at equilibrium the amounts of butyl alcohol and methyl alcohol which are present will bear the same ratio to each other as the inverse ratio of their reactivities. The equilibrium constant is then given by

$$K = \frac{0.80 \times 0.80}{1.0 \times 1.0} = 0.64$$

In other words, K in each case is the square of the relative reactivity value. The logarithms of K (x 100) given in the last column of Table II are perhaps the fairest measure of the differences in chemical reactivity of the alkyl group in alcoholysis.

From the relative reactivities, however calculated, certain general conclusions may be drawn. The substitution of any group for a hydrogen of methyl results in reduction in reactivity. The primary straight chain alkyl groups are similar and show comparatively small difference, yet there can be no question that *n*-heptyl is distinctly more reactive than *n*-propyl. A branching of the chain, or the presence of an unsaturated linkage adjacent to the carbinol, distinctly lowers the reactivity of an alcohol. The simple secondary alcohols show decidedly lower reactivity than do the primary alcohols but octanol-2, as in the acetal reaction, is distinctly more reactive than certain primary alcohols.

It is not worth while at the present time to make a comparison between Menschutkin's figures upon the extent of the ester reaction with various alcohols and the extent of alcoholysis in systems involving these same alcohols except to say that the relative reactivities are similar in the two systems.[1]

It should be pointed out that the statement given in various textbooks that secondary alcohols react to the extent of only 40 to 50% to form an ester with an equimolecular amount of acetic acid is not correct and is based upon a misreading of Menschutkin's papers. He really gave the figures 60.3% for isopropyl and 59.3 for *s*-butyl at 155°. Measurements in this Laboratory gave a value of about 58% for isopropyl at 200°.

It is interesting to note that the relative replacing power of hydrogen for methyl is 0.44 calculated upon the basis of the concentrations at equilibrium as given by Menschutkin for the reaction

$$\overset{0.305}{\mathrm{HOH}} + \overset{0.305}{\mathrm{MeOAc}} \rightleftharpoons \overset{0.695}{\mathrm{AcOH}} + \overset{0.695}{\mathrm{MeOH}}$$

The figure 0.44 for hydrogen is distinctly lower than that for any alkyl group given in Table II, but considerably higher than those for phenyl or *t*-butyl. One may then say that primary and secondary alkyl groups are more reactive while tertiary groups are less reactive in alcoholysis than hydrogen.

Summary

The extent of replacement of one alkyl group by another in the alcoholysis of various acetates has been ascertained. The relative replacing powers of fourteen alkyl groups referred to methyl have been calculated and recorded in Table II.

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[1] Menschutkin, *Ber.*, **11**, 1507 (1878); *Ann.*, **197**, 193 (1879); *Ann. chim. phys.*, [5] **23**, 14 (1881); *ibid.*, [5] **30**, 81 (1883).

MADISON, WISCONSIN RECEIVED NOVEMBER 1, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE B. F. GOODRICH COMPANY]

The Nitro and Amino Derivatives of *t*-Butylbenzene

BY DAVID CRAIG

In connection with studies involving certain aromatic amines it became necessary to investigate the nitration[1,2,3,4,5] of *t*-butylbenzene. The rather meager work reported in this field is in some cases conflicting and is entirely inadequate from the viewpoint of the preparation of *o*-nitro-*t*-butylbenzene. Accordingly it seems well to report the following studies which confirm and extend the early investigations of Senkowski.

t-Butylbenzene when nitrated is found to give a mixture of about 77% of *p*-nitro-*t*-butylbenzene with about 23% of the ortho isomer.[6] The presence of *m*-nitro-*t*-butylbenzene[7] was not noticed although it may have been present in small amounts. The use of mixed acid at room temperature is satisfactory for the nitration, a fact which does not seem to have been recognized thus far.

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[1] Senkowski, *Ber.*, **23**, 2412 (1890).

[2] Baur, *ibid.*, **27**, 1610 (1894).

[3] Henderson and Boyd, *J. Chem. Soc.*, **97**, 1665 (1910).

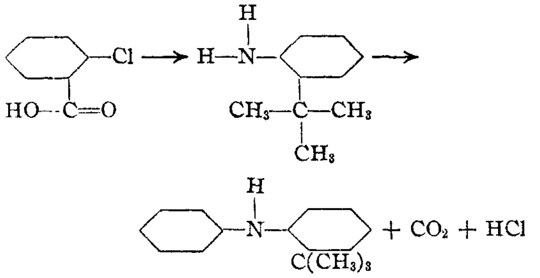
[4] Malherbe, *Ber.*, **52**, 319 (1919).

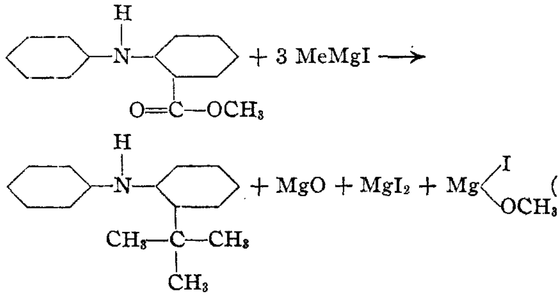
[5] Shoesmith and Mackie, *J. Chem. Soc.*, 2334 (1928).

[6] Under the same conditions of nitration the amount of para substitution increased with different alkylbenzenes in the following order: methyl, ethyl, isopropyl, *t*-butyl. See (a) Le Fèvre, *ibid.*, 981 (1933); (b) Brady *et al.*, *ibid.*, 114 and 121 (1934).

[7] Gelzer, *Ber.*, **21**, 2947 (1888).

The reduction of the nitro bodies with iron and hydrochloric acid in the usual manner leads to the formation of the corresponding amines which have been prepared by a variety of methods.[8,9] A proof of the structure of *o*-amino-*t*-butylbenzene[5] is found in the preparation of *o*-*t*-butyldiphenylamine (I) by the Ullmann[10] reaction (1). This diarylamine can be prepared by an independent method, namely, by the reaction of methylmagnesium iodide[11] with methyl N-phenylanthranilate (2). Other products secured from this reaction will be described in a later paper.


(1)


(2)

The preparation of the α-naphthyl and β-naphthyl derivatives of *p*-amino-*t*-butylbenzene takes place in the presence of hydrochloric acid. However, the yields are low. This may be due to the splitting off of butylene, since in the case of *o*-amino-*t*-butylbenzene and β-naphthol the main product is phenyl-β-naphthylamine. The activity of the *t*-butyl radical in N-*t*-butylaniline has been discussed recently by Hickinbottom,[12] who found that butylene is split off under the action of aqueous acid. Other *t*-butyl derivatives of diarylamines[13] that were prepared are *p*-*t*-butyldiphenylamine, *p*,*p*′-di-*t*-butyldiphenylamine, and *p*,*p*′-di-*t*-butyl-N,N′-diphenyl-*p*-phenylenediamine.

Experimental Part

The Nitration of *t*-Butylbenzene.—*t*-Butylbenzene, b. p. 166–169°, was prepared by the Friedel–Crafts reaction in 79% yield by the addition of one mole of *t*-butyl chloride to five moles of benzene and 0.08 mole of aluminum chloride. A considerable quantity of *p*-di-*t*-butylbenzene was obtained as a by-product. Other methods which gave lower yields involved the reaction of benzene, sulfuric acid and *t*-butanol[14] or the reaction of di- or tri-isobutylenes with benzene in the presence of aluminum chloride.[15]

A mixture of 900 g. (10 moles) of concentrated nitric acid with 1080 cc. of concentrated sulfuric acid was added to 1340 g. (10 moles) of *t*-butylbenzene with efficient agitation and cooling to 20–30° during 1.1 hours. The mixture was then agitated for one hour at 40°. The product was separated and washed free of acid with dilute caustic. Distillation without efficient fractionation being attempted produced 46 g. of recovered *t*-butylbenzene and 1680 g. (94% conversion) of mixed mononitro-*t*-butylbenzenes This was fractionated in a suitable column. After 18 g. of forerunnings a fraction (157 g.) consisting mainly of *o*-nitro-*t*-butylbenzene came over at 143–145° (45 mm.). An intermediate fraction (212 g.) was collected at 136–155° (30 mm.) and finally a fraction (1264 g.) consisting mainly of *p*-nitro-*t*-butylbenzene distilled at 155–158° (30 mm.). This product melted at 22° and at 28° after recrystallization from petroleum ether (Senkowski gave 30°). Assuming the crude products to be 90% pure and the intermediate fraction to be a 50% mixture, about 23 parts of *o*-nitro-*t*-butylbenzene for 77 parts of the para isomer were obtained.

The Reduction of the Nitro-*t*-butylbenzenes.—The reduction of the crude nitro-*t*-butylbenzenes was carried out in the usual manner by adding 179 g. of iron powder and 5 cc. of concentrated hydrochloric acid to one mole (179 g.) of vigorously agitated nitro compound during two hours. A temperature of 100° was maintained by a steam-bath. The mixture was then agitated for two hours at 100°. The amines were obtained by steam distilling and extracting the distillate with benzene; yield about 85% in both cases. The *p*-nitro-*t*-butylbenzene reduced smoothly with tin and hydrochloric acid, but the ortho isomer gave considerable amounts of a halogen-containing product (possibly an amino-chloro-*t*-butylbenzene).

The amino-*t*-butylbenzenes were not further purified for use in subsequent reactions. The crude *p*-amino-*t*-butylbenzene melted at 9° and after crystallizing from petroleum ether, 15–16° (Senkowski gave 17°). The acetyl derivatives of the two amines were prepared by reaction with

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(8) Senkowski, *Ber.*, **24**, 2974 (1891); Hickinbottom and Preston, *J. Chem. Soc.*, 1566 (1930).

(9) See Refs. 1, 4, 5, 7 and (a) Studer, *Ann.*, **211**, 234 (1882); (b) Gasiorowski and Merz, *Ber.*, **18**, 1009 (1885); (c) Louis, *ibid.*, **16**, 114 (1883); (d) Lloyd, *ibid.*, **20**, 1254 (1887).

(10) Ullmann, *Ann.*, **355**, 312 (1907).

(11) In addition to the customary preparation of alcohols from esters, Grignard reagents have been used for the direct removal of oxygen from (a) dimethylaminobenzaldehyde, Sachs *et al.*, *Ber.*, **40**, 4361 (1907); from (b) amides, Montagne, *Compt. rend.*, **183**, 216 (1926), and *Ann. chim.*, [10] **13**, 40 (1930), and references therein contained and Paraskova, *Compt. rend.*, **198**, 1701 (1934); and from (c) pyrrolones, Lukeš, *Coll. Czechoslov. Chem.*, *Comm.*, **4**, 181 (1932).

(12) Hickinbottom, *J. Chem. Soc.*, 1070 (1933).

(13) The use of these compounds as antioxidants has been patented: Craig, Canadian Patent 339,068, Jan. 30, 1934; French Patent 750,473, Aug. 11, 1933.

(14) Meyer, *Monatsh.*, **53** and **54**, 721 (1929).

(15) See Tilicheev and Kuruindin, *Neftyanoe Khozyaistvo*, **19**, 586 (1930); *Chem. Abs.*, **25**, 3469 (1931), for the preparation of amylbenzene by a similar method. See also Davidson, U. S. Patent 1,953,702, April 3, 1934.

acetyl chloride. The melting point of acetyl-*o*-amino-*t*-butylbenzene was found to be 159–161°, and of the corresponding para derivative 169–170°. These values agree with those previously reported.

o-*t*-**Butyldiphenylamine.**—The reaction of *o*-chlorobenzoic acid with *o*-amino-*t*-butylbenzene[10] gave in low yield a product which melted at 70–71° when crystallized from alcohol. This product was also prepared by the Grignard reaction using the following materials: 85.2 g. (0.6 mole) methyl iodide, 14.6 g. (0.6 mole) magnesium turnings, 150 cc. of dry ether and 30 g. (0.132 mole) of methyl N-phenylanthranilate (see last section of Experimental Part) dissolved in 150 cc. of dry ether. The addition of the ester to the Grignard reagent (twenty minutes required) produced a fairly vigorous reaction and caused the appearance of a yellow color. The mixture was stirred for one hour and allowed to stand overnight. The ether was then evaporated and the residue baked on the steam-bath for two hours. After cooling, 250 cc. of ether was added. Hydrolysis of the magnesium compounds was effected by gradually adding a mixture of 150 cc. water with 40 cc. acetic acid. A red solid came down during the hydrolysis. It was found in later experiments that this red solid did not form when only water or ammonium chloride solution was used for the hydrolysis. The compound contained halogen and was probably the hydriodide of an unidentified base; yield 9 g., m. p. 180–200°. The ether layer was separated, dried over potassium carbonate and distilled. Seventeen grams of a clear oil, b. p. 180–185° (18 mm.), was obtained. It did not crystallize when cooled in an ice–salt mixture. After dissolving in 80 cc. of concentrated sulfuric acid and allowing to stand for forty-five minutes the solution was poured onto cracked ice whereupon it crystallized completely. After filtering and washing with water it was taken up in benzene and dried over potassium carbonate. The benzene was evaporated and the product crystallized from about 3 volumes of hexane. The crystals were filtered off and were found to melt at 122–124°. On evaporating the mother liquor a further quantity of these resulted. The hexane was then evaporated and the resulting oil crystallized from ice cold alcohol. The crystals obtained melted at 71–72°. By working up the mother liquors in this way the total yield of the crystals from hexane (to be described more completely in a later paper) was 4.5 g. The total yield of the product melting at 71–72° was 10 g. (33%).

Anal. Calcd. for $C_{16}H_{19}N$: C, 85.3; H, 8.51; N, 6.31. Found: C, 85.17; H, 8.50; N, 6.55.

By its analysis and method of synthesis the compound is seen to be *o*-*t*-butyldiphenylamine. It did not depress the melting point secured by the above-described Ullmann reaction. The acetyl derivative melted at 88–89° after three crystallizations from hexane.

Phenyl-β-naphthylamine from *o*-Amino-*t*-butylbenzene.—Fifteen grams (0.1 mole) of *o*-amino-*t*-butylbenzene, 17.3 g. (0.12 mole) of β-naphthol, and a drop of concentrated hydrochloric acid were heated to the refluxing point of β-naphthol for two hours. The excess β-naphthol was extracted with dilute alkali. The product was then washed with water and distilled; yield 7 g., b. p. 170–176° (1 mm.) and 4 g., b. p. 176–190° (1 mm.). Both fractions gave phenyl-β-naphthylamine when crystallized from alcohol; m. p. 106–107° alone or when mixed with an authentic specimen.

p-*t*-**Butyldiphenylamine.**—This compound was prepared in low yield by refluxing mixed amino *t*-butylbenzenes with their hydrochlorides. In this experiment it is probable that butylene was split off from one or both of the amino-*t*-butylbenzenes. The amine was also obtained in small amounts by the condensation of diphenylamine with *t*-butyl chloride ($AlCl_3$) or with *t*-butanol (H_3PO_4) and by the reaction of *p*-amino-*t*-butylbenzene with *o*-chlorobenzoic acid. The compound was crystallized from alcohol, m. p. 66–67°, b. p. 170–173° (3 mm.).

Anal. Calcd. for $C_{16}H_{19}N$: C, 85.33; H, 8.53; N, 6.31. Found: C, 85.57; H, 8.48; N, 6.35.

p,p′-**Di-*t*-butyldiphenylamine.**—This compound different from Lloyd's[9d] "diphenisobutylamine" was prepared by heating *p*-amino-*t*-butylbenzene (2 moles) with its hydrochloride (1 mole) at the refluxing point for fourteen hours. After washing out the acid the product was isolated by distillation and crystallization from alcohol; b. p. 190–195° (3 mm.), m. p. 107–108°.

Anal. Calcd. for $C_{20}H_{27}N$: C, 85.41; H, 9.68; N, 4.98. Found: C, 85.77; H, 9.80; N, 4.94.

By working up the mother liquors from this compound some *p*-*t*-butyldiphenylamine was isolated. The structure of the *p,p*′-di-*t*-butyldiphenylamine was proved by converting it into the benzoyl derivative by the action of benzoyl chloride at 160–170°, m. p. 191° from toluene. The same derivative was then prepared by the Chapman[16] synthesis starting with *p*-*t*-butylphenol, phosphorus pentachloride, and benzoyl-*p*-amino-*t*-butylbenzene. The melting point of the intermediate *p*-(*t*-butylphenyl)-iminophenylmethyl-(*p*′-*t*-butylphenyl) ether was 134–136° from alcohol. Rearrangement of this by heating to 300° produced the benzoyl derivative in nearly theoretical yield, m. p. 192–193°, alone or mixed with the compound prepared directly from the diarylamine. The melting point of the acetyl derivative of *p,p*′-di-*t*-butyldiphenylamine was found to be 160–161° when crystallized twice from hexane.

p,p′-**Di-*t*-butyl-N,N′-diphenyl-*p*-phenylenediamine.**—This compound was prepared by refluxing 1.5 moles of the primary amine with 0.5 mole of hydroquinine and a trace of hydrochloric acid for five hours. The product was crystallized from toluene and washed with methanol. A yield of 24% was isolated, m. p. 176–177°.

Anal. Calcd. for $C_{26}H_{32}N_2$: C, 83.87; H, 8.65; N, 7.53. Found: C, 83.50; H, 8.59; N, 7.87.

p-*t*-**Butylphenyl-α-naphthylamine.**—Five tenths of a mole of α-naphthylamine, 1.5 moles of mixed amino-*t*-butylbenzenes and a trace of hydrochloric acid were refluxed for thirty-seven hours. The yield of *p*-*t*-butylphenyl-α-naphthylamine after distilling off the unreacted starting materials and crystallizing from alcohol was about 20%, m. p. 91–92°, b. p. about 205° (2 mm.).

Anal. Calcd. for $C_{20}H_{21}N$: C, 87.27; H, 7.71; N, 5.09. Found: C, 86.96; H, 7.75; N, 5.54.

p-*t*-**Butylphenyl-β-naphthylamine.**—This compound was prepared by heating 1.0 mole of mixed amino-*t*-butyl-

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[16] (a) Chapman, *J. Chem. Soc.*, 569 (1929); (b) Gibson, *ibid.*, 1474 and 2747 (1929).

benzenes, 1.2 moles of β-naphthol, and a trace of hydrochloric acid together for five and one-half hours. The yield after extracting the mixture with dilute alkali, distilling and crystallizing from methanol was about 40%, m. p. 76–78° and 80–81° after recrystallizing, b. p. 213° (3 mm.). A side product of the reaction was phenyl-β-naphthylamine.

Anal. Calcd. for $C_{20}H_{21}N$: C, 87.27; H, 7.71; N, 5.09. Found: C, 87.30; H, 7.74; N, 5.24.

The Preparation of Methyl-N-phenylanthranilate.—Baeyer and Villiger[17] prepared this compound as an oil in 60% yield by the saturation of a solution of N-phenylanthranilic acid in methanol with dry hydrogen chloride. The following directions give a better yield and also a product which is crystalline.

Dry hydrogen chloride was passed into 963 cc. of methanol until the weight had increased 289 g. One hundred and forty-seven grams (0.69 mole) of N-phenylanthranilic acid was then added and the mixture allowed to stand overnight and then refluxed for three hours. The mixture was cooled, 500 cc. of benzene added, then shaken with water (two volumes) and the layers separated. The water layer was then washed with benzene. The benzene layers were united, washed with dilute caustic until free of acid and finally with water. After drying over potassium carbonate the benzene solution was distilled. The product solidified in the receiver; yield 115 g. (91% after allowing for 27 g. of N-phenylanthranilic acid recovered from the alkaline wash water). After crystallizing from hexane 111 g. of pure product was obtained, m. p. 58–59°.

Anal. Calcd. for $C_{14}H_{13}NO_2$: C, 74.10; H, 5.77; N, 6.17. Found: C, 74.11; H, 5.78; N, 6.55.

The compound was also prepared in 93% yield (60% conversion) from the reaction of 21.3 g. (0.1 mole) of phenylanthranilic acid, 6 g. of potassium hydroxide, and 12.6 g. (0.1 mole) of methyl sulfate dissolved in 125 cc. of methanol. The mixture warmed up and after about an hour a considerable amount of solid had separated. It was allowed to stand overnight and worked up as in the case of the hydrochloric acid method.

Summary

1. The nitration of *t*-butylbenzene has been found to yield a mixture of *o*- and *p*-nitro-*t*-butylbenzenes, as reported by Senkowski.

2. *o*-Amino-*t*-butylbenzene was converted into *o*-*t*-butyldiphenylamine, which was also prepared by the reaction of methylmagnesium iodide with methyl-N-phenylanthranilate.

3. The following new diarylamines were prepared: *p*-*t*-butyldiphenylamine, *p*,*p*′-di-*t*-butyldiphenylamine, *p*,*p*′-di-*t*-butyl-N,N′-diphenyl-*p*-phenylenediamine, *p*-*t*-butylphenyl-β-naphthylamine and *p*-*t*-butylphenyl-α-naphthylamine.

4. The method for the preparation of methyl-N-phenylanthranilate was improved.

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[17] Baeyer and Villiger, *Ber.*, **37**, 3201 (1904).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ST. JOHN'S COLLEGE]

The Preparation of Some Normal Aliphatic Thiocyanates

BY PAUL ALLEN, JR.

In connection with other work straight-chain thiocyanates have been prepared to complete the series through the thirteen carbon member. The method of synthesis was to treat an alkyl bromide with potassium thiocyanate in alcohol.

Bromides.—Cyclohexyl, *n*-amyl and *n*-octyl bromides were Eastman Kodak Co. chemicals and were used without further purification. The others were made from the corresponding alcohols using hydrobromic acid.

Alcohols.—The nonyl alcohol was an Eastman product; decyl and dodecyl (lauryl) alcohols were prepared by reduction of the methyl esters[1] of the corresponding acids by sodium and absolute alcohol; undecyl and tridecyl alcohols were made by the reaction between formaldehyde and decyl and dodecyl magnesium bromides, respectively.

Thiocyanates.—The proportions of materials were one mole of bromide to one and a half moles of potassium thiocyanate to about 340 cc. of ethanol. About a third of the potassium salt dissolves in this amount of boiling alcohol. To the mixture, boiling under reflux, was added the alkyl bromide drop by drop; refluxing was continued for two hours. When small quantities of material were involved water was added at this point, without distilling off any of the alcohol, and the mass extracted with ether. The extract was dried over calcium chloride, the ether evaporated off and the residue distilled under vacuum. Usually one fractional distillation sufficed, but in a few cases two were needed to obtain a product boiling over a narrow range.

THIOCYANATES

	Yield, %	B. p., °C.	Pressure, mm.	d_4^{25}	n_D^{25}	Sulfur, %	
						Calcd.	Found
Amyl	84.5	90–91	16	0.9412	1.4620	24.8	24.8
Octyl	83.5	141–142	19	.9149	1.4642	18.7	18.5
Nonyl	67.3	156–157	19	.9091	1.4649	17.3	17.4
Decyl	95.3	154–155	15	.9047	1.4652	16.1	16.0
Undecyl	86.5	160–161	10	.9007	1.4653	15.0	14.7
Dodecyl	92.9	170–172	10	.8958	1.4657	14.1	14.1
Tridecyl	88.0	173–176	7	.8935	1.4661	13.3	13.1
Cyclohexyl	31.2	111–112	16	1.0402	1.5055	22.7	22.8

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[1] Noller, Millner and Gordon, THIS JOURNAL, **55**, 1227 (1933).