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# THE NITRATIONS OF 2,4,5-TRIISOPROPYLACETANILIDE

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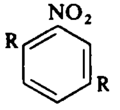
**Abstract**—The nitrations of 2,4,5-triisopropylacetanilide give mainly 2,4,5-triisopropyl-6-nitroacetanilide in acetic anhydride and mainly 2,4-diisopropyl-5-nitroacetanilide in conc sulphuric acid. An attempt has been made to interpret the direction of substitution in sulphuric acid in terms of the dominant influence of the 2-isopropyl group in substitutions in the conjugate acid. 2,4,5-Triisopropyl-6-nitroacetanilide loses a nitro group in boiling ethanolic HCl and this may represent the first reported case of protodenitration.

## INTRODUCTION

IN CONTRAST to the ease of the alkylations of mono- and dihydric phenols the direct nuclear alkylations of arene-amines and particularly of arenediamines are not readily accomplished except by using special catalysts at high temperatures.[1,2] Therefore common methods for the unambiguous synthesis of nuclearly alkylated amines involve reductions of appropriately alkylated nitro compounds. Such a method previously has provided[3] 2,5-dimethyl-1,4-benzenediamine (IV; R = Me) from *p*-xylene by a route through I, II and III (R = Me) and now we have shown that similar routes are convenient laboratory procedures for 2,5-diethyl- and 2,5-di-t-butyl-1,4-benzenediamines (IV; R = Et and $Me_3C$). In the last case the method is an alternative to the direct nitration of 2,5-di-t-butylnitrobenzene (I; R = ($Me_3C$) which gives[4,5] the dinitro-compound (V; R = $Me_3C$).

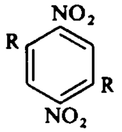


I

II

III

IV

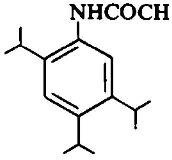


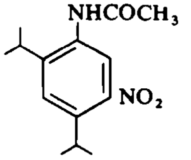
V

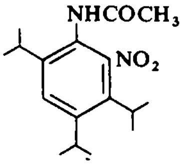
However, it is known[5–7] that nuclear isopropyl groups are readily displaced under the conditions of nitrations and thus although it has been claimed[7,8] that *p*-diisopropylbenzene can provide 2,5-diisopropylnitrobenzene (I; R = $Me_2CH$) we and others[9] have found that it is difficult to separate this compound from the major product, *p*-nitrocumene. Dealkylations of this type might intervene also in the further nitration of 2,5-diisopropylacetanilide (II; R = $Me_2CH$) as they do[5] in the nitration of 2,5-diisopropylnitrobenzene and therefore it is considered that the route through I, II and III (R = $Me_2CH$) is unsuitable for 2,5-diisopropyl-1,4-benzenediamine.

Surprisingly, in view of the difficulty of direct alkylations of amines under acidic conditions, acetanilide is alkylated readily by 2-propanol in cold, concentrated sulphuric acid to give a good yield of 2,4,5-triisopropylacetanilide (VI). And since

4-isopropylacetanilide undergoes[10] nearly quantitative nitrodealkylation in sulphuric acid to give 4-nitroacetanilide it seemed to be possible that VI might give 2,5-diisopropyl-4-nitroacetanilide (III; R = $Me_2CH$) directly. However we have shown that the nitration of VI by a mixture of nitric and sulphuric acids gives mainly the *m*-nitrodealkylation product (VII) and that the nitration of VI in acetic anhydride containing acetic acid gives mainly 2,4,5-triisopropyl-6-nitroacetanilide (VIII). This paper describes the results and attempts to interpret the directions of the substitutions.


VI


VII

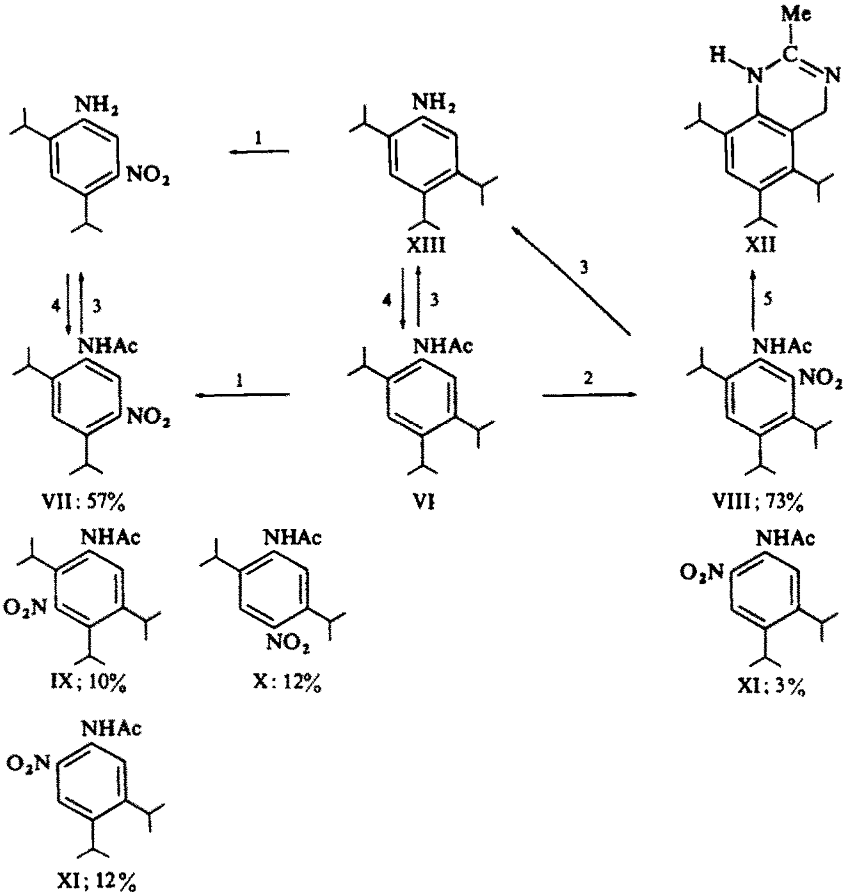

VIII

## RESULTS AND DISCUSSION

The scheme depicts the products and it shows that all the five possible mononitro derivatives have been obtained. The approximate proportions that are given in the scheme were obtained by using gas-chromatography except in the cases of the products of 5- and 3-nitration (VII and IX). These two compounds were not separated by gas chromatography and so the proportion of VII is the isolated yield and the proportion of IX is an approximation allowing for losses of VII during isolation; VII and IX together comprised 76% of the total product. All the compounds were isolated from the reaction mixtures and their structures were established by chemical and spectroscopic methods as is described in (i) through (iii).

(i) The major product of nitration by conc nitric acid in conc sulphuric acid is 2,4-diisopropyl-5-nitroacetanilide (VII). This is identical with the compound that can be obtained from the product of nitration under similar conditions of 2,4,5-triisopropylaniline (XIII) and its structure was assigned by Newton[7] as the result of interrelationships observed in the nitrations of polyisopropylbenzenes. The present work in which all the five possible products have been isolated confirms that assignment.

(ii) 2,5-Diisopropyl-4-nitroacetanilide (X) and 4,5-diisopropyl-2-nitroacetanilide (XI) are two of the minor products from sulphuric acid and they were distinguished readily by using UV and IR spectroscopy. The UV spectra of nitroacetanilides have been discussed recently.[11] 2-Nitroacetanilides which do not have substituents in the 6-position characteristically have a strong absorption band near 360 mμ which is owing to the formation of an intramolecular H-bond. Compound XI gives rise to such an absorption band as is shown in Fig. 1 whereas X gives rise to only minor absorption in this region. The IR spectra[12,13] are equally characteristic. Dyall and Kemp[12] have shown how the four possible conformations of the acetylamino-group in *o*-substituted compounds should give rise to four absorption bands in the range 3300–3500 $cm^{-1}$. These are observed for 2-methylacetanilide and deuteriation suggests that they genuinely represent the N—H stretching vibrations of the conformers.



1 $HNO_3$—$H_2SO_4$; 2 $HNO_3$—$Ac_2O$—AcOH; 3 HCl—EtOH; 4 $Ac_2O$; 5 $H_2$—Pd; Al/Hg—$Et_2O$

Fig. 2 gives a schematic representation of the IR spectra of the relevant compounds in very dilute solutions (0·002M) in carbon tetrachloride. 2,4,5-triisopropylacetanilide (VI), 2,4-diisopropyl-5-nitroacetanilide (VII) and compound X all give rise to three absorption bands and since for VI and VII, first, all three bands move to lower frequencies as the solvent becomes more basic[12] and are replaced by a single absorption band in dioxan, and, second, all three bands are reduced in intensity by deuteriation and then three new bands appear in the range 2500–2600 $cm^{-1}$, they are considered to represent three conformations of the acetylamino group in these compounds. Evidently the single *o*-isopropyl substituent is not sufficiently bulky to cause the adoption of only two conformations in the ground state, but it is notable that IX gives rise to only two absorption bands presumably owing to a buttressing effect of the adjacent substituents. The completely contrasting behaviour of XI for which only a single absorption band is observed at a significatly lower frequency (which is close to that for *o*-nitroacetanilide) is taken to indicate the formation of an intramolecular H-bond and to characterize XI as an *o*-nitroacetanilide.

(iii) The major product of nitrations by nitric acid in $Ac_2O$–AcOH (4:1) mixtures

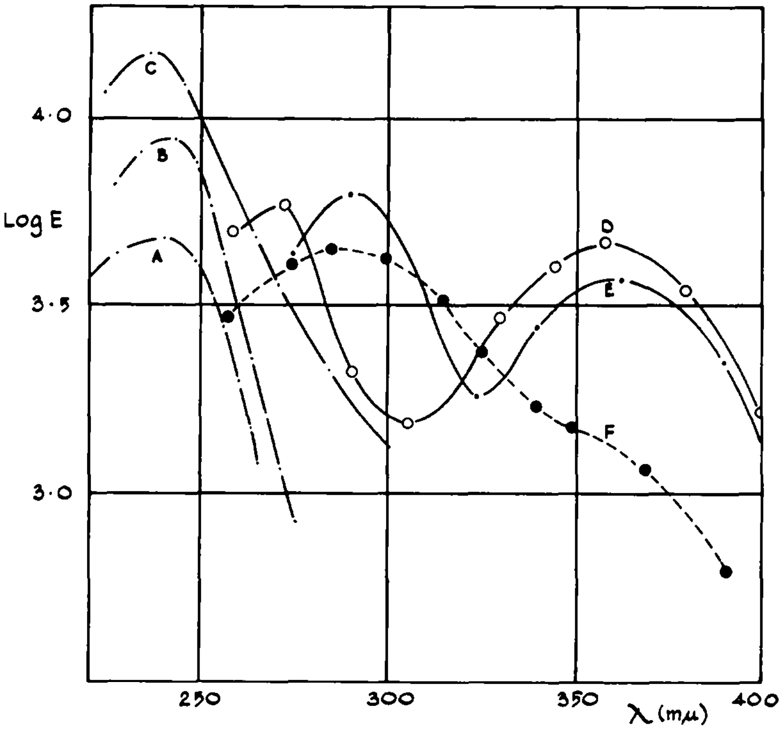


FIG. 1.

A. 2,4,5-Triisopropylacetanilide (VI)
B. 2,4,5-Triisopropyl-3-Nitroacetanilide (IX)
C. 2,4-Diisopropyl-5-Nitroacetanilide (VII)
D. 2-Nitroacetanilide
E. 4,5-Diisopropyl-2-Nitroacetanilide (XI)
F. 2,5-Diisopropyl-4-Nitroacetanilide (X)

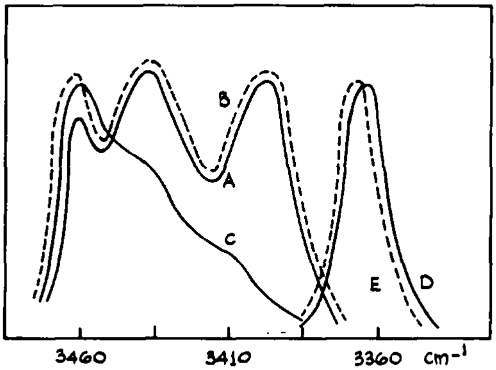


FIG. 2.

A. 2,4,5-Triisopropylacetanilide (VI)
B. 2,4-Diisopropyl-5-Nitroacetanilide (VII)
C. 2,5-Diisopropyl-4-Nitroacetanilide (X)
D. 4,5-Diisopropyl-2-Nitroacetanilide (XI)
E. 2-Nitroacetanilide

is 2,4,5-triisopropyl-6-nitroacetanilide (VIII) as is proved conclusively by its reduction to 4,6,7-triisopropyl-2-methylbenzimidazole (XII) and it follows that IX obtained from nitration in sulphuric acid must be 2,4,5-triisopropyl-3-nitroacetanilide. Gas chromatography indicates that the product from acetic anhydride consists of VIII (73%), XI (3%) and unchanged 2,4,5-triisopropylacetanilide (20%), but although VIII therefore constitutes 96% of the nitration products it has not been possible to increase the isolated yield beyond 59% by increasing reaction times or by increasing the concentration of nitric acid. It is notable that the nitro group is displaced during attempted deacetylations by HCl–EtOH and it is possible that owing to steric crowding VIII undergoes protodenitration in acidic solutions and that this is the factor which restricts the conversion of 2,4,5-triisopropylacetanilide. Steric crowding in VIII apparently reveals itself also in the UV, IR and NMR spectra. Thus there is no discrete absorption beyond 225 mμ by VIII in cyclohexane and therefore presumably intramolecular H-bonding, such as is observed for XI and for *o*-nitroacetanilide, is absent. There are two absorption bands at 3425 and 3390 $\text{cm}^{-1}$ which behave properly under the influence of solvent basicity and on deuteriation. The two *o*-substituents probably restrict the rotation of the acetylamino group around the $C_{ar}$—N bond and therefore cause this group to adopt a non-planar situation for which there are just two conformations in which N—H and C=O are in *cis* and *trans* positions relative to each other. Similar observations have been made by Kessler[14] in interpreting the NMR spectra of 2,6-diisopropylacetanilides. Kessler observed two signals representing the protons of the acetyl groups in the two possible conformations of the nonplanar acetylamino group and from the relative intensities of these signals he showed that the *cis* conformer became relatively less stable as the dielectric constant of the solvent increased. The NMR spectra of VIII (Experimental) in $CDCl_3$, pyridine and $CD_3COCD_3$ may be interpreted similarly: the two signals are observed distinctly in $CDCl_3$ and that assigned to the *cis* conformer is decreased in intensity in pyridine and in $CD_3COCD_3$.

The nitration of 2,4,5-triisopropylacetanilide in acetic anhydride presumably represents a further case of initial nucleophilic displacement of the nitrate ion from $N_2O_5$ by —NHAc, followed by intramolecular transfer of $NO_2$ to the *ortho* positions;[15] the transfer to the vacant *ortho* position evidently is preferred. But superficially there is a contrast between the nitrations in sulphuric acid of the 2,5-dialkyl acetanilides (II; R = Me, $Me_3C$) for which the major products appear to be the 4-nitro derivatives and the nitration of 2,4,5-triisopropylacetanilide for which the major substitutions take place at positions *meta* to NHAc. However, it is possible to derive a crude appreciation of the differences between the two cases by assuming kinetically controlled products and the applicability of the additivity principle. It is necessary to consider substitutions in the free bases and in the corresponding conjugate acids. If the rate of substitution at a particular position (x) in the conjugate acid is represented by $(R_{N^+})_x$ and in the free base by $(R_N)_x$ then the expressions (1) for substitutions in 2,4,5-triisopropylacetanilide, (2) and (3) for substitutions in acetanilide and in 2,5-dialkylacetanilides, and (4) for *meta* substitutions generally, may be derived; $f$ denotes partial rate factors and $c_{BH^+}$ and $c_B$ denote respectively the concentrations of the conjugate acids and of the free bases.

For acetanilide ($pK_{BH^+} = 1$)[16] in 98% $H_2SO_4$ ($H_0 = -10{\cdot}4$)[17] the ratio $c_{BH^+} : c_B = 2{\cdot}5 \times 10^{11}$ and if the partial rate factor for nitration *meta* to a positive pole ($f_m^{N^+}$) is taken as the smallest value determined by Ridd[18] for anilinium ions ($4 \times 10^{-8}$), it follows from (2) that $f_p^{\mathrm{NHAc}}$ must exceed $10^4$ in order that the rate of substitution in the *para* position of the free base $(\mathrm{R_N})_4$, should exceed the rate at the *meta* position in

$$\frac{(\mathrm{R_{N+}})_5}{(\mathrm{R_N})_4} = \frac{c_{\mathrm{BH+}}}{c_{\mathrm{B}}} \cdot \frac{f_{\mathrm{m}}^{\mathrm{N+}} \cdot f_o^{\mathrm{Pr}} \cdot f_p^{\mathrm{Pr}}}{f_p^{\mathrm{NHAc}} \cdot f_o^{\mathrm{Pr}} \cdot f_{\mathrm{m}}^{\mathrm{Pr}}} = \frac{c_{\mathrm{BH+}}}{c_{\mathrm{B}}} \cdot \frac{f_{\mathrm{m}}^{\mathrm{N+}}}{f_p^{\mathrm{NHAc}}} \cdot \frac{f_p^{\mathrm{Pr}}}{f_{\mathrm{m}}^{\mathrm{Pr}}} \tag{1}$$

$$\frac{(\mathrm{R_{N+}})_3}{(\mathrm{R_N})_4} = \frac{c_{\mathrm{BH+}}}{c_{\mathrm{B}}} \cdot \frac{f_m^{\mathrm{N+}}}{f_p^{\mathrm{NHAc}}} \cdot \frac{f_o^{\mathrm{R}} f_{\mathrm{m}}^{\mathrm{R}}}{f_o^{\mathrm{R}} f_{\mathrm{m}}^{\mathrm{R}}} = \frac{c_{\mathrm{BH+}}}{c_{\mathrm{B}}} \cdot \frac{f_{\mathrm{m}}^{\mathrm{N+}}}{f_p^{\mathrm{NHAc}}} \tag{2}$$

$$\frac{(\mathrm{R_{N+}})_5}{(\mathrm{R_N})_4} = \frac{c_{\mathrm{BH+}}}{c_{\mathrm{B}}} \cdot \frac{f_{\mathrm{m}}^{\mathrm{N+}}}{f_p^{\mathrm{NHAc}}} \cdot \frac{f_p^{\mathrm{R}}}{f_o^{\mathrm{R}} \cdot f_{\mathrm{m}}^{\mathrm{R}}} \tag{3}$$

$$\frac{(\mathrm{R_{N+}})_{\mathrm{m}}}{(\mathrm{R_N})_{\mathrm{m}}} = \frac{c_{\mathrm{BH+}}}{c_{\mathrm{B}}} \cdot \frac{f_{\mathrm{m}}^{\mathrm{N+}}}{f_{\mathrm{m}}^{\mathrm{NHAc}}} \tag{4}$$

the conjugate acid, $(\mathrm{R_{N+}})_3$, and thus lead to the observed dominant 4-nitration. If 2,5-dialkylacetanilides may be taken to be basic to a comparable extent then the observed formation of 4-nitro derivatives follows from the identical expression (2) since contributions from the alkyl substituents ($f^{\mathrm{R}}$) are eliminated. This interpretation is acceptable for 2,5-dimethylacetanilide for which steric effects to the full operation of the activating influence of NHAc and to the basicity should be relatively small. But the situation may be marginal for 2,5-di-t-butylacetanilide and different considerations may be applicable in this case since even 2,5-di-t-butylnitrobenzene gives dominant 4-nitration.[5]

Substitutions at *meta* positions apparently must always take place in the conjugate acids since the derived relative rates (expression 4) show that $f_{\mathrm{m}}^{\mathrm{NHAc}}$ must exceed approximately $4 \times 10^3$ ($10^{11} \times 4 \times 10^{-8}$) in order to allow preferential *meta* substitutions in the free bases; whereas *m*-NHAc is likely to be deactivating through the operation of an inductive effect as it is in chlorination.[19] Therefore it follows from (1) that the observed 5-nitration for 2,4,5-triisopropylacetanilide may be owing to the dominant influence of the 2-isopropyl substituent in substitutions in the conjugate acid. The powerful activating influence of alkyl substituents in otherwise deactivated systems has been demonstrated[20] for anilinium ions. It is interesting that equation (3) which relates to 5-substitution in the conjugate acid of 2,5-dimethylacetanilide suggests a balanced situation which presumably is not achieved owing to the difficulty in displacing Me groups as carbonium ions. But, as is suggested in the introduction, the nitration of 2,5-diisopropylacetanilide in sulphuric acid might lead at least partly to a displacement of the 5-isopropyl group.

## EXPERIMENTAL

The UV spectra (solns in cyclohexane except where stated; in some cases the compounds were not completely soluble and the values of the molar absorptivities therefore are minimum values) were obtained by using a Unicam SP800 spectrometer. The IR spectra (dilute solns in $\mathrm{CCl_4}$) in the range 3300–3500 cm$^{-1}$ were obtained by using a Unicam SP100/130 spectrometer; association was evident in some cases even for 0·01M solns and usually 0·002M solns in 3 cm cells were used; the solvent was dried over molecular sieve, Deuteriations were done by using the methods described.[12] The $^1H$ NMR spectra (5–10% solns in $CD_3COCD_3$, $CDCl_3$ or pyridine) were measured by using a Perkin Elmer R10 spectrometer at 60 Mc/s and TMS as an internal reference. Gas chromatography was done with 6 ft of ¼ in (od) stainless steel packed with 3% OV-1 (silicone gum rubber) on 60–80 mesh Gas Chrom Q at 170° (inlet, 250°; detector, 225°) and a flame ionization detector; the analytical results were derived simply from the relative peak-areas. The NMR spectra and the gas chromatographic results were supplied by Dr. J. Newton of these laboratories and we are grateful for his interest and for discussions.

2,5-*Diethyl*-1,4-*benzenediamine* (IV; R = Et). *p*-Diethylbenzene[22] was obtained from *p*-ethylacetophenone[21] and converted to 2,5-diethylacetanilide.[23] A mixture of conc $H_2SO_4$ (55 ml) and conc $HNO_3$ (*d*, 1·42; 26 g) was added during 2 hr to 2,5-diethylacetanilide (55 g, 0·29 mole) in conc $H_2SO_4$ (230 ml) maintained at 0°. The resultant dark liquid was poured on to crushed ice and the ppt extracted into ether–benzene, washed with $NaHCO_3$ aq, dried, and the solvent removed to give a solid residue which crystallized from aqueous EtOH as white needles, m.p. 141·5–144·5° (27 g, 39%). Recrystallization from aqueous EtOH gave 2,5-*diethyl*-4-*nitroacetanilide*, m.p. 147·5–148·5°. (Found: C, 60·9; H, 6·6; N, 11·9. $C_{12}H_{16}N_2O_3$ requires: C, 61·0; H, 6·8; N, 11·9%). This acetanilide (26 g, 0·11 mole) after heating under reflux with a mixture of conc HCl (150 ml) and EtOH (200 ml) for 15 hr followed by basification with NaOH aq gave a yellow solid which crystallized from aqueous EtOH as bright yellow needles m.p. 81–83° (16 g, 75%) of 2,5-*diethyl*-4-*nitroaniline*. (Found: C, 62·1; H, 7·5; N, 15·6. $C_{10}H_{14}N_2O_2$ requires: C, 61·9; H, 7·3; N, 14·4%). This amine (14 g, 0·072 mole) in EtOH was hydrogenated at room temp by using 5% Pd–C and it provided a brown solid which crystallized from petrol (b.p. 60–80°) as buff needles m.p. 80–81° (7·6 g, 65%) of 2,5-*diethyl*-1,4-*benzenediamine*. (Found: C, 73·1; H, 9·8; N, 17·1. $C_{10}H_{16}N_2$ requires: C, 73·1; H, 9·9; N, 17·1%).

2,5-*Di-t-butyl*-1,4-*benzenediamine* (IV; R = ($Me_3C$). t-BuOH (160 g, 2·16 moles) was added during 2 hr to a vigorously stirred mixture of benzene (78 g, 1 mole) and conc $H_2SO_4$ (200 ml) maintained at 10°. After a further 20 min the mixture was poured on to ice and the solid was crystallized from MeOH to give *p*-di-t-butylbenzene, m.p. 75–78° (85 g, 50%). Potts and Carpenter[24] give m.p. 75° for a product made by using 2-methyl-2-propene and $AlCl_3$; the present procedure apparently has not been described previously. 2,5-Di-t-butylacetanilide was obtained from *p*-di-t-butylbenzene by using the method of Legge[25] and this acetanilide (84·5 g, 0·34 mole) in conc $H_2SO_4$ (500 ml) was nitrated at 10° by the addition of conc $HNO_3$ (*d*, 1·42; 22 ml) during 2 hr. After a further 2 hr at 10° the mixture was poured on to ice and the ppt was crystallized from MeOH to give a product, m.p. 145–150° (60 g, 67%). Recrystallization from MeOH gave 2,5-*di-t-butyl*-4-*nitroacetanilide*, m.p. 155–156°. (Found: C, 65·6; H, 9·6; N, 8·2. $C_{16}H_{24}N_2O_3$ requires: C, 66·0; H, 9·4; N, 7·9%). This was hydrolysed according to the previous section to provide 2,5-*di-t-butyl*-4-*nitroaniline*, m.p. 121–123°. (Found: C, 67·1; H, 9·0; N, 11·4. $C_{14}H_{22}N_2O_2$ requires: C, 67·2; H, 8·9; N, 11·2%) and this nitroamine (5 g, 0·02 mole) in EtOH (200 ml) was hydrogenated at room temp in the presence of 5% Pd–C (1 g). It formed a pale brown solid which crystillized from aqueous MeOH as buff crystals, m.p. 173–175° (2·2 g, 50%) of 2,5-di-t-butyl-1,4-benzenediamine. (Found: C, 76·2; H, 11·1; N, 12·9; M (Mechrolab osmometer), 217. Calc for $C_{14}H_{24}N_2$: C, 76·3; H, 11·0; N, 12·7%; M, 220). Bell[4] gives m.p. 172–173° for the product obtained from the reduction of 2,5-di-t-butyl-1,4-dinitrobenzene.

2,4,5-*Triisopropylacetanilide* (VI)[26]. 2-Propanol (480 g, 6 moles) was added during 4 hr to acetanilide (270 g, 1·86 moles) in conc $H_2SO_4$ (2500 ml) maintained below 30° (ice-bath). after an additional 1·5 hr at room temp the mixture was poured on to ice and the ppt was washed with $NaHCO_3$aq and crystallized from aqueous EtOH to give white needles, m.p. 144·5–145° (380 g, 78%) of 2,4,5-tri-isopropylacetanilide. (Found: C, 78·2; H, 10·6; N, 5·6; M, 262. Calc. for $C_{17}H_{27}NO$: C, 78·1; H, 10·4; N, 5·4%; M, 261). Yasue[26] gives m.p. 141–142° for the product obtained by using the above procedure and Newton[7] gives m.p. 142° for a product obtained from 1,2,4,5-tetraisopropylbenzene.

*The nitration of* 2,4,5-*triisopropylacetanilide in sulphuric acid.* A mixture of conc $HNO_3$ (*d*, 1·42; 20 ml) and conc $H_2SO_4$ (50 ml) was added during 2·5 hr to 2,4,5-triisopropylacetanilide (50 g, 0·19 mole) in conc $H_2SO_4$ (400 ml) maintained at 0–7°. Then the temp was allowed to rise to room temp and the mixture was stored at this temp for 16 hr when it was poured on to ice, extracted into ether, washed with $NaHCO_3$ aq, dried and evaporated to give a dark viscous oil (51 g). This oil was anlysed by gas chromatography to give the results discussed. The viscous oil ultimately solidified and crystallization from benzene–petrol gave VII, m.p. 115–116° (30 g, 57%; Newton[7] gives m.p. 116–117°). This was hydrolysed to give 2,4-diisopropyl-5-nitroaniline, m.p. 76·5–78°. (Found: C, 65·0; H, 8·3; N, 12·7. Calc for $C_{12}H_{18}N_2O_2$: C, 64·8; H, 8·2; N, 12·6%) which was identical (m.p. mixed m.p. and IR spectrum) with the product obtained (see later) from the nitration of XIII.

The mother liquors from the crystallizations of VII after concentration deposited a yellow solid which crystallized from aqueous MeOH (m.p. 163–165°; 2 g) as *2,5-diisopropyl-4-nitroacetanilide*. (Found: C, 63·2; H, 7·4; N, 10·6. $C_{14}H_{20}N_2O_3$ requires: C, 63·6; H, 7·6; N, 10·6%). And further concentration gave a solid which also crystallized from aqueous MeOH to give *2,4,5-triisopropyl-3-nitroacetanilide*, 1·5 g, m.p. 206–209°. (Found: C, 67·1; H, 8·7; N, 9·1 $C_{17}H_{26}N_2O_3$ requires: C, 66·6; H, 8·6; N, 9·2%). Then the solvent was removed from residual mother-liquors and the resultant black tar (1·9 g) was dissolved in benzene (70 ml) and part of this soln (35 ml) was filtered through neutral alumina (9 in × $\frac{3}{4}$ in) by using benzene as eluant. A yellow solid was recovered from the early fractions which crystallized from petrol as pale yellow crystals (0·5 g), m.p. 83–86° of *4,5-diisopropyl-2-nitroacetanilide*. (Found: C, 64·0; H, 7·6; N, 10·3. $C_{14}H_{20}N_2O_3$ requires: C, 63·6; H, 7·6; N, 10·6%).

*The nitration of* 2,4,5-*triisopropylaniline in sulphuric acid* 2,4,5-Triisopropylacetanilide was hydrolysed by HCl–EtOH as described to give 2,4,5-triisopropylaniline, b.p. 144–145° 13 mm, $n_D^{24}$ 1·5200 (Newton[7] gives $n_D^{20}$ 1·5215), and this amine (10 g, 0·046 mole) in conc $H_2SO_4$ (100 ml) was nitrated at 5–10° by conc $HNO_3$ (*d*, 1·42; 3·5 ml). The product crystallized from petrol as red-orange plates, m.p. 75–76° (5 g, 49%) of 2,4-diisopropyl-5-nitroaniline which was identical with the compound obtained from the nitration of 2,4,5-triisopropylacetanilide.

*The nitration of* 2,4,5-*triisopropylacetanilide in acetic anhydride*. Fuming $HNO_3$ (5 ml) in AcOH (50 ml) was added during 1·5 hr to a soln of 2,4,5-triisopropylacetanilide (20 g, 0·077 mole) in a mixture of $Ac_2O$ (400 ml) and AcOH (100 ml) maintained at 15°. After a further 1 hr at room temp the mixture was poured into cold (0°) 1% NaOHaq and the ppt was filtered off, washed with water, dried, and analysed by gas chromatography. The solid crystallized from petrol (b.p. 80–100°) as pale yellow crystals, m.p. 184–185° (14 g, 59%) of *2,4,5-triisopropyl-6-nitroacetanilide*. (Found: C, 67·0; H, 8·6; N, 9·2; M, 324. $C_{17}H_{26}N_2O_3$ requires: C, 66·6; H, 8·6; N, 9·2%, M, 306).

*Attempted hydrolysis of* 2,4,5-*triisopropyl-6-nitroacetanilide*. The acetanilide (16 g, 0·052 mole) was heated under reflux with a mixture of conc HCl (250 ml) and EtOH (300 ml) for 20 hr. The mixture was poured into NaOHaq and the organic phase extracted into ether, washed with water, dried, and the ether removed to give a dark oil. Distillation gave three fractions: (i) b.p. 96°/0·4 mm (5·4 g), (ii) b.p. 96–98°/0·4 mm (7·0 g), (iii) b.p. 96–108°/0·4 mm (1·0 g) and a residue (1 g). Fraction (ii) had an IR spectrum closely similar to that of 2,4,5-triisopropylaniline and it formed white crystals of 2,4,5-triisopropylacetanilide, m.p. and mixed m.p. 143–144°.

4,6,7-*Triisopropyl-2-methylbenzimidazole* (XII). 2,4,5-Triisopropyl-6-nitroacetanilide (14·3 g, 0·047 mole) in EtOH (100 ml) was hydrogenated at 65° in the presence of 5% Pd–C. Removal of catalyst and solvent gave a glass which crystallized from aqueous MeOH as buff crystals, m.p. 172–173° (6·5 g, 54%) of *4,6,7-triisopropyl-2-methylbenzimidazole*. (Found: C, 79·4; H, 10·0; N, 11·0; M, 248. $C_{17}H_{26}N_2$ requires: C, 79·0; H, 10·2; N, 10·8%; M, 258). $\lambda_{max}$ (EtOH) 250 (8000), 274 (4290) and 283 mμ (3900); NMR spectrum ($CDCl_3$): τ, 2·85 (=CH, s), 6·45 (NH, s) 7·45 (=C—Me, s), 8·60 ($CMe_2$, m); the signal at 6·45 disappeared on deuteriation to leave a multiplet arising from the tertiary protons of the isopropyl groups.

Al-Hg (100 g) was added to 2,4,5-triisopropyl-6-nitroacetanilide (50 g, 0·16 mole) suspended in moist ether (3500 ml) at room temp. After 4 hr the Al salts and the excess of Al-Hg were filtered off and the solvent removed from the filtrate to give a yellow solid (39 g) which crystallized from MeOH as needles, m.p. 173–176° (21 g, 50%); this was identical (IR spectrum) with the product obtained by catalytic hydrogenation.

*Spectra*. 2,4,5-*Triisopropylacetanilide* (VI): $\lambda_{max}$ 240 mμ (5200); IR spectrum: 3460, 3438 and 3396 $cm^{-1}$ moving to 3458, 3422 and 3387 in chlorobenzene and reduced to a single band at 3336 $cm^{-1}$ in dioxan; deuteriation caused the appearance of three new bands at 2570, 2556 and 2524 $cm^{-1}$. 2,4-*Diisopropyl-5-nitroacetanilide* (VII): $\lambda_{max}$ 235 mμ (17,400); IR spectrum: 3464, 3435 and 3398 $cm^{-1}$ moving to 3453 and 3420 $cm^{-1}$ in chlorobenzene and reduced to a single band at 3316 $cm^{-1}$ in dioxan; deuteriation caused the appearance of three new bands at 2570, 2554 and 2524 $cm^{-1}$. 2,5-*Diisopropyl-4-nitroacetanilide* (X): $\lambda_{max}$ 287 (4870); IR spectrum: 3460, 3440 and 3400 $cm^{-1}$. 4,5-*Diisopropyl-2-nitroacetanilide* (XI): $\lambda_{max}$ 290 (6700) and 364 mμ (4070); IR spectrum: a single band at 3367 $cm^{-1}$; *o*-nitroacetanilide has $\lambda_{max}$ 272 (5900) and 358 mμ (4560) with a single band in the IR spectrum at 3370 $cm^{-1}$. 2,4,5-*Triisopropyl-3-nitroacetanilide* (IX): $\lambda_{max}$ 242 mμ (9140); IR spectrum: 3484 and 3410 $cm^{-1}$. 2,4,5-*Triisopropyl-6-nitroacetanilide* (VIII): No discrete absorption beyond 225 mμ. IR spectrum: 3425 and 3390 $cm^{-1}$ moving to chlorobenzene and to 3285 $cm^{-1}$ in dioxan; deuteriation caused the appearance of two new bands at 2545 and 2520 $cm^{-1}$. NMR spectra: signals for the protons of the acetyl groups at τ, 7·83 and 8·11 with relative intensities 82:18 in $CDCl_3$; at τ, 7·80 and 8·11 with relative intensities 94:6 in $CD_3COCD_3$; and at τ, 7·80 and 8·02 with relative intensities 94:6 in pyridine.

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