot was removed and titrated in absolute ethanol at -20° . The initial sample required 1.00 ml. of base; at 1 hr. the titer was 1.0 ml.; in 2 hr., 1.2; in 3 hr., 1.1. Complete hydrolysis (2 hr. at 25°) required 11.8 ml. Therefore solvolysis of the tertiary chloride does not proceed at any appreciable rate under these conditions.

In the same way $\alpha,2,4,6$ -tetramethylstyrene was treated with hydrogen chloride and the product added to 95% ethanol at -80° . A small amount of the product did not dissolve at this temperature. However, aliquots were removed and titrated: 0 min., 4.43 ml.; 20 min., 4.29; 40 min., 4.44; 60 min., 4.29. The residual solution (with suspended solid) was permitted to warm up to room temperature. The "infinity" titer obtained in this way is 5.49. The increase over the other values is probably due to the solution of the suspended material.

The large amount of hydrogen chloride absorbed at -30° is far greater than can be accounted for in terms of mere solubility.²⁵ The results suggest two possible conclusions:

(25) The solubility of hydrogen chloride in olefins at low temperatures has been examined: H. C. Brown and J. Brady, *THIS JOURNAL*, **74**, 3570 (1952).

either the tertiary chloride is formed in equilibrium concentrations at -30° and undergoes practically instantaneous solvolysis in 95% ethanol at -80° or the tertiary chloride is not formed and the high "solubility" is result of the formation of a carbonium ion salt. The product is red in color and this observation has led us to adopt the latter interpretation for the present. We hope to investigate the phenomenon in greater detail later.

Attempted *t*-Butylation of Mesitylene.—*m*-Xylene, 101 g. (0.95 mole), was treated with 23 g. (0.25 mole) of *t*-butyl chloride and 12 g. (0.075 mole) of anhydrous ferric chloride at -5° for 2.5 hours. The mixture was stirred at 0° for an additional four hours and hydrolyzed. The product was distilled: 53.6 g. (0.5 mole) of *m*-xylene (b.p. $60-62^{\circ}$ at 52 mm., n_D^{20} 1.4964) and 30.5 g. (0.19 mole) of 1,3-dimethyl-5-*t*-butylbenzene (b.p. $74-75.5^{\circ}$ at 8 mm., n_D^{20} 1.4962). This represents a 76% yield, based on *t*-butyl chloride, with 0.69 mole (74%) of the original *m*-xylene accounted for.

Mesitylene, 112.8 g. (n_D^{20} 1.4980), was treated in precisely the same manner with *t*-butyl chloride and ferric chloride. Distillation of the product yielded 96.6 g. of mesitylene (n_D^{20} 1.4987), 85% of the starting material. A few ml. of a viscous tarry residue which could not be distilled was dissolved in hot 95% ethanol and cooled. About 0.2 g. of a brown solid was obtained, m.p. $92-94^{\circ}$. Successive recrystallization from 95% ethanol and ligroin raised the m.p. to 100° . *Anal.* Calcd. for $C_{10}H_{12}$: C, 90.69; H, 9.31. Found: C, 90.37; H, 9.52.

The solid is evidently bimesityl (2,2',4,4',6,6'-hexamethylbiphenyl).²⁶

(26) F. Ullmann and G. M. Meyer, *Ann.*, **332**, 49 (1904), report a m.p. of 100.5° for bimesityl.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Reaction of Methyl Iodide with *o*-Phenylenediamine; Homomorphs of *o*-Di-*t*-butylbenzene^{1,2}

BY HERBERT C. BROWN AND K. LEROI NELSON³

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o-Phenylenediamine in methanol solution reacts with one mole of methyl iodide; *p*-phenylenediamine reacts with two moles. This unique ortho effect is attributed to hydrogen bonding in the conjugate acid of *N*-methyl-*o*-phenylenediamine which effectively deactivates both amino groups. In the presence of alkali the reaction can be made to proceed to the formation of *N,N,N',N'*-tetramethyl-*o*-phenylenediamine. This compound reacts at low temperature with an additional mole of methyl iodide. The reaction is reversible at 50° and at higher temperatures the quaternary salt dissociates completely into its components. All attempts at formation of *o*-phenylenediamine-bis-trimethylammonium iodide (a homomorph of *o*-di-*t*-butylbenzene) were unsuccessful, whereas the corresponding *m*- and *p*-compounds form easily. Similarly, *o*-*t*-butyl-*N,N*-dimethylaniline does not react with methyl iodide. Treatment of $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-*o*-xylene- α,α' -diol with hydrogen chloride gives not the homomorphous bis-*t*-chloride, but instead the stable cyclic tertiary ether, $\alpha,\alpha,\alpha',\alpha'$ -tetramethylphthalan. It follows that no homomorph of *o*-di-*t*-butylbenzene has been synthesized.

Introduction

The failure of 2-*t*-butylpyridine to react with trimethylboron⁴ places a lower limit of 17 kcal. on the strain present in homomorphs⁵ of *o*-di-*t*-butylbenzene. Failure of boron trifluoride to add to *o*-*t*-butyl-*N,N*-dimethylaniline⁴ raises the estimated strain to a minimum of 25 kcal. Strains of this magnitude (Fig. 1) suggest that the preparation of such homomorphs should be a difficult matter.

(1) Studies in Stereochemistry. XXI. Strained Homomorphs. VII.

(2) Based upon a thesis submitted by K. LeRoi Nelson to the Faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) A.E.C. Fellow (1950-1952).

(4) H. C. Brown and R. B. Johannesen, *THIS JOURNAL*, **75**, 16 (1953).

(5) H. C. Brown, G. K. Barbaras, H. L. Berneis, W. H. Bonner, R. B. Johannesen, M. Grayson and K. L. Nelson, *ibid.*, **75**, 1 (1953).

A search of the literature revealed two reports of the preparation of compounds of this kind. Rate data are reported for the reaction of *o*-*t*-butyl-*N,N*-dimethylaniline with methyl iodide.⁶ The preparation of 3,4-di-*t*-butyltoluene is claimed by the treatment of toluene with 2 moles of *t*-butyl chloride in the presence of either aluminum chloride or ferric chloride.⁷

Unfortunately, Brown and Fried did not attempt to isolate the ammonium salt presumably formed in the reaction and de Capeller based the structure of his product on the belief (now known to be erroneous) that aluminum chloride and ferric chloride direct an entering alkyl group to different positions in the aromatic ring. Since *t*-butylation of toluene, using boron trifluoride or aluminum chlo-

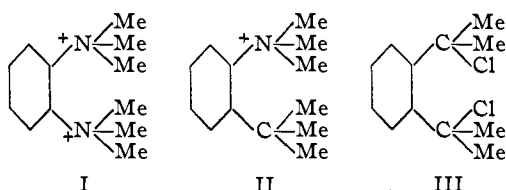
(6) W. G. Brown and S. Fried, *ibid.*, **65**, 1841 (1943).

(7) R. de Capeller, *Helv. Chim. Acta*, **11**, 168 (1928).

ride as catalyst, forms only a mixture of the *m*- and *p*-*t*-butyltoluenes with none of the ortho isomer,⁸ and *m*-xylene gives only 1,3-dimethyl-5-*t*-butylbenzene on *t*-butylation using either ferric chloride or aluminum chloride as catalyst,⁹ it appears certain that de Capeller's product cannot have the structure he proposed, but is probably the 3,5-di-*t*-butyltoluene.

That considerable difficulty is to be anticipated in any synthesis of a homomorph of *o*-di-*t*-butylbenzene is indicated by the experience of workers who prepared *o*-bis-trifluoromethylbenzene.¹⁰ In the photochlorination of *o*-xylene, only five chlorine atoms could be introduced into the side chains. The last remaining hydrogen could not be replaced. Only after the five chlorine atoms (van der Waals radius 1.80 Å.) had been replaced by five smaller fluorine atoms (1.35 Å.), could the last hydrogen atom be replaced by chlorine.

In the present study we investigated the reactions of methyl iodide with *o*-phenylenediamine and *o*-*t*-butyl-N,N-dimethylaniline and the reaction of $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-*o*-xylene- α,α' -diol with hydrogen chloride in an attempt to prepare a homomorph of *o*-di-*t*-butylbenzene (I-III).



Although we failed to synthesize any homomorphs of this kind, we did encounter some interesting reactions of the compounds under investigation.

Results and Discussion

***o*-Phenylenediamine and Methyl Iodide.**—Treatment of *o*-phenylenediamine with excess methyl iodide in methanol solution leads to a relatively rapid reaction until one mole of methyl iodide has reacted per mole of amine. This 1:1 stoichiometry is surprising in view of the observation that *p*-phenylenediamine reacts with two moles of methyl iodide under the same conditions. This unique ortho effect is presumably due to hydrogen bonding (IV) which effectively deactivates the second amino group.¹¹

Study of the reaction of *o*-phenylenediamine with methyl iodide was complicated by the fact that

(8) K. T. Serijan, H. F. Hipsher and L. C. Gibbons, *THIS JOURNAL*, **71**, 873 (1949).

(9) D. Nightingale, H. D. Radford and O. G. Shanholzer, *ibid.*, **64**, 1662 (1942).

(10) I. G. Farbenindustrie Aktiengesellschaft, British Patent 465,885 (May 18, 1937).

(11) The phenomenon appears to be a general one for ortho diamines since we also observed that one mole of acid effectively halts the further reaction of methyl iodide with N,N,N',N'-tetramethyl-*o*-

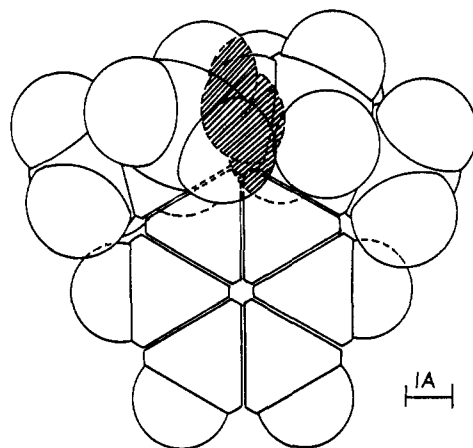
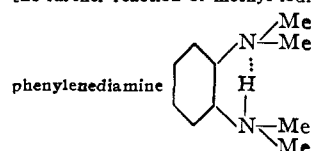
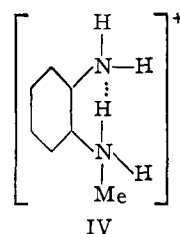


Fig. 1.—Molecular model of *o*-di-*t*-butylbenzene.

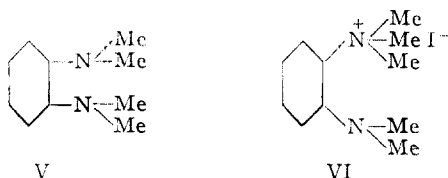
many of the intermediate methylated products have quite similar boiling points and poorly characterized properties. It was therefore impossible to follow the progress of the reaction between methyl iodide and the amine by isolation of products. An ebullioscopic method was developed whereby the extent of reaction could be ascertained at any time merely by observing the reflux temperature and referring to a standard curve of reflux temperature *vs.* composition for the system of the volatile components (methanol and methyl iodide). The method proved highly convenient and should be adaptable to a variety of reactions involving a volatile reagent and a relatively non-volatile reactant and product.



Treatment of *o*-phenylenediamine with methyl iodide in the presence of sodium carbonate leads to further methylation and N,N,N',N'-tetramethyl-*o*-phenylenediamine (V) is readily prepared. The optimum reaction procedure takes advantage of the peculiar 1:1 stoichiometry. A total of $n - 1$ equivalents of sodium carbonate is placed in the reaction flask in order that the reaction will essentially cease when n moles of methyl iodide have reacted.¹²

N,N,N',N'-Tetramethyl-*o*-phenylenediamine can be potentiometrically titrated with anhydrous perchloric acid in glacial acetic acid. Only a slight inflection in the titration curve was observed for half neutralization, but a good end-point was obtained for complete neutralization. The free amine (V) reacts easily with additional methyl iodide (in excess) at relatively low temperatures to give a quantitative yield of 2-(dimethylamino)-N,N,N-trimethylanilinium iodide (VI).

(12) In the general case not involving ortho amino groups, the proportion should be $n - 1$ equivalents of sodium carbonate per amino group.



The specific rate constant for this reaction in acetonitrile at 50° is 2.0×10^{-4} l. mole⁻¹ sec.⁻¹. An equilibrium state was apparently attained after about 50 hours, even in the presence of excess methyl iodide, with approximately 13% of the amine unreacted. The calculated equilibrium constant is 16.8 l. mole⁻¹ and the rate of the reverse reaction is 1.2×10^{-5} sec.⁻¹. When carried out in concentrated solution with a very large excess of methyl iodide, the reaction is forced to virtual completion. The salt is stable at room temperature and can be recrystallized from absolute ethanol and vacuum desiccated without decomposition. On heating the salt slowly loses methyl iodide, the dissociation being almost instantaneous at the melting point, 220°.

The easy formation of the monoquaternary salt (VI) observed in the present investigation contrasts with the failure of previous investigators.¹³ The difference is probably a consequence of the dissociation of the salt at elevated temperatures. Thus, Pinnow mentioned the formation of a small amount of the salt, but gave no supporting experimental evidence. In view of the reaction temperature he used (180°), it is probable that little, if any, salt was actually formed. The corresponding meta and para compounds, however, form without difficulty and are quite stable.¹⁴

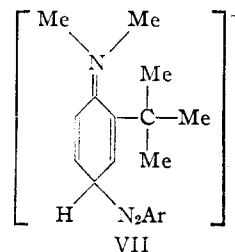
All attempts at formation of *o*-phenylene-bis-trimethylammonium (I) iodide met with conclusive failure. Both gravimetric and kinetic investigations gave no evidence of any methylation beyond the pentamethyl stage (VI).

***o*-*t*-Butyl-*N,N*-dimethylaniline and Methyl Iodide.**—Our failure to observe a reaction between 2-(dimethylamino)-*N,N,N*-trimethylanilinium iodide and methyl iodide was puzzling in view of the rate data reported for the reaction of *o*-*t*-butyl-*N,N*-dimethylaniline with methyl iodide.⁶ We at first considered the possibility that the positive charge at the quaternary nitrogen was deactivating the lone pair of the second nitrogen atom. However, both *m*- and *p*-phenylenediamine readily react with six moles of methyl iodide to form diquaternary salts.¹⁴ To clarify the situation we undertook a study of the reaction of *o*-*t*-butyl-*N,N*-dimethylaniline and methyl iodide.

o-*t*-Butyl-*N,N*-dimethylaniline was synthesized and refluxed with a large excess of methyl iodide for 12 days. After removal of the excess methyl iodide, the gain in weight of the reaction flask indicated a reaction of at most 4.4%. Since this small apparent reaction could conceivably be the result of impurities in the amine, the base was carefully purified and its purity established as 99.3 mole per cent. by cryoscopic measurements. A precise rate study was then made for the reaction of the

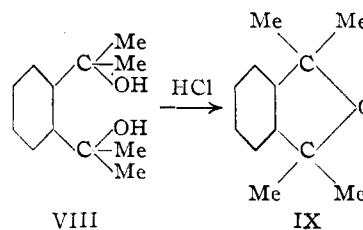
amine and methyl iodide in acetonitrile as solvent at 25°. In 84 days no reaction was observed. We therefore believe that the rate data reported in the literature must be in error.

The report that *o*-*t*-butyl-*N,N*-dimethylaniline couples normally with diazonium salts¹⁵ appeared questionable in view of the probable strain in the transition state (VII).



Under reaction conditions which give a good yield of methyl orange, little or no coupling was observed with either *o*-*t*-butyl-*N,N*-dimethylaniline or 2,6-*N,N*-tetramethylaniline.

$\alpha,\alpha,\alpha',\alpha'$ -Tetramethyl-*o*-xylene- α,α' -diol.—The glycol (VIII) was treated with gaseous hydrogen chloride and with aqueous hydrochloric acid under conditions which readily convert phenyldimethylcarbinol and related model compounds into the corresponding tertiary chlorides. However, the bis-*t*-chloride (III) was not obtained. Instead the unusually stable tertiary ether¹⁶ (IX) was formed.



Experimental Part

Ebullioscopic Technique.—Since this technique should be adaptable to a variety of reactions involving a volatile reagent and a relatively non-volatile reactant and product, the procedure will be described. The reflux temperature of a solution of the reactants is observed and the amount of unreacted reagent determined by reference to a standard reflux temperature *vs.* composition curve for the system, volatile solvent–volatile reagent. Since a distillative separation of the order of one plate is involved, the standard curve should be prepared using a system having essentially the same vapor volume as the reaction system. A small total-condensation variable-takeoff distilling head (low vapor volume and liquid holdup) mounted in one of the side necks of a regular 3-necked round-bottomed flask is suitable for both the standardization and reaction. A volume of the volatile solvent (in this report, methanol) comparable to that used under reaction conditions is placed in the flask and the null value of the reflux temperature observed. Successive aliquots of the volatile reagent (in this report, methyl iodide) are added and the respective reflux temperatures observed. Five or six points are sufficient to define the standard curve. It is usually preferable to add the volatile reagent in several portions, since the depression of the reflux temperature is most pronounced at lower concentrations. In many applications, the time for completion of reaction will be of primary interest and in such cases all of the reagent will be added initially. The reflux temperature will increase as the reaction proceeds and will become constant

(13) (a) O. Fischer and M. Woldenberg, *Ber.*, **25**, 2839 (1892); (b) J. Pinnow, *ibid.*, **32**, 1401 (1899).

(14) A. W. Hofmann, *Compt. rend.*, **56**, 994 (1863).

(15) C. D. Nenitzescu and V. Vantu, *Ber.*, **77**, 705 (1944).

(16) G. M. Bennett and R. L. Wain, *J. Chem. Soc.*, 1114 (1936).

when the reaction is essentially complete. The citation of precision limits for various concentrations in the methanol-methyl iodide system should assist the adaptation of the technique to other systems. The following limits are based on a precision of $\pm 0.5^\circ$ in the measurement of the reflux temperature.

Reflux temperature, $^\circ\text{C}$.	Composition, MeI by weight, %	Precision, %
64.0	0	± 0.2
60.0	1	± 0.3
53.0	5	± 0.6
49.0	10	± 1
44.0	20	± 1.5
38.5	40	± 2.5
36.5	60	± 8

Reactions of *o*- and *p*-Phenylenediamine with Methyl Iodide.—The ebullioscopic technique was applied to the study of the reaction in methanol of *o*- and *p*-phenylenediamine with methyl iodide in the absence of added alkali.

In a 250-ml. round-bottomed flask equipped with a reflux head were placed 8.9 g. (0.082 mole) of *o*-phenylenediamine (Eastman Kodak Co., White Label), 100 ml. of absolute methanol, a boiling chip and 2.57 ml. (0.041 mole) of methyl iodide (Columbia). After refluxing 2 hours, the reflux temperature had increased to 63.5° . The system was partially cooled and 2.57 ml. (0.041 mole) of methyl iodide added. After refluxing for an additional 12 hours, the reflux temperature was constant at 63.2° . The further addition of 0.97 ml. of methyl iodide gave a reflux temperature which was constant at 55.6° for 24 hours. The reaction does not proceed beyond the 1:1 stoichiometry.¹⁷

In an analogous experiment, 10.8 g. (0.10 mole) of *p*-phenylenediamine (Paragon) was refluxed with 28.4 g. (0.20 mole) of methyl iodide (Columbia) in 100 ml. of absolute methanol. Reference to the standard curve indicated the progress of the reaction. The reflux temperature was constant after about 8 hours and indicated essentially complete utilization of the methyl iodide. The amine-methyl iodide stoichiometry in this case is clearly 1:2.

***N,N,N',N'*-Tetramethyl-*o*-phenylenediamine.**—Into a tared 500-ml. 4-necked round-bottomed flask was distilled 40.6 g. (0.376 mole) of *o*-phenylenediamine (b.p. $159\text{--}160^\circ$ at 45 mm.). The flask was equipped with a sealed stirrer, addition funnel, reflux head, stopper and provision for maintaining nitrogen atmosphere. Anhydrous methanol, 160 g., and 59.8 g. of sodium carbonate (1.13 eq.) were added to the amine in the flask. Moderate stirring was maintained while 213.5 g. (1.50 moles) of freshly distilled methyl iodide (b.p. 41.5° , n_D^{20} 1.5306) was slowly added over a period of four hours. The mixture was brought to a gentle reflux and maintained there for nine hours until the temperature of the vapor had increased from 42° to a constant value of 64.2° , corresponding to complete utilization of the methyl iodide. The flask was cooled, an additional 53.4 g. (0.346 mole) of methyl iodide was added, and the reaction mixture refluxed for two additional hours. However, no change in the temperature of the vapor was observed, indicating that the excess methyl iodide did not react.¹⁸

The volatile components were removed by simple distillation, the remaining slush was slurried with 100 ml. of water and 19.9 g. (0.376 eq.) of sodium carbonate. The mixture was extracted with ethyl ether, the extract washed with water and dried over potassium hydroxide followed by calcium hydride. Distillation (over phosphorus pentoxide) gave 51.5 g. (84%) of *N,N,N',N'*-tetramethyl-*o*-phenylenediamine, b.p. 92.0° at 10 mm., n_D^{20} 1.5434, d_4^{20} ,

(17) There is, however, a slow reaction between the 1:1 product and methanol which, in effect, regenerates the free amine species and converts the hydrogen iodide into methyl iodide. Thus, a fair yield of *N,N,N,N'*-tetramethyl-*o*-phenylenediamine may be obtained (without added alkali) by using a very large excess of methyl iodide and refluxing the mixture for several weeks.

(18) It follows that one equivalent of acid effectively prevents reaction of the *o*-bis-*t*-amine with additional methyl iodide. The result must here also be attributed to hydrogen bonding, such as was postulated to be present in the conjugate acid of *N*-methyl-*o*-phenylenediamine (IV). The treatment with excess methyl iodide minimizes the presence of traces of primary or secondary amine in the product.

0.956, m.p. (cor. to zero impurity) $8.9 \pm 0.9^\circ$. The purity was estimated from cryoscopic data¹⁹ as 96.4 ± 1.8 mole %.

Anal. Calcd. for $\text{C}_{10}\text{H}_{16}\text{N}_2$: N, 17.07; mol. wt., 164.3. Found: N, 17.07, 17.21; mol. wt. (from titration with anhydrous perchloric acid in glacial acetic acid), 166.

2-(Dimethylamino)-*N,N,N'*-trimethylanilinium Iodide.—In a tared 50-ml. flask were placed 5.7 g. (0.0347 mole) of *N,N,N',N'*-tetramethyl-*o*-phenylenediamine and 39.4 g. (0.278 mole) of freshly distilled methyl iodide. The reaction mixture became cloudy almost immediately and was a white slush in 5 hours at room temperature. After a total of 23 hours, the methyl iodide was removed under reduced pressure, residual material being removed by pumping to constant weight at 0–1 mm. The increase in weight, 4.9 g., corresponded exactly to the calculated value for the monoquaternary salt. The product was recrystallized from absolute alcohol. It was obtained as white leaflets, m.p. 220° (with dissociation).

Anal. Calcd. for $\text{C}_{11}\text{H}_{19}\text{N}_2\text{I}$: N, 9.15. Found: N, 9.08, 9.13.

Rate of Reaction of *N,N,N',N'*-Tetramethyl-*o*-phenylenediamine with Methyl Iodide.—Solutions of the amine and methyl iodide in acetonitrile were prepared and mixed. Aliquots were introduced into capsules, which were then sealed and maintained at 50° . The solutions were 0.442 *M* in methyl iodide and 0.0638 *M* in amine. At measured intervals of time, a capsule was opened and analyzed for iodide ion by the Volhard procedure. Data for a typical study are summarized in Table I.

TABLE I

RATE DATA FOR THE REACTION OF *N,N,N',N'*-TETRAMETHYL-*o*-PHENYLENEDIAMINE WITH EXCESS METHYL IODIDE IN ACETONITRILE AT 50°

Time, hr.	Iodide ion, % ^a	Time, hr.	Iodide ion, % ^a
0	0	6	2.42
1	0.87	53	2.83
2	1.44	168	2.83 ^b
3	1.86	504	2.84 ^b
4	2.14	1008	2.89 ^b
5	2.30	2016	2.89 ^b

^a Expressed as ml. of 0.2021 *N* silver nitrate. In these units the initial concentrations of methyl iodide and amine are 22.81 and 3.30 ml., respectively. ^b Increasing relative error due to slight deterioration.

The specific rate constant established by these data is 2.0×10^{-4} l. mole⁻¹ sec.⁻¹. Even after 80 days, the reaction was not complete at the first amino group. Apparently an equilibrium state is reached, even in the presence of the excess methyl iodide, with 13% of the amine unreacted. It follows that the equilibrium constant is 16.8 l. mole⁻¹ and the rate of the reverse reaction is 1.2×10^{-6} sec.⁻¹.

***o*-Phenylene-bis-trimethylammonium Iodide.**—In an attempt to drive the reaction to completion, 2.19 g. (0.0139 mole) of *N,N,N',N'*-tetramethyl-*o*-phenylenediamine was treated with a large excess of methyl iodide (29.5 g., 0.208 mole) and 8.5 g. of acetonitrile. The reaction mixture was refluxed, for three months (with protection from radiation) and the volatile contents removed by aspiration and pumping. The weight increase was 1.84 g. as compared to 3.68 g. calculated for the formation of the diammonium derivative.

***o*-*t*-Butyl-*N,N*-dimethylaniline.**—*t*-Butylbenzene was nitrated and the ortho isomer separated in pure form by distillation.²⁰ The nitro compound was reduced to *o*-*t*-butylaniline with iron and hydrochloric acid in 70% yield. The amine was carefully fractionated in a Miniature Podbielniak Column (8 mm. \times 24" Heligrad packing); b.p. 106.5° at 10 mm., n_D^{20} 1.5453, m.p.²¹ approx. -60° .

The equipment was similar to that described for methyl-

(19) The equipment and techniques were modified from those of Rossini and co-workers [*J. Research Natl. Bur. Standards*, **26**, 591 (1941); **35**, 355 (1945)]. These simplified procedures will be described in a paper now in process of publication by K. L. Nelson.

(20) K. L. Nelson and H. C. Brown, *THIS JOURNAL*, **73**, 5605 (1951).

(21) The high viscosity of the liquid at low temperatures made it impossible to carry out a cryoscopic determination of purity.

tion of *o*-phenylenediamine. In a 100-ml. flask were placed 18.4 g. (0.123 mole) of *o*-*t*-butylaniline, 6.6 g. (0.123 eq.) of sodium carbonate, 35 g. of dry methanol and 35.0 g. (0.246 mole) of methyl iodide. After refluxing for 24 hours the vapor temperature was constant at 64°. An additional 10.0 g. (0.0704 mole) of methyl iodide was added and the reaction mixture refluxed for an additional 24 hours. There was no further reaction. The amine was isolated and rectified over phosphorus pentoxide in the Podbielniak Heligrad Column. There was obtained 15.7 g. (72%) of *o*-*t*-butyl-N,N-dimethylaniline: b.p. 91.0° at 10 mm., n_D^{20} 1.5040, m.p. (corrected to zero impurity) $2.8 \pm 0.2^\circ$ and purity 99.3 ± 0.4 mole %, both from cryoscopic data.¹⁹

Reaction of *o*-*t*-Butyl-N,N-dimethylaniline with Methyl Iodide.—Crude *o*-*t*-butyl-N,N-dimethylaniline and 45.6 g. of methyl iodide were heated under reflux for 12 days. After removal of the volatile constituents, the flask and its contents had increased in weight by 0.28 g. versus 6.21 g. calculated for formation of the quaternary salt.

Solutions of *o*-*t*-butyl-N,N-dimethylaniline and excess methyl iodide in acetonitrile were prepared, placed in sealed ampules, and maintained at 25°. From time to time an ampule was opened and analyzed for iodide ion. At 741 hours, an ampule required 0.12 ml. of 0.0988 *N* silver nitrate solution; at 1118 hr., 0.03 ml.; at 2006 hr., 0.09 ml. This compares to 10.43 ml. estimated for complete reaction. Within the precision of the measurements there is obviously no reaction.

Comparison of Coupling Reaction.—In each case, the coupling agent was prepared by adding 1.73 g. (0.01 mole) of sulfanilic acid (Baker C.P.) to 20 ml. of 2.5% sodium carbonate solution and dissolved by heating. The solution was cooled and 0.75 g. (0.011 mole) of sodium nitrite was added with stirring to effect complete solution. This solution was poured into a beaker containing 10 g. of crushed ice and 2 ml. of concentrated hydrochloric acid. The resulting suspension of diazotized sulfanilic acid was used without isolation.

In each case, 0.01 mole of tertiary amine (1.21 g. of N,N-dimethylaniline, 1.77 g. of *o*-*t*-butyl-N,N-dimethylaniline

and 1.49 g. of 2,6,N,N-tetramethylaniline²²) was dissolved in 0.6 g. of glacial acetic acid and the solution added with stirring to the suspension of diazotized sulfanilic acid.

A thick red paste was formed almost immediately from N,N-dimethylaniline. The addition of 7 ml. of 20% sodium hydroxide solution and subsequent boiling and slow cooling yielded about 2 g. of crystalline methyl orange. When *o*-*t*-butyl-N,N-dimethylaniline was treated in the same way, about half of the tertiary amine was recovered and no solid product was obtained. Nearly half of the 2,6,N,N-tetramethylaniline was recovered and only about 0.3 g. of orange solid was obtained.

Reaction of $\alpha,\alpha,\alpha',\alpha'$ -Tetramethyl-*o*-xylene- α,α' -diol²² with Hydrogen Chloride.—In a 50-ml. separatory funnel were placed 20 ml. of concentrated hydrochloric acid and 2.0 g. (0.0103 mole) of $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-*o*-xylene- α,α' -diol. A little ethyl ether was added to make the system homogeneous. The mixture was shaken at room temperature at frequent intervals over a period of 24 hours, diluted (1:1) with water and extracted with three portions of ethyl ether. The extract was washed with water and dried over calcium chloride. After removal of the ether by simple distillation, the remaining solid was sublimed at 28 mm. (bath at 70°). The white crystalline product (m.p. 71.5–72.0°) was obtained in a yield of 1.5 g. (83%) and was identified as the stable cyclic ether, $\alpha,\alpha,\alpha',\alpha'$ -tetramethylphthalan.¹⁶

In a tared 50-ml. round-bottomed flask was placed 1.80 g. (0.0093 mole) of $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-*o*-xylene- α,α' -diol. A slow stream of anhydrous hydrogen chloride was passed over the material at room temperature for 12 hours. The pink solid glycol was completely converted to liquid (one phase). The increase in weight was 0.15 g. which is consistent with the solubility of hydrogen chloride in the water produced if the ether was formed. The weight increase would have been approximately 0.5 g. if the monochloride was formed and 1.0 g. for the dichloride.

(22) Supplied by Mr. M. Grayson (b. p. 80° (15 mm.), n_D^{20} 1.5138).

(23) Supplied by Mr. W. H. Bonner (m. p. 163–165°).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS, FORDHAM UNIVERSITY AND BROOKHAVEN NATIONAL LABORATORY]

Studies in the Mechanism of the Willgerodt Reaction. II. Direction of Migration of the Functional Group in Aliphatic Ketones¹

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The direction of migration of the functional group during the transformation of normal aliphatic ketones into amides by the Willgerodt reaction has been studied with carbon-14. For unsymmetrical di-*n*-alkyl ketones the functional group shows a preferential tendency to migrate to the shorter end of the chain. This preferential tendency gradually increases as the number of carbon atoms is increased in the longer alkyl chain.

When a dialkyl rather than an aryl alkyl ketone undergoes the Willgerodt reaction the product is a corresponding alkyl carbonamide, as has been shown previously.^{4,5} Thus, pinacolone (CH₃)₂CCOCH₃ gives *t*-butyl acetamide⁴ (CH₃)₃CH₂CONH₂, while methyl isobutyl ketone CH₃CH(CH₃)-CH₂COCH₃ gives isocaproamide,⁵ CH₃CH(CH₃)-CH₂CH₂CONH₂. In these cases the migration of the functional group is to the structurally simple end of the molecule. Since neither α,α -dimethylbutyramide, CH₃CH₂C(CH₃)₂CONH₂ is obtained from pinacolone nor α -methylvaleramide CH₃CH₂-CH₂CH(CH₃)CONH₂ from methyl isobutyl ke-

tone, this migration is essentially unidirectional and therefore is similar to the behavior of aryl alkyl ketone. As predicted by the mechanisms proposed by Carmack and DeTar^{6,7} and McMillan and King⁸ no migration can occur past a quaternary carbon and thus the result with pinacolone is explicable. The case of the methyl isobutyl ketone has not been explored as far as a rationale for the mechanism is concerned. It is not possible with this example to separate factors influencing migration such as a structural feature (a secondary carbon in the chain) or probability (assuming, for example, equal chance of migration to either side of the original carbonyl group).

A straight chain aliphatic ketone, however,

(6) M. Carmack and D. F. DeTar, *ibid.*, **68**, 2029 (1946).

(7) M. Carmack and M. A. Spielman, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, chap. II.

(8) J. A. King and F. H. McMillan, *This Journal*, **68**, 632 (1946); F. H. McMillan and J. A. King, *ibid.*, **70**, 4143 (1948).

(1) Work carried out under the auspices of the Atomic Energy Commission.

(2) A.E.C. Predoctoral Fellow, 1949–1951.

(3) Brookhaven National Laboratory.

(4) L. Cavallieri, D. B. Pattison and M. Carmack, *This Journal*, **67**, 1783 (1945).

(5) J. A. King and F. H. McMillan, *ibid.*, **68**, 1269 (1946).