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Oxidation Reactions of 2,4,6-Tri-*t*-butylaniline

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Oxidation reactions of 2,4,6-tri-*t*-butylaniline with lead tetraacetate (LTA), lead tetrabenzoate (LTB), peroxybenzoic acid (PBA) and benzoyl peroxide (BPO) were studied and mechanisms of these reactions were briefly discussed. In the reaction with LTA, 4-acetoxy-1-imino-2,4,6-tri-*t*-butyl-2,5-cyclohexadiene (I), 2-acetamido-3,5-di-*t*-butylphenol (II) and 2-acetylimino-3,5-di-*t*-butyl-3,5-cyclohexadienone(III) were produced. Oxidation with LTB gave 4-benzoyloxy-1-imino-2,4,6-tri-*t*-butyl-2,5-cyclohexadiene (VI, major product) and 2-benzamido-3,5-di-*t*-butylphenol (VII). The reaction products with PBA were 2,4,6-tri-*t*-butylnitrosobenzene (VIII) and VII. In addition to the last two compounds, VI and 2,2′,4,4′,6,6′-hexa-*t*-butylazobenzene (XI) were obtained in the case of BPO.

2,4,6-Tri-*t*-butylaniline (TBA) has been studied by many workers who expected unusual properties due to the steric effects of the bulky *t*-butyl groups. There have been only a few reports on the chemical reactions, although there have been several investigations on the physical properties such as basic strength,[1-3] IR,[2] UV[2] and NMR[4] spectra. The reactions reported so far are conversion *via* diazotization[1,5] and preparation of the *N*-acyl and the *N*-alkyl derivatives.[2a]

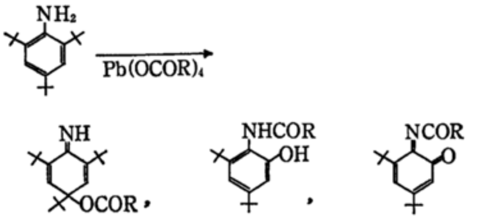
Oxidation reactions of TBA were focused only on the ESR studies of the corresponding anilino radical,[6] although Cauquis *et al.* have isolated some products in the electrochemical oxidation.[7]

We have studied the reactions of TBA with some oxidizing agents such as lead tetraacetate (LTA), lead tetrabenzoate (LTB), peroxybenzoic acid (PBA) and benzoyl peroxide (BPO), and found that the reactions are different in many respects from those of sterically unhindered anilines.

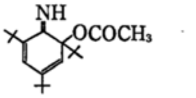
Results

The structures of the reaction products were determined by elemental analyses, IR and NMR spectra.

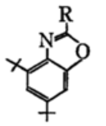
Reactions with LTA or LTB. TBA reacted with LTA in benzene at 5°C to give 4-acetoxy-1-imino-2,4,6-tri-*t*-butyl-2,5-cyclohexadiene (I, 47%), 2-acetamido-3,5-di-*t*-butylphenol (II, 11%) and 2-acetylimino-3,5-di-*t*-butyl-3,5-cyclohexadienone (III, 8%).



I: $R=CH_3$ VI: $R=C_6H_5$ II: $R=CH_3$ VII: $R=C_6H_5$ III: $R=CH_3$



IV



V: $R=CH_3$
X: $R=C_6H_5$

Although an isomeric structure (IV) is possible for I, IV was ruled out by the NMR spectrum which exhibited five singlets (τ 9.10, 9H, *t*-butyl protons at 4-position; 8.72, 18H, *t*-butyl protons at 2- and 6-positions; 8.05, 3H, acetyl protons; 4.04, 2H, olefinic protons; 0.48, 1H, imino proton), for the NMR spectrum of IV would be expected to show three kinds of the *t*-butyl protons, and AB type quartet of the olefinic protons.

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[1] P. D. Bartlett, M. Roha and R. M. Stiles, *J. Am. Chem. Soc.*, **76**, 2349 (1954).

[2] a) J. Burgers, M. A. Hoefnagel, P. E. Verkade, H. Visser and B. M. Wepster, *Rec. Trav. Chim.*, **77**, 491 (1958). b) P. J. Krueger, *Can. J. Chem.*, **40**, 2300 (1962); **41**, 363 (1963).

[3] F. E. Condon, *J. Am. Chem. Soc.*, **87**, 4494 (1965).

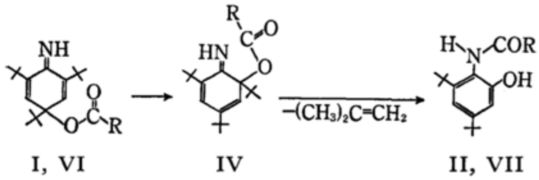
[4] V. M. S. Gil and W. A. Gibbons, *Mol. Phys.*, **8**, 199 (1964); W. A. Gibbons and V. M. S. Gill, *ibid.*, **9**, 163, 167 (1965).

[5] E. E. Betts and L. R. C. Barclay, *Can. J. Chem.*, **33**, 1768 (1955); F. E. Condon, *J. Org. Chem.*, **30**, 3946 (1965).

[6] E. J. Land and G. Porter, *J. Chem. Soc.*, **1961**, 3540; N. M. Atherton, E. J. Land and G. Porter, *Trans. Faraday Soc.*, **59**, 818 (1963); K. Mukai, H. Nishiguchi, K. Ishizu and Y. Deguchi, This Bulletin, **40**, 2731 (1967); G. Cauquis and M. Geniès, *C. R. Acad. Sci., Paris, Ser. C*, **265**, 1340 (1967).

[7] G. Cauquis, G. Fauvelot and J. Rigaudy, *ibid.*, **264**, 1758, 1958 (1967).

The imine (I) decomposed about 150°C into II and isobutylene. The reaction proceeds presumably *via* an intermediate (IV) as shown below.



The structure of II was confirmed by comparison with that of an authentic sample, which was synthesized by the acetylation of 2-amino-3,5-di-*t*-butylphenol.

The hydrolysis of II by hydrochloric acid gave 4,6-di-*t*-butyl-2-methylbenzoxazole (V) instead of expected 2-amino-3,5-di-*t*-butylphenol.

The reduction of III with lithium aluminum hydride yielded II, and conversely, the oxidation of II with LTA gave III.

LTB oxidized TBA in dichloromethane at room temperature to yield 4-benzoyloxy-1-imino-2,4,6-tri-*t*-butyl-2,5-cyclohexadiene (VI, 65%) and 2-benzamido-3,5-di-*t*-butylphenol (VII, 1.4%). Their characterization will be described later.

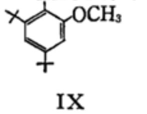
Reaction with PBA. The oxidation of TBA with two mole equivalents of PBA at 0°C gave 73% of 2,4,6-tri-*t*-butylnitrosobenzene (VIII) and a trace of VII. Use of excess PBA or higher temperatures produced 2,4,6-tri-*t*-butylnitrobenzene as by-product. On the other hand, use of an equimolar amount of PBA enhanced the yield of VII; VIII and VII being produced in 18 and 10% yields, respectively. The formation of *o*-*N*-acylaminophenols has not yet been observed for the ordinary anilines.

Furthermore, II was produced instead of VII, in the case of the reaction with an equimolar amount of PBA in the presence of a large excess of acetic acid. Oxidation of TBA with 30% hydrogen peroxide in acetic acid by the procedure of Holmes and Bayer[8] produced no nitroso compound.

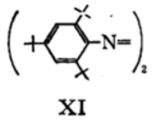
The nitrosobenzene (VIII) is emerald-green crystals and monomeric even in the solid state.[9]

The structure of VII was characterized by comparison with that of an authentic sample, which was prepared by benzoylation of 2-amino-3,5-di-*t*-butylphenol. The phenol (VII) was converted into the methyl ether (IX) by diazomethane and cyclized to 2-phenyl-3,5-di-*t*-butylbenzoxazole (X) by hydrochloric acid as in the case of II.

VIII



IX



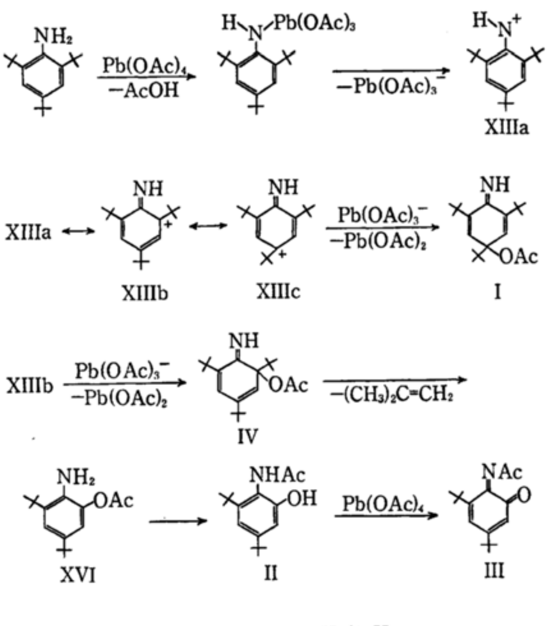
XI

Reaction with BPO. TBA reacted with BPO in benzene at room temperature to yield VIII, VII, VI and 2,2′,4,4′,6,6′-hexa-*t*-butylazobenzene (XI) in 2, 49, 38 and 2% yields, respectively.

The imine (VI) was undistilled even under high vacuum owing to its facile decomposition into VII at about 100°C. Moreover, it could not be purified by column chromatography on silica gel, because of easy decomposition into VII (37%) and 4-benzoyloxy-2,6-di-*t*-butylaniline (XII, 39%). However, petroleum ether soluble part of the reaction products, after extraction of benzoic acid by aqueous alkali, was almost pure VI.

Discussion

It is known that the reactions of the primary aromatic amines with LTA produce azo compounds in poor yields.[10] Products other than azo compound were obtained in the case of TBA. The difference can be attributed to the steric hindrance around the amino group of TBA. The following mechanism is considered to account for the results, although a homolytic mechanism involving anilino



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[8] R. R. Holmes and R. P. Bayer, *J. Am. Chem. Soc.*, **82**, 3454 (1960).

[9] R. Okazaki, T. Hosogai, E. Iwadare, M. Hashimoto and N. Inamoto, This Bulletin, **42**, 3611 (1969).

[10] K. H. Pausacker and J. G. Scroggie, *J. Chem. Soc.*, **1954**, 4003; E. Baer and A. L. Tosoni, *J. Am. Chem. Soc.*, **78**, 2857 (1956).

radical (XIV) or aniline radical-cation (XV) cannot be ruled out. Rearrangement of *O*-acetylated aminophenols such as XVI into the corresponding *N*-acetylated aminophenols is well known.[11]

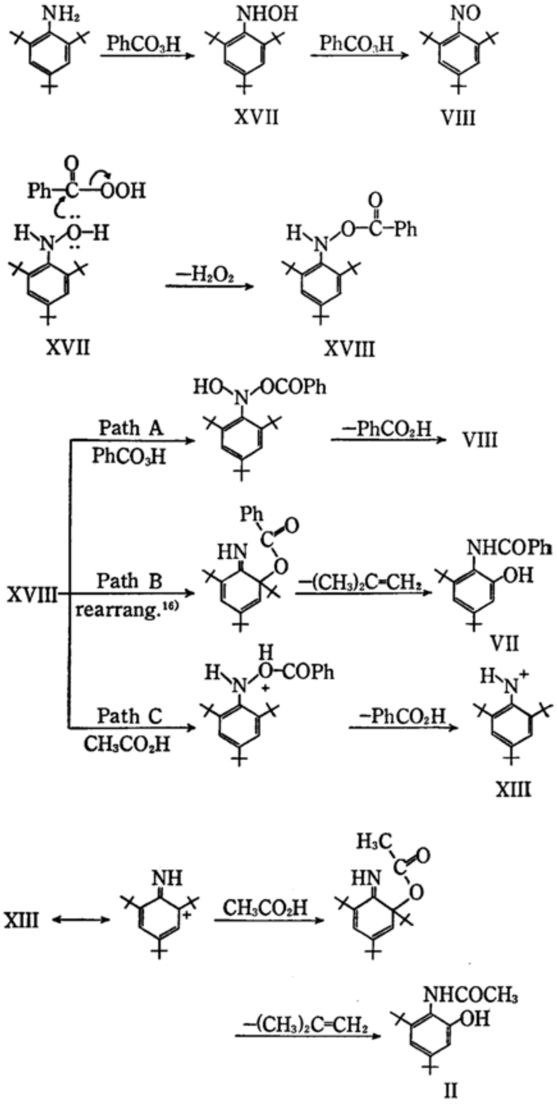
In the reactions of the ordinary anilines the intermediate anilino cations readily attack the unchanged anilines followed by further oxidation to give azobenzenes, while the intermediate (XIII) generated from TBA cannot react with another TBA molecule owing to the steric hindrance by the *t*-butyl groups.

Reaction with LTB is likely to proceed *via* the same mechanism as that with LTA. It is different, however, in two respects; the product ratio of the aminophenol (VII or II) to the imino compound (VI or I) is rather low and no *o*-benzoquinone acylimine analogous to III is produced. The low product ratio in the case of LTB is obviously due to the more bulky attacking species such as $Pb(OCOPh)_3^-$.

It is known that the reaction products of primary aromatic amines with peroxyacids are different depending upon the kinds of peroxyacids and the reaction conditions.[12] Caro's acid oxidizes the anilines to the nitroso compounds in usually poor yields. Oxidation with peroxyacetic acid affords nitrosobenzenes, nitrobenzenes and/or azoxybenzenes depending upon the reaction conditions; higher temperatures favor the production of the latter two and lower temperatures that of the former.[8,13] For PBA there have been a few investigations[14] which have dealt with the reaction only qualitatively except for the study by Horner and Kirmse, who reported azobenzene and azoxybenzene as the reaction products with aniline.[15]

However, PBA oxidized TBA into the nitroso compound (VIII) in a high yield.[9] This is because the bulky *t*-butyl groups at *ortho*-positions disturb the condensation of the unchanged TBA with the corresponding nitroso or hydroxylamino compound produced.

As for formation of VII and II under various conditions, the following scheme is plausible, although not conclusive.



The unusual formation of VII is likely to be due to the steric hindrance which makes the rate of the reaction XVII→XVIII comparable to that of the reaction XVII→VIII, for the steric congestion around the oxygen atom in XVII is fairly less than that around the nitrogen atom.

Horner and Kirmse have concluded that the reactions of the anilines with BPO proceed by both homolytic and heterolytic mechanisms.[17]

Our results for TBA are also explicable by the following mechanism involving both homolytic and heterolytic reactions, the former being predominant. The imine (VI), the benzamidophenol (VII) and the azobenzene (XI) are products *via*

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[11] W. Böttcher, *Ber.*, **16**, 629 (1883); J. T. Edward, *J. Chem. Soc.*, **1954**, 1464; J. H. Ransom, *Ber.*, **33**, 199 (1900); K. Auwers, *Ann.*, **332**, 159 (1904); M. Bergmann, R. Ulpts and F. Camacho, *Ber.*, **55**, 2805 (1922).

[12] P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. 2, W. A. Benjamin, Inc., New York (1966), p. 355; B. G. Gowenlock and W. Lüttke, *Quart. Rev.*, **12**, 321 (1958).

[13] J. D'Ans and A. Kneip, *Ber.*, **48**, 1136 (1915); F. P. Greenspan, *Ind. Eng. Chem.*, **39**, 847 (1947); W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 5528 ,6522 (1957); H. R. Gutmann, *Experientia*, **20**, 128 (1964); A. J. Boulton, P. B. Ghosh and A. R. Katritzky, *Tetrahedron Letters*, **1966**, 2887; H. Meister, *Ann.*, **679**, 83 (1964).

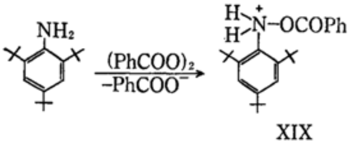
[14] A. Baeyer and V. Villiger, *Ber.*, **33**, 1569 (1900); N. Prileschajew, *ibid.*, **42**, 4811 (1909).

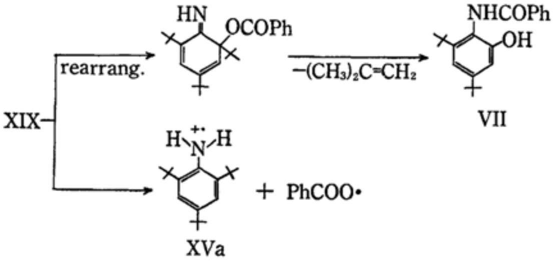
[15] L. Horner and W. Kirmse, *Ann.*, **597**, 70 (1955).

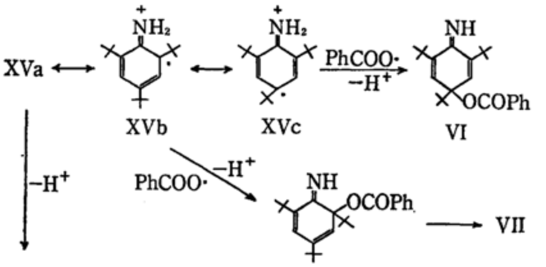
[16] P. B. Denney and D. Z. Denney, *J. Am. Chem. Soc.*, **82**, 1389 (1960).

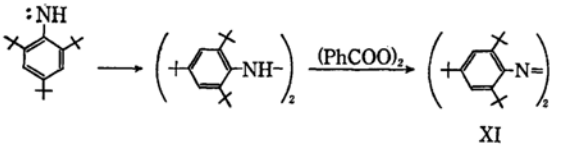
[17] L. Horner and W. Kirmse, *Ann.*, **597**, 66 (1955) and references cited therein.

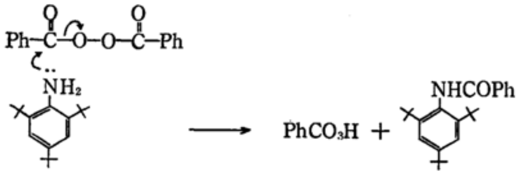
homolytic processes and the nitroso compound (VIII) is that *via* heterolytic one.











The formation of the nitrosobenzene (VIII) is reasonably explained by oxidation of TBA with PBA which is yielded by aminolysis of BPO, although the full characterization of the benzamide was unsuccessful (see Experimental).

A high product ratio of VII to VI as compared with that in the case of LTB suggests the existence of another route to VII probably *via* rearrangement of an intermediate (XIX).

Experimental

Melting points and boiling points are uncorrected. The NMR spectra were taken on a Japan Electron Optics Laboratory spectrometer Model JNM-C-60H using tetramethylsilane as an internal standard. Unless otherwise indicated, the solvent was carbon tetrachloride, and the signals were singlet. The electronic and the infrared spectra were recorded on a Hitachi spectrophotometer Model EPS-3 and EPI-G2, respectively.

2,4,6-Tri-*t*-butylaniline,[2a] lead tetraacetate,[18] lead tetrabenzoate[19] and peroxybenzoic acid[20] were prepared by the reported methods.

Reaction of 2,4,6-Tri-*t*-butylaniline (TBA) with Lead Tetraacetate (LTA). To a solution of TBA (9.2 g, 0.035 mol) in 250 m*l* of dry benzene, was added LTA (18.7 g, 0.042 mol) in 250 m*l* of benzene with stirring at 5°C. The mixture was stirred successively for 3 hr. After filtration of lead diacetate (10.6 g, 0.033 mol), the filtrate was shaken with 300 m*l* of water, and the benzene layer was dried over anhydrous sodium sulfate. After removal of benzene *in vacuo* below 50°C, petroleum ether (100 m*l*) was added and the insoluble crystals were recrystallized from chloroform to yield 2-acetamido-3,5-di-*t*-butylphenol (II, 1.0 g, 11%) as white solid, mp 214—216°C, which was identical with a compound obtained from acetylation of 2-amino-3,5-di-*t*-butylphenol (see below).

Found: C, 72.77; H, 9.62; N, 5.26%. Calcd for $C_{16}H_{25}NO_2$: C, 72.96; H, 9.57; N, 5.32%. Mol wt (Rast method) Found: 261. Calcd: 263.

The petroleum ether solution was chromatographed on silica gel. An oily material (5.3 g, 47%), eluted with petroleum ether, was purified by distillation to give 4-acetoxy-1-imino-2,4,6-tri-*t*-butyl-2,5-cyclohexadiene (I, 3.4 g, 31%), bp 90°C (0.28 mmHg). NMR: τ 0.48 (1H, broad), 4.04 (2H), 8.05 (3H), 8.72 (18H) and 9.10 (9H). IR (neat): 3330(N-H) and 1745 cm^{-1} (C=O).

Found: C, 75.38; H, 10.34; N, 4.54%. Calcd for $C_{20}H_{33}NO_2$: C, 75.19; H, 10.41; N, 4.38%.

Another material eluted with benzene was recrystallized from 70% ethanol to give 2-acetylimino-3,5-di-*t*-butyl-3,5-cyclohexadienone (III, 0.7 g, 8%) as orange-red crystals, mp 81—85°C. NMR: τ 3.29 (1H), 3.90 (1H), 7.86 (3H), 8.65 (9H) and 8.77 (9H).

Found: C, 73.26; H, 9.04; N, 5.27%. Calcd for $C_{16}H_{23}NO_2$: C, 73.53; H, 8.87; N, 5.36%.

Pyrolysis of I and 4-Benzoyloxy-1-imino-2,4,6-tri-*t*-butyl-2,5-cyclohexadiene (VI). Cyclohexadiene (I, 1.00 g, 3.1 mmol) was heated to 148°C in the course of 15 min in a test tube connected to a trap cooled with Dry Ice - ethanol mixture. The sample suddenly solidified with evolution of gas. The solid was washed with petroleum ether and recrystallized from methanol to give II (0.56 g, 70%), mp 215—217°C. To the liquid collected in the trap was added bromine in carbon tetrachloride to yield isobutylene dibromide (0.38 g, 57%), the amount of which was determined by means of VPC (succinic polyester of diethylene-glycol).

The cyclohexadiene (VI, 1.09 g, 2.86 mmol) obtained in the reaction of TBA with BPO was pyrolyzed by the same procedure to give isobutylene (47%) and 2-benzamido-3,5-di-*t*-butylphenol (VII, 0.57 g, 62%), which was identical with an authentic sample synthesized from benzoylation of 2-amino-3,5-di-*t*-butylphenol. VI began to decompose at about 100°C and decomposed vigorously at 130°C.

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[18] J. C. Bailar, Jr., *Inorg. Synth.*, **1**, 47 (1939).

[19] R. Criegee, P. Dimroth, K. Noll, R. Simon and C. Weis, *Chem. Ber.*, **90**, 1070 (1957).

[20] G. Braun, "Organic Syntheses," Coll. Vol. 1, p. 431 (1956).

Oxidation of II. To a solution of II (0.5 g, 1.9 mmol) in 10 m*l* of dry benzene was added LTA (1.0 g, 2.3 mmol) in 30 m*l* of dry benzene at room temperature, and the mixture was allowed to stand at room temperature overnight. After filtration of lead diacetate (0.7 g, 2.2 mmol) and removal of benzene, petroleum ether was added and insoluble LTA was filtered off. The filtrate was chromatographed on silica gel with benzene-ether (9 : 1) to give III (0.3 g, 60%), mp 81—85°C.

Reduction of III. To a solution of lithium aluminum hydride (0.1 g, 2.6 mmol) in 6 m*l* of anhydrous ether was added dropwise III (0.1 g, 3.8 mmol) in 5 m*l* of ether at room temperature with stirring. After usual working up, II (0.02 g, 20%), mp 214—216°C, was obtained.

Preparation of 2-Amino-3,5-di-*t*-butylphenol. To 3,5-di-*t*-butyl-2-nitrophenol[21] (10 g, 0.040 mol) in 20 m*l* of ethanol, was added sodium hydroxide (2 g, 0.050 mol) in 20 m*l* of water and then sodium hydrosulfite (14 g, 0.080 mol) in 100 m*l* of water was added dropwise at room temperature. Another sodium hydroxide (3 g, 0.075 mol) was added in portions to keep the mixture slightly alkaline, and the solution was stirred overnight. The reaction mixture was poured into 2 *l* of water and neutralized with dilute hydrochloric acid. The precipitate (10 g) was recrystallized from carbon tetrachloride to give 2-amino-3,5-di-*t*-butylphenol (2 g, 23%), mp 165—167°C. IR: 3330, 3430 (N-H) and 3110 cm^{-1} (O-H).

Found: C, 75.85; H, 10.25; N, 6.26%. Calcd for $C_{14}H_{23}NO$: C, 75.97; H, 10.47; N, 6.33%.

Acetylation and Benzoylation of 2-Amino-3,5-di-*t*-butylphenol. To a mixture of 2-amino-3,5-di-*t*-butylphenol (0.44 g, 2.0 mmol) and triethylamine (1.36 g, 3.6 mmol) in 5 m*l* of ether, acetyl chloride (0.16 g, 2.0 mmol) in 5 m*l* of ether was added with stirring at room temperature. After usual working up, II (0.1 g, 20%), mp 212—214°C, was obtained.

Found: C, 72.93; H, 9.56; N, 5.56%. Calcd for $C_{16}H_{25}NO_2$: C, 72.96; H, 9.57; N, 5.32%.

The benzoyl derivative (VII) was prepared by a similar method in 42% yield, mp 231—232°C (from chloroform).

Found: C, 77.21; H, 8.38; N, 4.36%. Calcd for $C_{21}H_{27}NO_2$: C, 77.50; H, 8.36; N, 4.30%.

4,6-Di-*t*-butyl-2-methylbenzoxazole (V). II (1.2 g, 4.6 mmol) was refluxed for 7 hr in 50 m*l* of absolute methanol under a stream of dry hydrogen chloride. After usual treatment, crude product was purified by column chromatography on alumina with petroleum ether to yield V (0.85 g, 77%), mp 45—46°C. UV: $\lambda_{\max}^{\mathrm{MeOH}}$ 240 (log ε 4.11), 271 (3.65) and 280 mμ (3.62). The UV spectrum was in good agreement with that of 2-methylbenzoxazole.[22]

Found: C, 78.37; H, 9.68; N, 5.89%. Calcd for $C_{16}H_{23}NO$: C, 78.32; H, 9.45; N, 5.71%.

Reaction of 2,4,6-Tri-*t*-butylaniline (TBA) with Lead Tetrabenzoate (LTB). A mixture of TBA (13 g, 0.050 mol), LTB (36 g, 0.052 mol) and dichloromethane (400 m*l*) was stirred for 2 hr at room temperature and then allowed to stand overnight. After removal of dichloromethane, ether was added in order to precipitate lead dibenzoate (21 g, 94%) (Found: C, 36.95; H, 2.51; N, 0%). After evaporation of the solvent from the filtrate and addition of petroleum ether, resulting white precipitates were shaken with aqueous sodium carbonate to leave insoluble VII (0.23 g, 1.4%), which was identified by comparison of the IR spectrum with that of an authentic sample described above. Acidification of the aqueous layer gave benzoic acid (6.33 g, 101%). The petroleum ether soluble products (16.21 g) were found by the NMR spectrum to be a mixture of unchanged TBA and VI (12.0 g, 65%). For characterization of VI, see the reaction with BPO.

Oxidation of TBA with Peroxybenzoic Acid (PBA). a) PBA (0.148 mol) in 100 m*l* of ether was added to an ethereal solution (100 m*l*) of TBA (19.5 g, 0.0747 mol) cooled with ice-water, and the mixture was kept at 0°C overnight. After usual working up, the crude material was purified by means of column chromatography on alumina or silica gel. 2,4,6-Tri-*t*-butylnitrosobenzene (VIII), first eluted with petroleum ether, was recrystallized from ethanol as emerald-green crystals. The yield was 16.2 g (73%), mp 166—168°C. The molecular weight was found to be 303 (Rast method) or 244 (Beckmann method in benzene); Calcd for $C_{18}H_{29}NO$: 275. NMR: τ 2.75 (2H), 8.65 (9H) and 8.80 (18H).

Found: C, 78.25; H, 10.81; N, 5.09%. Calcd for $C_{18}H_{29}NO$: C, 78.49; H, 10.61; N, 5.09%.

b) To TBA (5.2 g, 0.020 mol) in 20 m*l* of dichloromethane was added PBA (0.020 mol) in 20 m*l* of dichloromethane under cooling with ice-water, and the mixture was kept at 0°C overnight. After usual working up, the remaining solid was dissolved in petroleum ether. 3,5-Di-*t*-butyl-2-benzamidophenol (VII, 0.6 g, 10%) was obtained as white solid insoluble in this solvent, and recrystallized from chloroform and then from methanol, mp 231—232°C. IR (in Nujol): 3340 (N-H), 3110 (O-H) and 1630 cm^{-1} (C=O).

Found: C, 77.38; H, 8.48; N, 4.59%. Calcd for $C_{21}H_{27}NO_2$: C, 77.50; H, 8.36; N, 4.30%.

A product soluble in petroleum ether was VIII (1.0 g, 18%) and some TBA (1.5 g, 29%) was recovered.

c) To TBA (5.0 g, 0.019 mol) in 50 m*l* of ether, 30 m*l* of glacial acetic acid and then PBA (0.020 mol) were added under cooling with ice-water. After being kept at 0°C overnight, the reaction mixture was neutralized with aqueous sodium carbonate and dried over anhydrous sodium sulfate. After removal of the solvent the residue was dissolved in petroleum ether. II (5 mg, 0.1%) was obtained as a material insoluble in this solvent. The structure was confirmed to be identical with that of an authentic sample by the IR spectrum. The yield of VIII was 2.2 g (42%).

Methyl Ether of VII (IX). To a solution of VII (0.6 g, 2 mmol) in 100 m*l* of ethanol, about 1 g (24 mmol) of diazomethane in ether - ethanol was added at 0°C. The mixture was maintained at 0°C for two days. The solvents and excess diazomethane were removed, and recrystallization of the residual solid from methanol yielded methyl ether (IX, 0.3 g, 50%), mp 245.0—245.5°C. NMR (in $CDCl_3$ at 56°C): τ 1.95—3.20 (m, 7H), 6.27 (3H), 8.62 (9H) and 8.69 (9H). IR (in Nujol): 3270 (N-H), 1640 (C=O) and 1043 cm^{-1} (OCH_3).

Found: C, 77.55; H, 8.84; N, 4.11%. Calcd for $C_{22}H_{29}NO_2$: C, 77.84; H, 8.61; N, 4.13%.

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4,6-Di-*t*-butyl-2-phenylbenzoxazole (X). To a solution of VII (1.0 g, 3.2 mmol) in 50 m*l* of ethanol, 50 m*l* of 8 N hydrochloric acid was added, and the solution was refluxed at 110—120°C for 4 hr. After usual working up, to the viscous oil thus obtained was added 100 m*l* of petroleum ether. After filtration of the precipitated starting material (0.1 g, 10%) and removal of the solvent, the residue (0.8 g) was purified by column chromatography on alumina with petroleum ether. The yield was 0.6 g (57%). Mp 82—84°C.
NMR: τ 1.59—2.00 (m, 2H), 2.40—2.90 (m, 5H), 8.40 (9H) and 8.60 (9H). IR (in Nujol): 1595 cm^{-1} (C=N). UV: $\lambda_{\max}^{\mathrm{EtOH}}$ 232 (log ε 4.20), 299 (4.49), 301 (4.50) and 321 mμ (4.21). The UV spectrum was in good agreement with that of 2-phenylbenzoxazole.[22]

Found: C, 81.96; H, 8.43; N, 4.51%. Calcd for $C_{21}H_{25}NO$: C, 82.04; H, 8.20; N, 4.56%.

Reaction of TBA with Benzoyl Peroxide (BPO). A mixture of TBA (13 g, 0.050 mol) and BPO (13 g, 0.054 mol) in 200 m*l* of benzene was allowed to stand overnight at room temperature. After a large amount of white crystals (ppt-1, 2.75 g) were filtered off, the reaction solution was shaken with aqueous sodium carbonate to remove benzoic acid (5.5 g, 83%) and then dried over anhydrous sodium sulfate. Again white crystals (ppt-2, 1.79 g) precipitated, after filtration of which the benzene was evaporated under reduced pressure and petroleum ether was added. After precipitates thus obtained (ppt-3, 3.40 g) were filtered off, the solvent was removed completely under reduced pressure, leaving slightly reddish oily material (7.66 g). The IR spectra of ppt-1, ppt-2 and ppt-3 (7.94 g, 49% in total) were in entire agreement with that of VII.

The slightly reddish oil, VI, showed satisfactory analytical result without further purification. IR (neat): 3310 (N-H) and 1720 cm^{-1} (C=O). NMR: τ 8.93 (9H), 8.55 (18H), 3.83 (2H), 2.35—2.70 (m, 3H), 1.75—2.10 (m, 2H) and 0.60 (1H, broad).

Found: C, 78.50; H, 9.70; N, 3.30%. Calcd for $C_{25}H_{35}NO_2$: C, 78.68; H, 9.25; N, 3.67%.

The oily material (5.6 g) was chromatographed on silica gel. 2,2′,4,4′,6,6′-Hexa-*t*-butylazobenzene (XI, 0.33 g, 2%), 2,6-di-*t*-butyl-4-benzoyloxyaniline (XII, 1.76 g, 39%) and VII (1.69 g, 37%), mp 230—232°C, were eluted with petroleum ether, benzene and ether, respectively.

The azobenzene (XI) was identified by comparison of the UV spectra ($\lambda_{\max}^{\mathrm{EtOH}}$, 470 ($\varepsilon$ 617) and 314 mμ (14, 200)), and the melting point (237—238°C) with data of an authentic sample.[7]

The aniline (XII) was a white solid and recrystallized from petroleum ether, mp 134—135°C. NMR: τ 8.51 (18H), 5.95 (2H), 2.95 (2H), 2.25—2.55 (m, 3H) and 1.50—1.85 (m, 2H).

Found: C, 77.82; H, 8.66; N, 4.09%. Calcd for $C_{21}H_{27}NO_2$: C, 77.50; H, 8.36; N, 4.30%.

When a mixture of ppt-2 and ppt-3 was chromatographed on alumina, a trace of white crystals was eluted with dichloromethane. It melted at 256—258°C after recrystallization from carbon tetrachloride. The IR spectrum showed strong bands at 3280 and 1638 cm^{-1}. It was tentatively identified as 2,4,6-tri-*t*-butylbenzanilide.

Found: C, 81.10; H, 10.02; N, 4.33%. Calcd for $C_{25}H_{35}NO$: C, 82.14; H, 9.65; N, 3.83%.

From the petroleum ether-soluble oil obtained by another experiment using 5.0 g (0.019 mol) of TBA and 5.0 g (0.021 mol) of BPO, VIII (0.1 g, 2%) was isolated by sublimation under vacuum, mp 167—170°C.

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