from 1–6%. Thus the precision in these measurements was essentially identical with that of the determinations of the rates of rearrangement of hydrazobenzene but of appreciably lower order than the precision of the rate measurements in the *o*-hydrazotoluene investigation. The precision of the rate measurements in the three investigations therefore reflects exactly the accuracy of the analytical methods used to follow the rates.

The close similarity of the rate expressions, rates, E^a and $\Delta S^{\ddagger}$ for the rearrangements of hydrazobenzene and of *o*- and *m*-hydrazotoluenes suggests that all proceed by the same mechanism. Even the observation that the rate expression for the rearrangement of *o*-hydrazotoluene contains acid concentration to the power 1.6, whereas the other two rates are proportional to the square of acid concentration, has been reconciled with the reaction sequence proposed by Hammond and his collaborators,[13,15] which seems compatible with the evidence now available.

Hammond has proposed that the rate determining step in the rearrangement sequence is not the molecular rearrangement step itself, but rather the interaction of acid with the first conjugate acid of the aromatic hydrazo compound.[13,15] A comparison of the $\Delta S^{\ddagger}$ values for the rearrangements of hydrazobenzene and of *m*-hydrazotoluene, which are identical kinetically, may afford evidence in support of Hammond's proposal. The ultraviolet absorption spectra of *m*-tolidine and of benzidine suggest steric interference by the methyl groups with ring coplanarity in *m*-tolidine which, of course, does not exist in benzidine. A similarly derived steric factor might well be expected to intervene in the transition state of the rearrangement, and if this be true, then $\Delta S^{\ddagger}$ for the rearrangement *step* by which *m*-tolidine is formed might be expected to be less than that for the rearrangement *step* which leads to benzidine. The fact that the observed $\Delta S^{\ddagger}$ for the *m*-tolidine rearrangement is not significantly less than that for the benzidine rearrangement might then be considered an argument against the postulate that the rearrangement step is rate controlling. The $\Delta S^{\ddagger}$ value for the *o*-tolidine rearrangement probably is not comparable in this sense with the $\Delta S^{\ddagger}$ values for the other two rearrangements for reasons which have been considered previously.[3] The foregoing argument must be advanced with caution because of uncertainty in the meaning of the observed $\Delta S^{\ddagger}$ values.

Acknowledgment.—The authors are grateful to the Research Corporation for a Frederick Gardner Cottrell grant in support of this work.

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[15] M. D. Cohen and G. S. Hammond, THIS JOURNAL, **75**, 880 (1953).

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

1,3,5-Tri-*t*-butylbenzene and Some Derivatives[1]

BY PAUL D. BARTLETT, MAX ROHA AND R. MARTIN STILES[3]

RECEIVED DECEMBER 1, 1953

The reaction of *t*-butyl chloride and aluminum chloride with *p*-di-*t*-butylbenzene yields *m*-di-*t*-butylbenzene and hydrocarbons melting at 72.5–73° and 209–210°. The product of m.p. 72.5–73° is 1,3,5-tri-*t*-butylbenzene. It has been converted to 2,4,6-tri-*t*-butylaniline and 2,4,6-tri-*t*-butylphenol. Bromination in the presence of iron displaces one *t*-butyl group yielding 1-bromo-3,5-di-*t*-butylbenzene. The tri-*t*-butylbenzene has been obtained also from the condensation of pinacolone by means of metallic sodium. Potentiometric titration in 90% methanol reveals that 2,4,6-tri-*t*-butylaniline is not detectably basic under the conditions used, *i.e.*, the pK_A of the anilinium ion is substantially less than 2.

In connection with interest in this Laboratory in the properties of highly branched molecules we sought to prepare derivatives of 1,3,5-tri-*t*-butylbenzene (III) other than the well-known 2,4,6-tri-*t*-butylphenol[4,5] (VII) which is readily available by the *t*-butylation of phenol and which is so highly hindered as not to be appreciably acidic. Attempts to dehydroxylate this phenol with zinc dust were unsuccessful and although phosphorus pentachloride and thionyl chloride both reacted with it we did not succeed in this way in obtaining the desired chloro compound. 2,4,6-Tri-*t*-butylphenyl chlorosulfinate was isolated as a solid melting at 100.5–101.5°.

Preparation and Properties of 1,3,5-Tri-*t*-butylbenzene.—By means of aluminum chloride and *t*-butyl chloride at temperatures below 5° *p*-di-*t*-butylbenzene (I) was about half converted into a mixture consisting of similar amounts of *m*-di-*t*-butylbenzene (II) and two solid hydrocarbons melting at 72.5–73° and 209–210°. Both these solids gave analytical figures close to those calculated for tri-*t*-butylbenzene. However, the higher melting hydrocarbon also was sufficiently higher boiling to indicate that it was not isomeric with the lower melting. Its structure was not established. The compound melting at 72.5–73.0° and boiling under 12 mm. pressure at 121–122° was shown to be 1,3,5-tri-*t*-butylbenzene (III) by two independent procedures. It was shown to be identical with a hydrocarbon found among the products of reaction between pinacolone and sodium react

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[1] Most of the material of this paper formed a part of the Ph.D. thesis of Max Roha at Harvard University in 1949. The preparation from pinacolone and the conversion of 1,3,5-tri-*t*-butylbenzene into 2,4,6-tri-*t*-butylphenol are from the Ph.D. thesis of R. Martin Stiles, 1954. In the interpretation of our results we were aided by exchange of information with the research group at the Standard Oil Co. (Indiana), headed by Dr. A. P. Lien,[2] and with Dr. B. M. Wepster of Delft.[10]

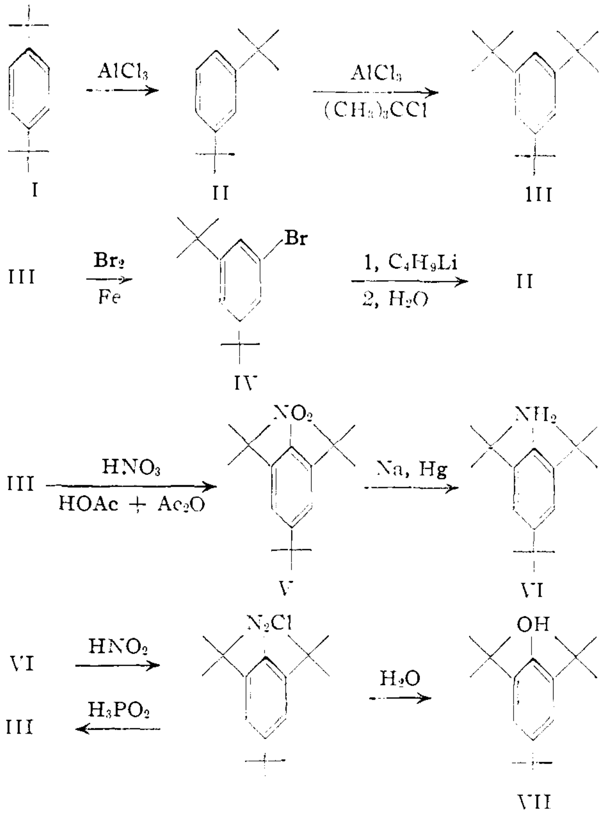
[2] D. A. McCaulay, A. P. Lien and Philip J. Launer, THIS JOURNAL, **76**, 2354 (1954).

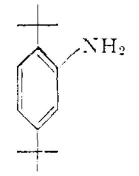
[3] National Science Foundation Predoctoral Fellow, 1952–1953.

[4] G. H. Stillson, D. W. Sawyer and C. K. Hunt, THIS JOURNAL, **67**, 303 (1945).

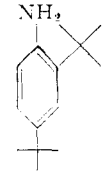
[5] D. R. Stevens and W. A. Gruse, U. S. Patent 2,248,828 (1941); *C. A.*, **35**, 7176^6 (1941).

ing together in the absence of solvent at 200°. Analogy to the condensation of acetone to yield mesitylene offers a possible explanation of this reaction and establishes a strong probability for the 1,3,5-orientation. It also was found possible to nitrate the hydrocarbon, reduce the nitro compound to 2,4,6-tri-*t*-butylaniline (VI) and convert the latter into the known 2,4,6-tri-*t*-butylphenol by means of nitrous acid.[10]

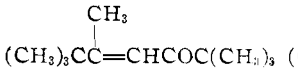




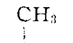
VIII



IX


$(CH_3)_3C\overset{\overset{CH_3}{|}}{C}{=}CHCOC(CH_3)_3$

X


$(CH_3)_3C\overset{\overset{CH_3}{|}}{C}HCH_2CHOHC(CH_3)_3$

XI

The infrared spectrum of 1,3,5-tri-*t*-butylbenzene obtained in this manner was identical with that determined by McCaulay, Lien and Launer[2] for the material prepared by disproportionation of *t*-butylbenzene with hydrogen fluoride and boron trifluoride. On treatment with aluminum chloride in excess benzene as solvent[6] 1,3,5-tri-*t*-butylbenzene yields *t*-butylbenzene as the principal or only product. On treatment with bromine in the presence of iron catalyst 1,3,5-tri-*t*-butylbenzene undergoes displacement of a *t*-butyl group, yielding a bromo-di-*t*-butylbenzene (IV) melting at 63–64°. Exhaustive bromination under these conditions has previously been observed[7] to result in the displacement of secondary and tertiary alkyl groups. By heating the bromo compound under reflux for 24 hours with *n*-butyllithium a product resulted which, on hydrolysis, yielded *m*-di-*t*-butylbenzene.[8,9]

Nitration in acetic acid and acetic anhydride converts tri-*t*-butylbenzene into a nitro compound V which still contains the three tertiary butyl groups. The nitro compound was resistant to catalytic hydrogenation both at low pressures over platinum and at high pressures over Raney nickel and also to reduction by stannous chloride. However, treatment with sodium amalgam in methanol brought about the reduction to 2,4,6-tri-*t*-butylaniline (VI). This could be converted by nitrous acid into the known 2,4,6-tri-*t*-butylphenol (VII), identified by mixed melting point with an authentic sample and by the identity of the infrared spectra of the two specimens. It was also possible to deaminate 2,4,6-tri-*t*-butylaniline in poor yield to 1,3,5-tri-*t*-butylbenzene.[10] The latter experiment tends to show that the symmetrical orientation of the tertiary butyl groups in the aniline is not the result of a molecular rearrangement attending nitration or reduction of the nitro compound.

Effect of Tertiary Butyl Groups on Basic Strength of Aniline.—Introduction of tertiary butyl groups into the ring of aniline might have several kinds of effect upon the basic strength. Both the inductive and resonance effects of alkyl groups are favorable to increased basicity. Severe steric hindrance in the immediate neighborhood of the amino group would be unfavorable to both the free aniline (because of prohibited coplanarity of the amino hydrogens with the ring) and the anilinium ion (because of the greater steric requirement of an NH_3^+ group compared to a non-coplanar NH_2).[11] In conditions of severe crowding the second effect might be more important than the first and might lead to a base-weakening effect of *ortho* tertiary butyl groups. Perhaps more important than these effects would be the fact that bulky hydrocarbon groups flanking the location of an electric charge would seriously interfere with solvation and shift any equilibrium toward the uncharged form. This may well be an important element in the great weakening effect of the tertiary butyl groups on the acid strength of phenol already commented upon.[4]

In order to study the effect of tertiary butyl groups on the basic strength of aniline we have pre-

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[6] E. Boedtker and O. M. Halse, *Bull. soc. chim.*, [4] **19**, 444 (1916).

[7] G. F. Hennion and J. G. Anderson, THIS JOURNAL, **68**, 424 (1946).

[8] C. E. Johnson and C. E. Adams, U. S. Patent 2,429,691 (Oct. 28, 1947); *C. A.*, **42**, 1005[a] (1948).

[9] H. Pines, G. J. Czajkowski and V. N. Ipatieff, THIS JOURNAL, **71**, 3798 (1949).

[10] Dr. B. M. Wepster of the Technische Hoogeschool, Delft, has established the orientation of 1,3,5-tri-*t*-butylbenzene by relating it to 3,5-di-*t*-butyltoluene, whose orientation he proved by an absolute method [private communication, 11 April, 1953]. Our work may thus be regarded as completing the proof of the orientation of 2,4,6-tri-*t*-butylphenol, previously assumed. Dr. Wepster has also obtained 3,5-di-*t*-butyl-1-bromobenzene, of known orientation, melting at 64–64.5°, in agreement with the properties of our product from the bromination of 1,3,5-tri-*t*-butylbenzene. The two samples had infrared peaks at identical wave lengths, with slight intensity differences.

[11] See H. C. Brown and A. Cahn, THIS JOURNAL, **72**, 2939 (1950).

pared 2,5-di-*t*-butylaniline[12] (VIII) and the compound, presumably 2,4-di-*t*-butylaniline (IX), prepared in similar fashion by the nitration of *m*-di-*t*-butylbenzene. The former was obtainable in a good state of purity as white needles melting at 104–105°. The latter, a liquid boiling at 152–154° at 32 mm., neutralized only about half the calculated quantity of acid and was accordingly very impure. It yielded an acetyl derivative melting at 83–84°.

Measurements of the basic strengths of aniline, *o*- and *p*-*t*-butylaniline, 2,5- and 2,4-di-*t*-butylaniline, and 2,4,6-tri-*t*-butylaniline were made by potentiometric titration in 90% methanol using an aqueous calomel half cell and a Beckman *p*H meter. Calculations and the plotting of model curves showed that under these conditions a base strong enough to have pK_A for the anilinium ion equal to 2 or more could be readily measured while if pK_A were equal to 1 or less the presence of the base would not affect the position or shape of the titration curve appreciably. The following pK_A's were observed

Aniline	4.14
p-*t*-Butylaniline	4.00
o-*t*-Butylaniline	3.39
2,5-Di-*t*-butylaniline	3.34
2,4,6-Tri-*t*-butylaniline	<2

The basic component of the presumed 2,4-di-*t*-butylaniline was indistinguishable in basic strength from 2,5-di-*t*-butylaniline. The non-basis component may have been 2,6-di-*t*-butylaniline which failed to undergo acetylation during the preparation of the derivative. No further evidence on this point was obtained.

The results confirm expectations from the work of Brown and Kanner[13] on the hindered pyridines, in that even one tertiary butyl group in the *ortho* position hinders the formation of an anilinium ion while tertiary butyl groups flanking the amino group on both sides present a large but unknown degree of hindrance to the uptake of a proton. Under the same conditions of titration which we used *m*-nitroaniline also appeared as a non-basis substance.

Some Related Hydrocarbons.—Senkowski in 1890[14] reported a solid hydrocarbon presumed to be tri-*t*-butylbenzene from the residues of a Friedel–Crafts reaction between benzene and isobutyl chloride. The same hydrocarbon has been obtained by Smith[15] from the treatment in benzene solution of isobutyl phenyl ether with aluminum chloride. Smith assigned to Senkowski's hydrocarbon the structure 1,2,4-tri-*t*-butylbenzene. We were unable to obtain this hydrocarbon from our reaction. We found it, however, in small quantities in residues from the preparation of *p*-di-*t*-butylbenzene kindly supplied to us by the Standard Oil Company of Indiana.[16] From 30 lb. of the residues 24 g. of the hydrocarbon was obtained, melting at 129.5–130°.

The Reduction of Pinacolone with Sodium.—The reaction of pinacolone with sodium in the absence of solvent at 200° yielded an initial salt-like product which could be decomposed with dilute acid to give three compounds: a diene boiling at 59–61° at 15 mm. which condensed with maleic anhydride to give an adduct, m.p. 128°; a ketone, b.p. 87–89° at 15 mm., whose dinitrophenylhydrazone melted at 115°; and 1,3,5-tri-*t*-butylbenzene, m.p. 73°, identical by mixed melting point and infrared spectrum with the product obtained from benzene. The diene was clearly identical with that obtained by Favorskiĭ and Nazarov[17] and shown by Backer and collaborators[18] to be 1,3-di-*t*-butyl-1,3-butadiene. The ketone was identified as 2,2,5,6,6-pentamethylheptane-3-one. It was reduced by the procedure of Favorskiĭ and Nazarov with sodium in ethanol to a secondary alcohol (XI) whose benzoate, m.p. 48°, proved to be identical with that obtained by reducing the known[19] 2,2,5,6,6-pentamethyl-4-heptene-3-one (X) to the saturated alcohol and esterifying the product.

Sodium methoxide in toluene, potassium *t*-butoxide in *t*-butyl alcohol or without solvent was incapable of producing tri-*t*-butylbenzene from pinacolone. The yield in the latter case was about 70% of the unsaturated ketone 2,2,5,6,6-pentamethyl-4-heptene-3-one (X).

Experimental

Thionyl Chloride Treatment of 2,4,6-Tri-*t*-butylphenol.—Tri-*t*-butylphenol (2.6 g., 0.01 mole) was refluxed with 3.5 g. (0.03 mole) of thionyl chloride. After 1.5 hours the evolution of hydrogen chloride had ceased and the resulting liquid was poured into water in order to decompose the excess thionyl chloride. The organic compound was extracted with ether. Evaporation of the ether yielded a solid which was recrystallized five times from petroleum ether but still melted from 79 to 90°. When the same preparation was made in a medium of dry pyridine it was possible to obtain a pale green solid, m.p. 100.5–101.5°.

Anal. Calcd. for $C_{18}H_{29}O_2SCl$: S, 9.3; Cl, 10.7. Found: S, 8.9, 8.9; Cl, 10.3.

Preparation of Tri-*t*-butylbenzene.—*p*-Di-*t*-butylbenzene (950 g., 5 moles) was dissolved in either 500 ml. of carbon disulfide or 2 l. of ethylene dichloride. After cooling the mixture to 0°, 800 g. (6.5 moles) of aluminum chloride was added. The temperature was maintained below 5° and 550 g. (6.0 moles) of cold *t*-butyl chloride was added. The reaction mixture was allowed to stand 4 hours and the organic layer was decanted into ice-water, washed free of acid with water and then dried over sodium carbonate. After evaporation of the solvent the following fractions were obtained by distillation

Fraction	Range, °C.	Pressure, mm.	Weight, g.	Major component
1	105–107	13	161	*m*-Di-*t*-butylbenzene[20]
2	110–111	12	117	*p*-Di-*t*-butylbenzene
3	121–122	12	160	1,3,5-Tri-*t*-butylbenzene
4	over 130	..	150	The higher hydrocarbon

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[12] D. I. Legge, THIS JOURNAL, **69**, 2089 (1947).

[13] H. C. Brown and B. Kanner, *ibid.*, **75**, 3865 (1953).

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

[15] R. A. Smith, THIS JOURNAL, **56**, 717 (1934).

[16] Through the courtesy of Dr. M. H. Arveson of the Indoil Chemical Division of the Standard Oil Company.

[17] A. E. Favorskiĭ and I. N. Nazarov, *Bull. soc. chim.*, [5] **1**, 46 (1934); *Compt. rend.*, **196**, 1229 (1933); *Bull. acad. sci. URSS, Class sci. math. nat.*, 1309 (1933) [*C. A.*, **28**, 2674 (1934)]; Nazarov, *Ann. Leningrad State Univ., Chem. Ser.*, **1**, 128 (1935) [*C. A.*, **31**, 6617 (1937)].

[18] (a) H. J. Backer, *Chem. Weekblad*, **36**, 205, 214 (1939); (b) H. J. Backer and J. Strating, *Rec. trav. chim.*, **56**, 1069 (1937); (c) H. J. Backer, *ibid.*, **57**, 967 (1938).

[19] J. Colonge, *Bull. soc. chim.*, [5] **2**, 57 (1935); V. M. Tolstopyatov and I. V. Voroshilova, *J. Gen. Chem. USSR*, **15**, 565 (1945); W. J. Hickinbottom and E. Schluchterer, *Nature*, **155**, 19 (1945).

[20] The *m*-di-*t*-butylbenzene prepared in this work was similar to that of Pines, Czajkowski and Ipatieff[9] except for having $n^{25}\text{D}$ 1.4847 instead of 1.4874, and for the lack of the infrared peaks at 9.8 and 12.5 μ, which occur in our *p*-di-*t*-butylbenzene but not in our pure *meta* isomer. They also have a small peak at 10.0 μ which is not found in either our pure *meta* or *para* isomer.

After four recrystallizations from ethanol, tri-*t*-butylbenzene melted at 72.5–73.0°.

Anal. Calcd. for $C_{18}H_{30}$: C, 87.74; H, 12.26; mol. wt., 246. Found: C, 87.70; H, 12.30; mol. wt., 237, 234.

After four recrystallizations from petroleum ether and two sublimations the higher hydrocarbon melted at 209–210°.

Anal. C, 88.28; H, 12.04.

Higher temperature or a longer reaction time reduced the yield of 1,3,5-tri-*t*-butylbenzene and produced a small increase in the yield of the higher hydrocarbon.

Isolation of Senkowski's Hydrocarbon.—The residue which was available from the preparation of *p*-di-*t*-butylbenzene by the Standard Oil Company of Indiana was treated as follows. Thirty pounds of this residue was distilled through a 2-ft. glass helix-packed column and the following fractions were obtained.

Fraction	Range, °C.	Pressure, mm.	Weight, g.	Major component
1	74–75	35	2247	*t*-Butylbenzene
2	83–86	35	1450	Tri-isobutylene
3	112–115	35	1298	*m*-Di-*t*-butylbenzene
4	120–130	35	5780	*p*-Di-*t*-butylbenzene
5	115–130	10	1105	Tri-*t*-butylbenzene

Fraction 5 on cooling deposited a solid which after three recrystallizations from ethanol melted at 129.5–130° and weighed 24 g.

Aluminum Chloride Treatment of 1,3,5-Tri-*t*-butylbenzene.—The tri-*t*-butylbenzene (24.6 g., 0.1 mole) was refluxed with 0.5 g. of aluminum chloride in 150 cc. of absolute benzene for 30 minutes. During this time the reaction mixture took on a deep orange-red coloration. After the addition of ice-water the mixture was taken up in ether and dried over sodium sulfate. Distillation through a modified Claisen flask gave, in addition to benzene, 9.65 g. of *t*-butylbenzene, b.p. 73° (40 mm.); 7.60 g. of di-*t*-butylbenzenes, b.p. 100–118° (30 mm.); and 3.80 g. of tri-*t*-butylbenzene, b.p. 135° (28 mm.).

Bromination of Tri-*t*-butylbenzene.—1,3,5-Tri-*t*-butylbenzene (50 g., 0.2 mole) was dissolved in 100 ml. of carbon tetrachloride in a blackened flask. After the addition of 12 g. of iron filings, 67.2 g. (0.42 mole) of bromine dissolved in 25 ml. of carbon tetrachloride was added dropwise. The reaction was moderated by cooling the reaction mixture in ice-water. After 4 hours the mixture was poured into cold water and the organic layer separated. The excess bromine was removed by shaking with a 10% sodium hydroxide solution followed by washing with water until neutral. The product was dried and distilled. The fraction boiling at 152–156° at 26 mm. solidified on cooling and yielded 38 g., 71%, of bromo-di-*t*-butylbenzene. Three recrystallizations from petroleum ether resulted in long, colorless prisms, m.p. 63–64°.

Anal. Calcd. for $C_{14}H_{21}Br$: C, 62.39; H, 7.85; Br, 29.76. Found: C, 62.23; H, 7.78; Br, 29.93.

Careful distillation of the products of another run through a 28-in. jacketed spiral column showed that this product was the only dialkylbromobenzene produced. Attempts to prepare a Grignard reagent or an organo-lithium compound from this substituted bromobenzene were unsuccessful, as were attempts to reduce the compound with sodium and ethanol or to debrominate it by the method of Busch and Stöve.[21]

Debromination of Bromo-di-*t*-butylbenzene by *n*-Butyllithium.—The lithium reagent was prepared from 1.65 g. of *n*-butyl bromide and 0.18 g. of lithium wire in 75 ml. of absolute ether under a nitrogen atmosphere. This reagent was added to a solution of 1.6 g. of bromo-di-*t*-butylbenzene in 25 ml. of ether. The mixture was heated under reflux for 14 hours, hydrolyzed with 10% hydrochloric acid, washed well with water, and dried over potassium carbonate. The solvent was evaporated, the residue distilled and the fraction boiling at 114° (30 mm.) was collected. It weighed approximately 0.4 g., 32%, $n^{25}D$ 1.4847. The infrared spectrum of this compound proved it to be *m*-di-*t*-butylbenzene.

Anal. Calcd. for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 87.47; H, 11.73.

When 38 g. of *m*-di-*t*-butylbenzene was brominated in the presence of iron filings by the same procedure as that used on tri-*t*-butylbenzene, distillation of the product yielded a fraction boiling at 147–148° (12 mm.) and weighing 10.4 g. The infrared spectrum of this fraction was consistent with its being a mixture of the bromo-di-*t*-butylbenzene just described and isomeric material.

The Di-*t*-butylaniline from *m*-Di-*t*-butylbenzene.—*m*-Di-*t*-butylbenzene[20] (74 g.) was dissolved in 78 ml. of glacial acetic acid and 58 ml. of acetic anhydride. Nitric acid (31 g.), 96%, was added with cooling so that the temperature of the reaction mixture did not rise above 45°. The mixture was allowed to stand overnight and the product then poured into ice-water. The yellow oil was separated and the aqueous layer extracted with petroleum ether. The combined organic layers were washed with water until neutral and dried over sodium sulfate. The crude nitro compound (90 g.) was obtained by evaporation of the solvent.

This nitro compound was dissolved in 500 ml. of 95% ethanol with 0.7 g. of platinum oxide added as catalyst. The compound was reduced to the amine with hydrogen at 4 atm. pressure. After the hydrogen uptake had ceased (about 8 hours) the solution was filtered and the alcohol evaporated. The amine was distilled under diminished pressure and a fraction boiling at 152–154° (32 mm.) was collected; weight, 32 g., $n^{25}D$ 1.5111.

The acetyl derivative was prepared by treatment with glacial acetic acid.[22] Recrystallization from 50% aqueous ethanol gave white flakes, m.p. 83–84°.

Anal. Calcd. for $C_{16}H_{25}ON$: N, 5.67. Found: N, 5.88.

Bromination of this di-*t*-butylaniline in acetic acid solution proceeded to a sharp end-point but yielded a deep red oil which did not solidify and was not further studied. Potentiometric titration of this aniline with 0.10 *N* hydrochloric acid in 90% methanol showed a break corresponding to the complete neutralization of all base present when 0.48 equivalent of acid had been added.

2,4,6-Tri-*t*-butylnitrobenzene.—A solution of 5.8 g. of 1,3,5-tri-*t*-butylbenzene in 4 ml. of glacial acetic acid and 3 ml. of acetic anhydride was treated with 1.6 g. of 96% nitric acid with cooling. A yellow precipitate was immediately formed. The mixture was allowed to stand for one-half hour, at which time the product was filtered. Recrystallization from petroleum ether (30–60°) gave a colorless solid which melted at 204–205° in 55% yield.

Anal. Calcd. for $C_{18}H_{29}NO_2$: N, 4.80. Found: N, 4.72.

2,4,6-Tri-*t*-butylaniline.—Unsuccessful attempts were made to reduce 2,4,6-tri-*t*-butylnitrobenzene by hydrogenation with Adams catalyst or with Raney nickel, by reduction with stannous chloride and by reduction with hydrazine. Sodium amalgam was found capable of bringing about this reduction. The nitro compound (10 g.) was dissolved in 200 ml. of absolute methanol. This was heated gently with 280 g. of 4% sodium amalgam. The mixture was refluxed for 5 hours. The hot solution was decanted through a filter and the contents of the filter washed with hot methanol. On cooling, the filtrate deposited glistening white plates which, after recrystallization from methanol, melted at 144.5–145.5°, yield 64%.

Anal. Calcd. for $C_{18}H_{31}N$: N, 5.35. Found: N, 5.12.

2,5-Di-*t*-butylnitrobenzene.—A solution of 74 g. of *p*-di-*t*-butylbenzene in 78 ml. of glacial acetic acid and 58 ml. of acetic anhydride was treated with 31 g. of 96% nitric acid. The temperature was maintained below 50° by cooling in an ice-bath. After standing at room temperature for 24 hours the product was poured into water and the pale yellow solid which formed was filtered and recrystallized from ethanol; yield 55 g., m.p. 75–78°.

Anal. Calcd. for $C_{14}H_{21}NO_2$: C, 71.45; H, 8.99. Found: C, 71.54; H, 9.11.

2,5-Di-*t*-butylaniline.—The nitro product was dissolved in 250 ml. of 95% ethanol and reduced with hydrogen at 4 atm. using 0.25 g. of platinum oxide as catalyst. When hydrogen was no longer taken up, the warm solution was filtered and the excess alcohol evaporated until crystallization began. The product which formed fine, long needles melted at 95–97° and after recrystallization from ethanol at 104–105°.

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[21] M. Busch and H. Stöve, *Ber.*, **49**, 1063 (1916).

[22] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 165.

Anal. Calcd. for $C_{14}H_{23}N$: C, 81.89; H, 11.29. Found: C, 81.90; H, 11.40.

On bromination in glacial acetic acid containing anhydrous sodium acetate 2,5-di-*t*-butylaniline decolorized two moles of bromine yielding a product which after recrystallization from ethanol formed pale pink prisms melting with decomposition at 256°.

Anal. Calcd. for $C_{14}H_{21}NBr_2$: N, 3.87; Br, 44.1. Found: N, 4.04; Br, 42.45.

***o*- and *p*-*t*-butylnitrobenzenes** were prepared following the instructions of Craig.[23] The dried product which weighed 302 g. was distilled through a Widmer column and small center cuts were selected from the fractions. *o*-*t*-Butylnitrobenzene was obtained, boiling at 140–141° (21 mm.), 21 g. being used. The center cut of *p*-*t*-butylnitrobenzene boiled at 150° (21 mm.) and was taken in the amount of 80 g.

***o*- and *p*-*t*-butylanilines** were prepared by the reduction of the separate nitro compounds by Adams catalyst in 95% ethanol. The products were distilled from zinc dust. *o*-*t*-Butylaniline boiled at 121–122° (21 mm.), 10.5 g. being obtained. *p*-*t*-Butylaniline gave a 57 g. fraction boiling at 125–126° (21 mm.).

Reaction of Pinacolone with Sodium.—Sodium (14 g.) in small pieces was placed in a dry flask under an atmosphere of nitrogen and to this was added 55 g. of pinacolone. Gas was evolved rather slowly and the flask became warm as the initial reaction proceeded. After 1 hour the mixture was heated to reflux, at which time a vigorous reaction occurred and the contents of the flask became pasty. Heating was continued for 12 hours and the temperature allowed to climb to 200°. After cooling the salt-like solid was decomposed by slow addition of water, acidified with dilute sulfuric acid and the mixture was extracted with ether. The ether extracts were washed with sodium carbonate solution, then with water, and dried over anhydrous sodium sulfate. After removal of the solvent the residue was fractionated through a 30-cm. column packed with glass helices. Fraction 1 was taken at atmospheric pressure, fraction 6 at 13 mm. and fractions 2 to 5 at 15 mm. The results of the distillation were

Fraction	Temp., °C.	Weight, g.	Fraction	Temp., °C.	Weight, g.
1	100–165	5.0	5	89–121	2.5
2	59–61	7.9	6	121–124	8.0
3	61–87	3 0	7	Residue	2.0
4	87–89	6.6			

Fraction 1 consisted of pinacolone and pinacolyl alcohol. Fraction 2 had an infrared spectrum indicative of a diene. When treated with maleic anhydride in benzene solution it yielded an adduct melting at 128°. Fraction 4 was a saturated ketone. A sample of its 2,4-dinitrophenylhydrazone melting at 115° was analyzed.

Anal. Calcd. for $C_{18}H_{28}O_4N_4$: C, 59.33; H, 7.74; N, 15.38. Found: C, 59.57; H, 7.58; N, 15.67.

Fraction 6 crystallized on standing and melted at 73° after one recrystallization from methanol. The infrared spectrum was identical with that of a sample of tri-*t*-butylbenzene prepared as reported above. The melting point of the mixture showed no depression.

Conversion of Tri-*t*-butylaniline to Tri-*t*-butylphenol.—Finely powdered tri-*t*-butylaniline (1.05 g., 0.004 mole), m.p. 144.5–145.5°, was suspended in a solution of 3 g. of concentrated sulfuric acid in 17 ml. of water and the mixture was cooled to 0°. A solution of 0.28 g. (0.0040 mole) of sodium nitrite in 2 ml. of water was added slowly with stirring. A yellow solid was precipitated during the addition. The mixture was then allowed to stand at room temperature for 30 minutes and steam distilled. The distillate was extracted with ether, the ether solution washed with aqueous sodium bicarbonate, then with water and dried over Drierite. After removal of the ether there remained 0.730 g. of semi-crystalline material. Chromatography of this material on an alumina column yielded 0.239 g. of unreacted amine, 0.201 g. of 2,4,6-tri-*t*-butylphenol, m.p. 129–130°, and 0.142 g. of the yellow substance whose infrared spectrum was suggestive of an amide. A mixed melting point of the phenol with a sample of the 2,4,6-tri-*t*-butylphenol prepared from phenol was undepressed and the infrared spectra of the two samples were identical.

Deamination of 2,4,6-Tri-*t*-butylaniline.—To a solution of 0.40 g. (0.0058 mole) of sodium nitrite in 125 ml. of 50% hypophosphorus acid which was cooled to −10° in an ice-salt bath, 0.50 g. (0.0019 mole) of 2,4,6-tri-*t*-butylaniline in 75 ml. of glacial acetic acid was added slowly with stirring. The mixture was allowed to stand for 3 hours at −10° after which 200 g. of crushed ice was added and the flask was placed in the refrigerator for 14 hours. The mixture was then extracted with 30–60° petroleum ether. The extracts were washed with 5% sodium hydroxide solution, then with water and dried over Drierite. Evaporation of the solvent left 0.355 g. of oil which was subjected to adsorption on an alumina column. The only hydrocarbon fraction consisted of 0.026 g. of 1,3,5-tri-*t*-butylbenzene, m.p. 68–69°, alone and when mixed with an authentic sample. Its infrared spectrum was also identical with that of the material described earlier.

2,2,5,6,6-Pentamethyl-4-heptene-3-one.—Potassium *t*-butoxide (0.54 mole) was prepared from 21 g. of metal and 150 ml. of dry *t*-butyl alcohol. After removing the excess alcohol by heating under vacuum, 18.0 g. (0.18 mole) of pinacolone was added and the resulting solid mixture was heated to 200° for 4 hours. After cooling the solid was decomposed with water, acidified with dilute sulfuric acid and the layers were separated. The organic layer was washed with water, dried over Drierite and distilled at atmospheric pressure. The product was obtained in a yield of 11.5 g.; 70%, b.p. 196–197°; oxime melting point, 123° (reported 125°)[24]; λ_{max} 238 mμ; 2,4-dinitrophenylhydrazone, m.p. 147–148° (reported 147°).[18a]

2,2,5,6,6-Pentamethyl-3-heptyl Benzoate.—2,2,5,6,6-Pentamethyl-4-heptene-3-one (1.0 g., 0.0055 mole) was dissolved in 20 ml. of absolute ethanol and 1.3 g. (0.057 mole) of sodium was added in small pieces. After the sodium dissolved (15–20 minutes) water was added and the mixture was extracted with petroleum ether. The extracts were washed with water, dried over Drierite, and the solvent was removed. The residue (0.92 g.) was treated with 1.3 g. of benzoyl chloride in 5 ml. of dry pyridine on the steam-bath for 30 minutes. The crude ester was purified by chromatography on alumina and subsequent recrystallization from methanol; yield 0.970 g., 61% based on ketone; m.p. 46–48°. A sample of this same benzoate identical by infrared spectrum and mixed m.p. was prepared from fraction 4 of the sodium reduction of pinacolone. This sample melted sharply at 48°.

CAMBRIDGE, MASS.

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(23) D. Craig, THIS JOURNAL, **57**, 195 (1935).

(24) J. Colonge, *Bull. soc. chim.*, [5] **2**, 57 (1935).