equilibrium had been reached. The decrease in pressure in SB gave the amount of trimethylboron introduced. After a correction for the quantity in the gas phase, the trimethylboron in solution was accurately known together with the equilibrium pressure. Additional quantities of trimethylboron could then be introduced to obtain a series of points for a pressure versus mole fraction graph.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Homomorphs of 2,6-Dimethyl-*t*-butylbenzene[1,2]

BY HERBERT C. BROWN AND MARTIN GRAYSON[3]

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2,6,N,N-Tetramethylaniline does not react with methyl iodide to form the quaternary ammonium salt, a homomorph of 2,6-dimethyl-*t*-butylbenzene. Similarly, mesitylene could not be *t*-butylated under conditions which result in the ready *t*-butylation of *m*-xylene to form 1,3-dimethyl-5-*t*-butylbenzene. Treatment of mesityldimethylcarbinol with hydrogen chloride results in the formation of α,2,4,6-tetramethylstyrene. The olefin does not add hydrogen chloride to form the tertiary chloride under a wide variety of conditions. At −30° considerable hydrogen chloride is absorbed with the formation of a red solid; the gas is evolved at higher temperatures. It is considered that the absorption is the result of the formation of a carbonium ion salt: $[2,4,6\text{-}Me_3C_6H_2CMe_2]^+Cl^-$. It is concluded that the high strain present in homomorphs of 2,6-dimethyl-*t*-butylbenzene accounts for the observations. Methyl 2,6-xylate could not be converted into 2,6-dimethylphenyldimethylcarbinol. No reaction occurred between the ester and methylmagnesium iodide; methyllithium yielded 2,6-dimethylacetophenone. The tertiary alcohol was prepared from 2,6-dimethylphenylmagnesium bromide and acetone in a yield of 4.5%. Mesityldimethylcarbinol was prepared from mesitylmagnesium bromide and acetone in 9% yield and from mesityllithium and acetone in 5.6% yield.

Introduction

Trimethylboron does not react with 2,6-lutidine.[4] Since pyridine, a somewhat weaker base,[5] readily reacts with trimethylboron to form a stable addition compound with a heat of dissociation of 17.0 kcal.,[6] steric strains of at least 17.0 kcal. are assigned to homomorphs[7] of 2,6-lutidine-trimethylboron (I) and 2,6-dimethyl-*t*-butylbenzene (II) (Fig. 1).

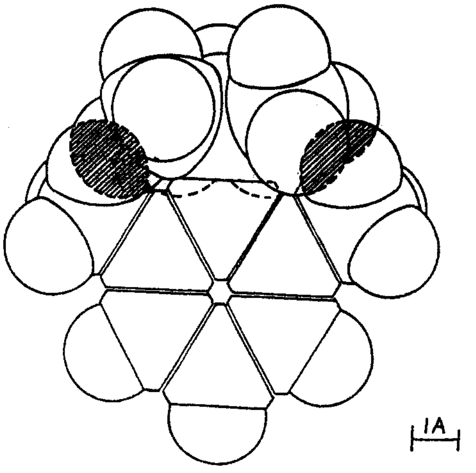
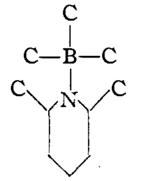
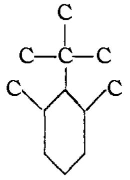


Fig. 1.—Molecular model of 2,6-dimethyl-*t*-butylbenzene.

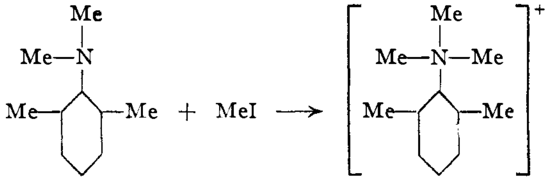


I



II

With one exception no homomorphs of 2,6-dimethyl-*t*-butylbenzene have been reported. Rate constants for the reaction of 2,6,N,N-tetramethylaniline (III) with methyl iodide at 35 and 45° in methanol have been reported.[8] From the data the reaction should proceed to the extent of 25% in nine days at 45°. However, the quaternary salt (IV) which is presumably formed in the course of the reaction has not been isolated. The situation is confused by the earlier report that treatment of the amine (II) with methyl iodide in anhydrous ether for two months led to the formation of only "a trace of a crystalline substance."[9] Accordingly it was decided to reinvestigate this reaction and to attempt the isolation of the homomorph (IV).



III IV

In the course of this study we also examined the reactions of 2,6-dimethylphenyldimethylcarbinol and mesityldimethylcarbinol with hydrogen chloride in an attempt to prepare the homomorphic tertiary chloride (V).

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(1) Studies in Stereochemistry. XX. Strained Homomorphs. VI.

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

(3) Standard Oil Company (Indiana) Fellow (1949-1950); A.E.C. Fellow (1950-1952).

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

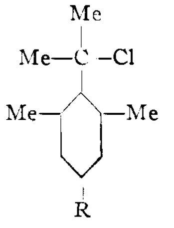
(5) Pyridine: pK_A 5.17 at 25°; 2,6-lutidine: pK_A 6.75 at 25°. Unpublished work with F. X. Mihm. Ph.D. Thesis, Purdue University, 1951.

(6) H. C. Brown and G. K. Barbaras, THIS JOURNAL, **69**, 1137 (1947).

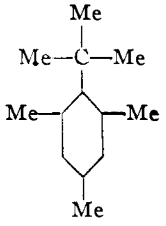
(7) H. C. Brown, G. K. Barbaras, H. L. Berneis, W. H. Bonner, R. B. Johannesen, M. Grayson and K. L. Nelson, *ibid.*, **75**, 1 (1953).

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

(9) W. C. Davies and H. W. Addis, *J. Chem. Soc.*, 1622 (1937).



V (R = Me or H)



VI

Finally we examined the *t*-butylation of mesitylene in an attempt to prepare a structure containing a *t*-butyl group flanked by two methyl groups in the ortho positions.

Results and Discussion

2,6,N,N-Tetramethylaniline and Methyl Iodide.—2,6,N,N-Tetramethylaniline was prepared from 2,6-xylidine by treatment with excess methyl iodide in the presence of aqueous sodium carbonate. After careful purification, freezing curve data indicated the purity to be 99.7 ± 0.2%. Acetonitrile was selected as the solvent for studying the reaction of the amine with methyl iodide. Under comparable conditions the reactions of amines with alkyl halides in acetonitrile proceed some fivefold faster than do the corresponding reactions in methanol. Moreover, methanol offers the possibility of a competing solvolytic reaction, whereas such reactions have not been observed with acetonitrile.

Accordingly solutions of amine (0.2 *M*) and methyl iodide (1.0 *M*) in acetonitrile were prepared and aliquots mixed and placed in ampules maintained at 25°. From time to time an ampule was opened and analyzed for iodide ion. There was observed a slow increase over a period of 18 days until the concentration of iodide ion corresponded to 4.5% reaction. No further increase was observed for several months thereafter.

It was considered that the small amount of apparent reaction might be the result of an unfavorable equilibrium. If so, an increase in the reaction temperature should increase the dissociation of the quaternary salt and shift the reaction to the left. Accordingly, an ampule which had been at 25° for 80 days was heated at 75–80° for 2 days. However, there was observed a slight increase in the iodide ion to 6.3%. Therefore, the small concentration of iodide ion cannot be attributed to a reaction which has proceeded only slightly toward the formation of the quaternary salt and must, instead, be the result of some side reaction or impurity.

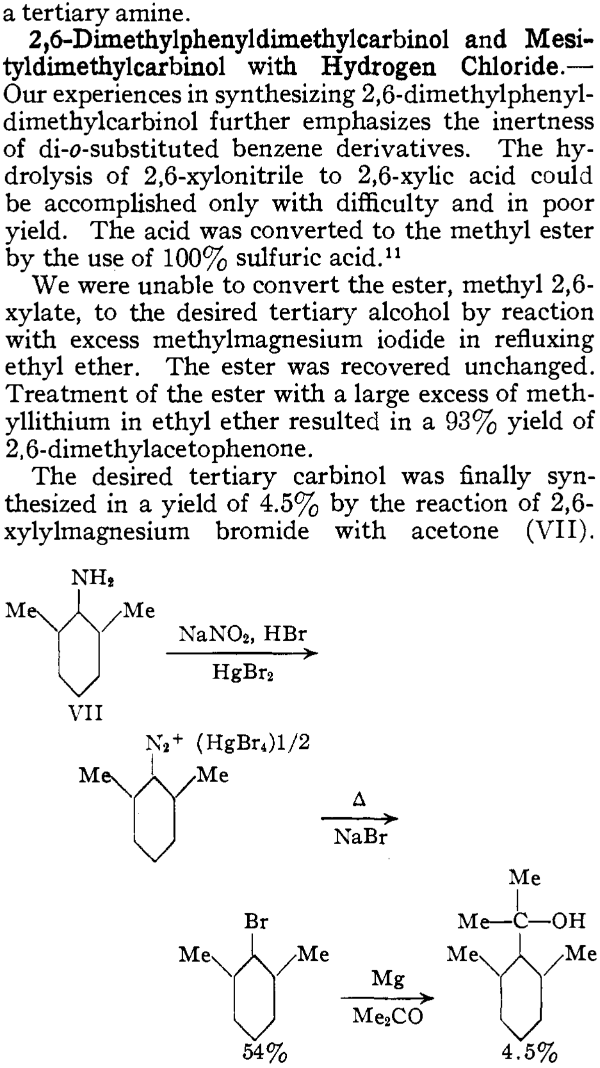
Repetition of the experiments after careful repurification of the amine, solvent, and methyl iodide did not eliminate this small formation of iodide ion. In the case of *o*-*t*-butyldimethylaniline,[10] using the same procedures and the same solvent and methyl iodide, this phenomenon was not observed. We can only conclude that in spite of the cooling curve data there must have been present in the amine a small amount of an impurity which reacts with methyl iodide. For example, the presence of 0.5% of water in the amine could account for the results.

In spite of this complication, it is apparent that 2,6,N,N-tetramethylaniline and methyl iodide do not react to any significant degree. It follows that the 17 kcal. of strain postulated for homomorphs of 2,6-dimethyl-*t*-butylbenzene is sufficient to prevent the usually easy reaction of methyl iodide and a tertiary amine.

2,6-Dimethylphenyldimethylcarbinol and Mesityldimethylcarbinol with Hydrogen Chloride.—Our experiences in synthesizing 2,6-dimethylphenyldimethylcarbinol further emphasizes the inertness of di-*o*-substituted benzene derivatives. The hydrolysis of 2,6-xylonitrile to 2,6-xylic acid could be accomplished only with difficulty and in poor yield. The acid was converted to the methyl ester by the use of 100% sulfuric acid.[11]

We were unable to convert the ester, methyl 2,6-xylate, to the desired tertiary alcohol by reaction with excess methylmagnesium iodide in refluxing ethyl ether. The ester was recovered unchanged. Treatment of the ester with a large excess of methyllithium in ethyl ether resulted in a 93% yield of 2,6-dimethylacetophenone.

The desired tertiary carbinol was finally synthesized in a yield of 4.5% by the reaction of 2,6-xylylmagnesium bromide with acetone (VII).



Because of the more ready availability of bromomesitylene, we decided to utilize mesityldimethylcarbinol[12] for a study of the possible preparation of a tertiary chloride with the strained 2,6-dimethyl-*t*-butylbenzene structure. The presence of the additional methyl group in the 4-position should not affect the reactions of the carbinol in any important manner. The action of mesitylmagnesium bromide on acetone gave the carbinol in 9% yield; the corresponding reaction of mesityllithium resulted in a yield of 5.6%.

Treatment of mesityldimethylcarbinol with dry hydrogen chloride gas at room temperature or at −30° gave only α,2,4,6-tetramethylstyrene (VIII).

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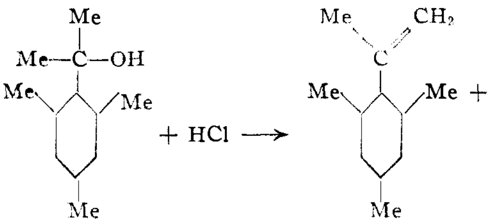
(10) H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 24 (1953).

(11) M. S. Newman, *ibid.*, **63**, 2431 (1941). Unfortunately, direct treatment of the nitrile by this procedure was unsuccessful. The nitrile was recovered unchanged.

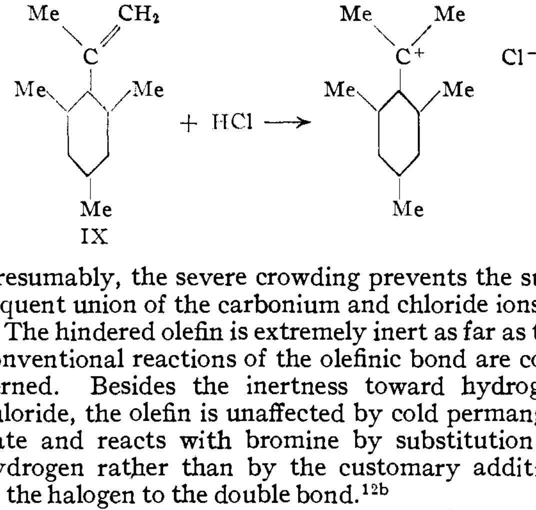
(12) (a) E. P. Kohler and L. W. Blanchard, Jr., *ibid.*, **57**, 367 (1935); (b) M. S. Newman and N. C. Deno, *ibid.*, **73**, 3644 (1951).



VIII

No evidence for the presence of an organic chloride could be obtained. When the olefin is treated at −30° with excess hydrogen chloride gas, a red solid is formed. (Newman and Deno[12b] report that mesityldimethylcarbinol dissolves in 100% sulfuric acid to give an orange-red solution.) The color of the solid disappears at once upon solution in 95% ethanol at low temperature (−80°) with the liberation of considerable quantities of hydrogen chloride. Under similar conditions α-methylstyrene adds hydrogen chloride to form 2-chloro-2-phenylpropane, which does not hydrolyze perceptibly in 95% ethanol at −80°.

The large quantity of hydrogen chloride which is absorbed without formation of a tertiary chloride together with the color of the product points to the addition of a proton to form the carbonium ion (IX)



IX

Presumably, the severe crowding prevents the subsequent union of the carbonium and chloride ions.

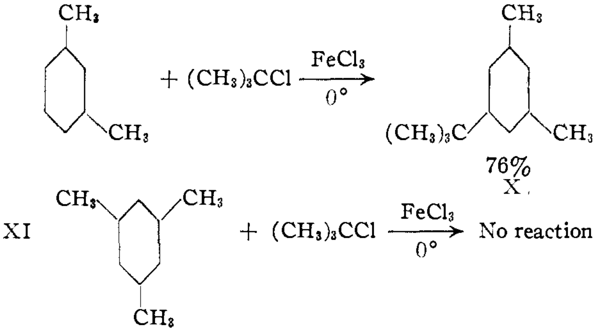
The hindered olefin is extremely inert as far as the conventional reactions of the olefinic bond are concerned. Besides the inertness toward hydrogen chloride, the olefin is unaffected by cold permanganate and reacts with bromine by substitution of hydrogen rather than by the customary addition of the halogen to the double bond.[12b]

In the case of dineopentylethylene,[13b] the hindered double bond shows similar characteristics. It neither reacts with permanganate nor adds bromine.[13b] Hydrogen chloride is added at low temperatures, but the tertiary chloride dissociates into its components at 25°.[13a]

It therefore appears that the increase in olefin formation in the solvolysis of tertiary chlorides with increasing B-strain[14] reaches a limiting condition in these compounds with the strain being sufficiently large in the hypothetical molecule, mesityldimethylcarbinyl chloride, that the equilibrium lies entirely in favor of the olefin and hydrogen chloride.

In connection with the concepts of steric assistance proposed earlier,[15] it is noteworthy that mesityldimethylcarbinol exhibited an unusual reactivity toward hydrogen chloride. Rapid conversion of the alcohol to the olefin occurs in the presence of traces of acid. Such behavior of a badly hindered tertiary alcohol is of course contrary to the classical concepts of steric hindrance.

Attempted Friedel–Crafts Reaction of Mesitylene and *t*-Butyl Chloride.—*m*-Xylene is readily alkylated with *t*-butyl chloride in the presence of anhydrous ferric chloride at 0° to give 1,3-dimethyl-5-*t*-butylbenzene[16] (X). Instead of the 67% yield previously reported[16] we realized a yield of 76% with 74% of the *m*-xylene either recovered or accounted for as product. However, under the same conditions mesitylene was not *t*-butylated (XI)



The mesitylene was recovered largely unchanged, 85%; no *t*-butylbenzene could be isolated in spite of a careful examination of the reaction mixture. A small quantity of 2,2′,4,4′,6,6′-hexamethylbiphenyl (bimesityl) was isolated from the residue. Thus, even under conditions sufficiently vigorous to permit coupling of two mesitylene molecules, alkylation does not occur. Evidently the large strain present in homomorphs of 2,6-dimethyl-*t*-butylbenzene is sufficient to prohibit direct formation of the strained structure through the Friedel–Crafts reaction.

Conclusions

It follows that no homomorphs of 2,6-dimethyl-*t*-butylbenzene are known. Apparently the postulated strains of 17 kcal. are sufficiently effective to prohibit the synthesis of the strained system by the reaction of the tertiary amine (III) with methyl iodide, reaction of the tertiary alcohol (VIII) with hydrogen chloride or reaction of *t*-butyl chloride with mesitylene. There is, of course, the possibility that homomorphs of this structure may be prepared by other more favorable synthetic procedures. Such possibilities are currently under examination.

Experimental Part

2,6,N,N-Tetramethylaniline.—One mole, 121 g., of 2,6-xylidine (Eastman Kodak Co., b.p. 216° at 747 mm., n^{20}_D 1.5602) was heated under reflux for four days with 500 g. (3.5 moles) of methyl iodide in the presence of 300 g. (2.8 moles) of anhydrous sodium carbonate. The liquid was separated by filtration and the solid residue was dissolved in water and extracted with ether. The ether extracts were dried, combined with the original liquid and the ether was removed by distillation. Solid material was observed to

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(13) (a) H. C. Brown and H. L. Berneis, THIS JOURNAL, **75**, 10 (1953); (b) P. D. Bartlett, G. L. Fraser and R. B. Woodward, *ibid.*, **63**, 495 (1941).

(14) H. C. Brown and R. S. Fletcher, *ibid.*, **72**, 1223 (1950).

(15) H. C. Brown, *Science*, **103**, 385 (1946). See also notes **19** and 22, ref. 7.

(16) D. V. Nightingale, H. D. Radford and O. G. Shanholtzer, THIS JOURNAL, **64**, 1662 (1942).

form in the course of removing the methyl iodide.[17] To complete the reaction, the crude product was treated with an aqueous solution of one mole of sodium carbonate and one mole of methyl iodide. After heating under reflux for 12 hours, the organic layer was separated, dried over potassium hydroxide, and the methyl iodide removed by distillation. No solid was observed to form. The product was distilled under reduced pressure through a short Vigreux column. The yield of product (b.p. 79–82° (15 mm.), n^{20}_{D} 1.5135) was 74%. To remove possible traces of secondary amine, the clear distillate was heated under reflux with 50 ml. of acetic anhydride for 48 hours and was then distilled through an 18-in. column packed with $^1/_{16}''$ helices. The purified product distilled at 195.0° at 740 mm., n^{20}_{D} 1.5133.

The purity of the material was examined by study of the cooling curve, using procedures modified from those of Rossini and co-workers.[18] The data indicate the correct freezing point to be −36°, with an estimated purity of 99.7 ± 0.2% based upon the 0.17° drop in temperature at the time of half freezing.

Reaction of 2,6,N,N-Tetramethylaniline with Methyl Iodide.—Solutions of the tertiary amine, 0.2006 *M*, and of methyl iodide, 1.000 *M*, in acetonitrile were prepared. Equal volumes of the two solutions were mixed and 10-ml. aliquots were placed in thin-walled glass ampules. The sealed ampules were maintained at 25.0°. From time to time an ampule was opened and iodide ion determined by the Volhard method.

Time, days	0	3.8	18.0	30.5	44.5	82.5
Reaction, %	0.3	2.0	4.7	5.8	4.5	4.6

A sample which had been at 25° for 80 days was heated at 75–80° for 2 days. The iodide analysis corresponded to a reaction of 6.3%. Blank experiments with methyl iodide and acetonitrile gave no significant quantities of methyl iodide under similar conditions.

2,6-Dimethylphenyldimethylcarbinol.—2,6-Xylidine (1.0 mole) was converted into the nitrile,[19] m.p. 89–90°, in yield of 53%. Hydrolysis of the nitrile to 2,6-xylic acid with 70% sulfuric acid with or without sodium nitrite gave at best 20 to 23% yields of crude acid.[20] More satisfactory results were obtained by a two step hydrolysis. The nitrile was converted to the amide in 67% yield by treatment with concentrated sulfuric acid at 75–80° for five hours. The crude amide, m.p. 120–125°, was then heated at 145–50° for one-half hour with 100% phosphoric acid. A 36% yield of acid, m.p. 115–16°, was obtained.[21] The acid was converted to the methyl ester by the procedure described by Newman[11] for mesitoic acid. The yield was 68% of ester of b.p. 94° at 9 mm., n^{20}_{D} 1.5052.

Methyl 2,6-xylate, 14 g. (0.085 mole), was treated in the conventional manner with a fourfold excess of methylmagnesium iodide in ethyl ether. After 36 hours, the unreacted Grignard was decomposed and the product isolated by distillation. Only unchanged ester was obtained: 11.8 g., b.p. 79–81° at 3 mm., n^{20}_{D} 1.5050.

Approximately 0.3 mole of methyllithium (assuming a 70% yield) was prepared from lithium and methyl iodide in ethyl ether. The ester, 11.8 g. (0.072 mole), was slowly added in ether solution. The reaction mixture was refluxed for four hours and left at room temperature overnight. After hydrolysis, the dried ether solution was distilled. There was isolated 9.1 g. of 2,6-dimethylacetophenone, b.p. 72–73° at 1.5 mm., n^{20}_{D} 1.5160, n^{25}_{D} 1.5138, m.p. 23.5–23.7°, d^{25}_4 0.9821.[22]

Diazotization of 2,6-xylidine and treatment with cuprous bromide in aqueous solution results largely in the production of 2,6-xylenol and very little of the bromide.[19] The desired bromide, b.p. 98–99° at 20 mm., n^{20}_{D} 1.5552, was prepared in 54% yield by the von Schwechten procedure.[23]

The Grignard reagent was prepared from 4.6 g. of magnesium turnings (0.19 g. at.) and 35 g. (0.19 mole) of 2,6-xylyl bromide in ethyl ether under a nitrogen atmosphere. Excess of acetone (0.3 mole) diluted with ether was added to the refluxing Grignard solution over a period of seven to ten hours. The product was hydrolyzed with water and the ether extract was distilled. There was obtained 1.4 g. (4.5% yield) of product, b.p. 81° at 2 mm., m.p. 52–53°. Recrystallization from petroleum ether raised the m.p. to 58°. *Anal.* Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.61; H, 10.02.

Mesityldimethylcarbinol.—Bromomesitylene (b.p. 100° at 13 mm., n^{20}_{D} 1.5500) was prepared in 72% yield by the bromination of 1.6 moles of mesitylene[24] (b.p. 162° at 741 mm.).

Mesityllithium was prepared from 50 g. (0.25 mole) of bromomesitylene and 3.5 g. (0.5 g. at.) of lithium in ethyl ether. Reflux was maintained for two hours to complete the reaction. Then 14.5 g. (0.25 mole) of acetone diluted with ether was added. Vigorous refluxing was observed and a gray precipitate formed. The reaction mixture was hydrolyzed with ice and the ether extracts dried over potassium carbonate and distilled. After removal of the ether, 23 g. (0.19 mole, 76%), of mesitylene was recovered. The residue deposited a solid after two days, m.p. 107–110°. The pure product melts at 113°.[12] The yield was 2.5 g., 5.6%.

A similar preparation from 0.9 mole of bromomesitylene through the Grignard reaction gave 14.5 g. (9% yield) of product, m.p. 108–110°. Recrystallization from petroleum ether raised the m.p. to 111–112°.

Mesityldimethylcarbinol and Hydrogen Chloride.—Mesityldimethylcarbinol, 2.04 g., was maintained in an atmosphere of hydrogen chloride for two days at room temperature. The white solid was converted to a clear, faintly colored liquid with a small lower layer of water. One ml. of the product was pipetted into 100 ml. of 90% acetone and aliquots were removed for titration. No increase in acid was observed with time.

In a similar experiment 1.478 g. of the carbinol was placed in a weighed vessel and treated with hydrogen chloride at 25°. The observed weight, 1.597 g. at 0.5 hr., 1.600 g. at 1.0 hr., 1.601 g. at 1.5 hr., corresponds closely to the 1.596 g. calculated for the formation of 1.229 g. of olefin and 0.249 g. of water saturated with hydrogen chloride (40% by weight).

The procedure is identical with that which we have utilized for the preparation of the tertiary chlorides from such compounds as *o*-tolyldimethylcarbinol and *o*-isopropylphenyldimethylcarbinol. Under similar conditions 1.717 g. of technical grade α-methylstyrene, treated with hydrogen chloride, increased in weight by 0.502 g. after 90 min. This corresponds to 0.530 g. calculated for 100% reaction.

α,2,4,6-Tetramethylstyrene.—Several grams of mesityldimethylcarbinol was treated with hydrogen chloride and the product was washed with water, dried over calcium chloride and distilled under reduced pressure. The product, α,2,4,6-tetramethylstyrene, distilled at 90–91° at 13 mm., n^{25}_{D} 1.5108.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.83; H, 10.20.

Several attempts were made to add hydrogen chloride to the olefin at −30°. After saturation with hydrogen chloride at this temperature, the product was cooled to −80° and evacuated to remove dissolved hydrogen chloride. The product, a red solid at −80°, was then warmed to room temperature and the gas evolved was collected and weighed.

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[17] The solid, m.p. 156° with decomposition, was soluble in water. Addition of aqueous sodium carbonate caused the solution to become turbid and carbon dioxide was evolved. The solid was evidently not a quaternary ammonium salt. Moreover, in several experiments we heated the pure tertiary amine and excess methyl iodide for extended periods of time without observing the formation of a crystalline quaternary salt.

[18] F. D. Rossini, *et al.*, *J. Research Natl. Bur. Standards*, **26**, 591 (1941); **35**, 355 (1945). These simplified procedures were developed by Mr. K. LeRoi Nelson and will be described by him in a paper in process of publication.

[19] R. C. Fuson, S. L. Scott, E. C. Horning and C. H. McKeever, THIS JOURNAL, **62**, 2091 (1940).

[20] In the case of 2,6-dimethyl-4-bromobenzonitrile the hydrolysis at 150° gives 70–90% yields of the acid: R. C. Fuson, S. L. Scott and R. V. Lindsey, Jr., *ibid.*, **63**, 1679 (1941). However, similar treatment of 2,6-xylonitrile results in large losses through sulfonation of the ring.

[21] G. Berger and S. C. J. Olivier [*Rec. trav. chim.*, **46**, 600 (1927)] report a 70% yield of acid by this procedure.

[22] The compound was previously prepared by P. DeJong [*ibid.*, **61**, 539 (1942)] by the reaction of 2,6-dimethylbenzoyl chloride and the methyl Grignard reagent: b. p. 111–112° at 23 mm., m.p. 23.0–23.6°.

[23] M. S. Newman and P. H. Wise, THIS JOURNAL, **63**, 2847 (1941).

[24] L. I. Smith, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 95.

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. Phenyldimethylcarbinyl 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 α,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: 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° at 52 mm., n^{20}_{D} 1.4964) and 30.5 g. (0.19 mole) of 1,3-dimethyl-5-*t*-butylbenzene (b.p. 74–75.5° at 8 mm., n^{20}_{D} 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^{20}_{D} 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^{20}_{D} 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°. Successive recrystallization from 95% ethanol and ligroin raised the m.p. to 100°. *Anal.* Calcd. for $C_{18}H_{22}$: 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]

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[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).

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

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[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]

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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 α,α,α′,α′-tetramethyl-*o*-xylene-α,α′-diol with hydrogen chloride gives not the homomorphic bis-*t*-chloride, but instead the stable cyclic tertiary ether, α,α,α′,α′-tetramethylphthalan. It follows that no homomorph of *o*-di-*t*-butylbenzene has been synthesized.

Introduction

The failure of 2-*t*-butylpyridine to react with trimethylboron[4] places a lower limit of 17 kcal. on the strain present in homomorphs[5] of *o*-di-*t*-butylbenzene. Failure of boron trifluoride to add to *o*-*t*-butyl-N,N-dimethylaniline[4] 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.

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-

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[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).

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

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