*The Nitration of Some Derivatives of 1, 3, 5-Tri-t-butylbenzene**

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In connection with the interesting problem of the possible existence of derivatives of *sym*-tri-*t*-butylbenzene with two or three functional groups, the nitration of some derivatives of 1, 3, 5-tri-*t*-butylbenzene has been undertaken.

Sym-tri-methyl-, or tri-isopropylbenzenes bearing three functional groups,(1) and *sym*-tri-*t*-butylbenzenes with one functional group(2) have already been known, but derivatives of the latter hydrocarbon bearing two or three functional groups have not yet been prepared. It has recently been suggested(3) that the steric requirements of the bulky *t*-butyl groups cause the distortion of the benzene ring in *o*-di-*t*-butylbenzene or in 1, 2, 4, 5-tetra-*t*-butylbenzene.

The nitration of 2, 4, 6-tri-*t*-butylphenol(4) has been shown to give various unusual nitration products. Among them, there were products in which original *t*-butyl groups were replaced by nitro groups, or, products of quinoid or quinolide structures, depending upon the conditions of nitration. Such a replacement of a *t*-butyl group by a nitro group has frequently been described in the literature(5) and has been found to be the case in the nitration of 2, 4, 6-tri-*t*-butylaniline.(6)

While 2, 4, 6-tri-*t*-butylnitrobenzene (I) can be obtained by a rather mild nitration of the corresponding hydrocarbon, the further nitration of I to a dinitro compound (m. p. 290~292°C) was found to require much more severe conditions using fum. nitric acid in sulfuric acid at 70°C. This dinitro compound II, when analyzed, is found to correspond to the molecular formula $C_{18}H_{28}O_4N_2$ and to have a molecular weight of 336 (Rast method), while still retaining three *t*-butyl groups.

The structure of II has been elucidated on the basis of the evidence given below.

The catalytic hydrogenations of the nitro compound II and the related nitro compounds shown in Fig. 1 were carried out under atmospheric pressure and at room temperature in the presence of the same amount of Raney nickel per each nitro group. II was found to resist hydrogenation very strongly, while all the nitro groups of *m*-dinitrobenzene (IIa) and of other *m*-di-nitro-*t*-butylbenzenes** (IIb and IIc) were readily reduced, absorbing theoretical quantities of hydrogen rapidly. On the other hand, the reduction of the nitro group substituted between the two ortho *t*-butyl groups in I proceeded very slowly, although it gave the expected reduced product. This experiment seems to indicate that both nitro groups in II are highly sterically hindered.

The steric hindrance of the nitro group was further supported by the infrared spectra of

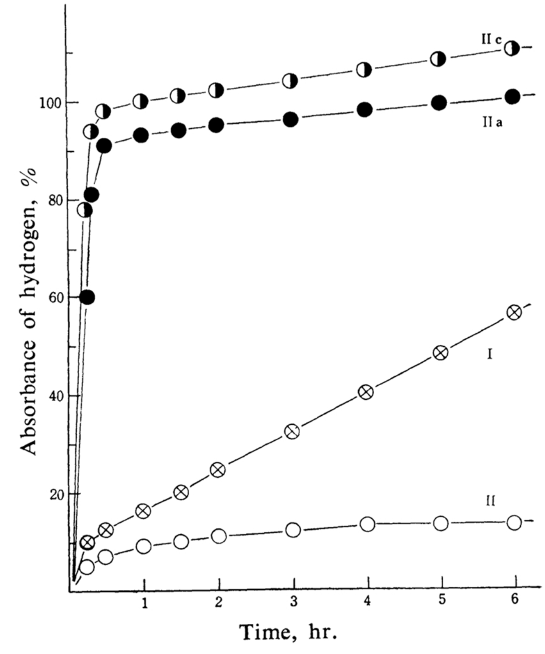

Fig. 1. Hydrogenations of *t*-butyl-*m*-dinitrobenzenes.

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1) For example: a) trinitromesitylene: Heilbron and Bunbury, "Dictionary of Organic Compounds," Eyre & Spottiswoode, London (1953), Vol. IV, p. 623; b) trinitro-*sym*-tri-isopropylbenzene: A. Newton, *J. Am. Chem. Soc.*, **65**, 2435 (1943).

2) E. E. Betts and L. R. C. Barclay, *Can. J. Chem.*, **33**, 1768 (1955).

3) C. Hoogzand and W. Hübel, *Tetrahedron Letters*, No. 18, 637 (1961).

4) K. Ley and E. Müller, *Chem. Ber.*, **89**, 1402 (1956).

5) P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Butterworths Scientific Publications, London (1959), p. 210; cf. also D. V. Nightingale, *Chem. Revs.*, **40**, 117 (1947).

6) B. M. Wepster et al., *Rec. trav. chim.*, **75**, 1327 (1956).

** The only curve of IIc is shown in Fig. 1, but almost the same one was also obtained in the case of IIb.

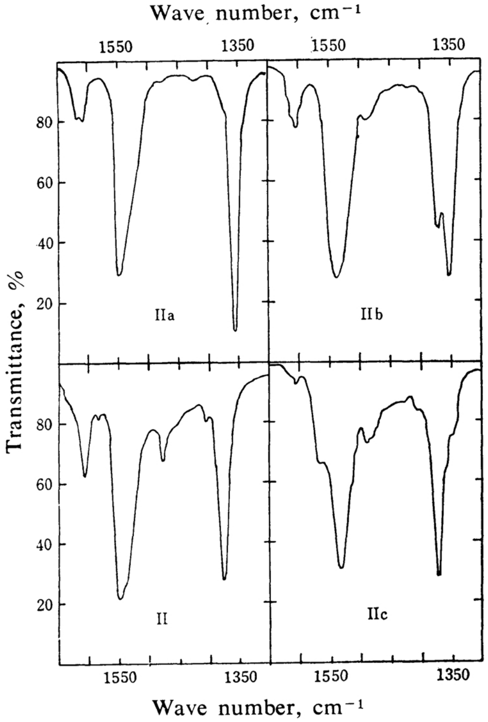

Fig. 2. Infrared spectra of *t*-butyl-*m*-dinitrobenzenes.

TABLE I. NO$_2$-STRETCHING VIBRATION BANDS OF *m*-DINITROBENZENES

m-Dinitrobenzenes	Band frequency cm^{-1}		Transmittance %	
	ν_a	ν_s	ν_a	ν_s
Unsubstituted, IIa	1545	1352	28.5	10.5
4-*t*-Butyl-, IIb	1537	1372 1354	28.0	44.0 27.5
4,6-Di-*t*-butyl, IIc	1535	1372	31.0	28.0
2,4,6-Tri-*t*-butyl-, II	1548	1375	22.0	28.0

N–O stretching vibrations shown in Fig. 2 and Table I. The most characteristic feature is the change in the N–O symmetric stretching vibration band of the dinitro-*t*-butylbenzenes from that of IIa. The shifts of these bands to higher frequencies, accompanied by the decreases in the apparent intensities relative to their N–O antisymmetric stretching bands, also suggest that the nitro groups in these compounds are sterically hindered.[7] Moreover, the N–O symmetric stretching band of IIb, in which only one nitro group is sterically hindered, splits into a doublet; on the contrary, that of II is a sharp singlet, as are those of IIa and IIc, in which the two nitro groups are indistinguishable.

On the basis of these data, the structure of II is assumed as 2,4,6-tri-*t*-butyl-*m*-dinitrobenzene.

An absolutely negative result for the high pressure catalytic hydrogenation of I over Raney nickel has been reported by other workers.[8] Indeed, we found I to be reduced very slowly in a low pressure and over this catalyst, as is shown in Fig. 1, but at a high pressure and over 50°C it was readily reduced under the same catalyst to afford almost quantitatively the corresponding aniline, 2,4,6-tri-*t*-butylaniline (III).

Nitration in acetic acid and acetic anhydride converted III into a di-*t*-butylnitroaniline (IV) in which a *t*-butyl group was replaced by a nitro group. The m.p. (256°C) of IV was distinctly different from that (89.5°C) of 2,4-di-*t*-butyl-6-nitroaniline,[9] one of the expected products in this dealkylnitration. Therefore, it was shown that the *t*-butyl group at the para-position of the amino group was replaced by the nitro group.

Several attempts to convert IV directly to a known 5-nitro-*m*-di-*t*-butylbenzene[9] by diazotization, under varying conditions, were unsuccessful. However, upon the reduction of the nitro group, the resulting diamine V could be converted, by oxidation with ferric chloride, to the known 2,6-di-*t*-butylbenzoquinone (VI).[10]

This experiment indicates that V is *p*-diamine and that, hence, IV is 2,6-di-*t*-butyl-4-nitroaniline. This result was in accordance with the assignment of the structure for IV made by other workers[6] on the basis of the rate constant of the catalytic deacetylation of the bisacetylamino compound derived from IV.

It is interesting to compare the present nitrations with those of the *sym*-tri-alkylbenzenes and with some of their amino derivatives.

Trinitro-derivatives have been obtained from mesitylene, triisopropylbenzene,[1b] and *t*-butyl-*m*-xylene[11] without any replacement of the alkyl groups; however, the introduction of more than two nitro groups into *m*-di-*t*-butyltoluene[12] has been shown to be unsuccessful. From mesidine, 2,4,6-tri-isopropylaniline,[1b] and 3,5-di-*t*-butyl-*o*-toluidine[12], only the usual nitration products have been reported.

Therefore, the failure to obtain the trinitro-derivative of *sym*-tri-*t*-butylbenzene, even with the application of drastic nitration conditions, may definitely be ascribed to the steric effect of the bulky *t*-butyl groups. The replacement

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[7] T. Kinugasa and S. Watarai, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **83**, 472, 476, (1962).

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

[9] T. Kinugasa and S. Watarai, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **83**, 333 (1962).

[10] G. R. Yohe et al., *J. Org. Chem.*, **21**, 1289 (1956).

[11] A. Baur, *Ber.*, **24**, 2841 (1891).

[12] B. M. Wepster et al., *Rec. trav. chim.*, **75**, 301 (1956).

of the *p-t*-butyl group by the nitro group, in the case of the nitration of IV, also seems to be caused by the steric effect of these groups. Undoubtedly the *t*-butyl group activated by the electron-releasing substiuent, such as the *p*-amino group, is displaced with remarkable ease in the electrophilic substitution.5)

Experimental

2, 4, 6-Tri-*t*-butylnitrobenzene (I), was prepared from 1,3,5-tri-*t*-butylbenzene13) in the manner described in the literature ;2) 80% of yield, m. p. 200～203°C.

Found: C, 74.37; H, 10.13; N, 5.08. Calcd. for $C_{18}H_{29}O_2N$: C, 74.18; H, 10.13; N, 4.81%.

The Nitration of I: 2, 4, 6-Tri-*t*-butyl-*m*-dinitrobenzene (III).—A finely ground mononitro derivative (7 g. of I) was added in small portions to the stirred mixture of 13 ml. of fuming nitric acid ($d=1.50$) and 36 ml. of concentrated sulfuric acid at 20°C. The reaction mixture was subsequently heated to 80°C for 5 hr.; the product, when cooled, was then poured onto a large amount of ice. The yellow solid was collected, washed with water, dilute ammonia and water, and then dried. It weighed 6.6 g. and melted at 220～269°C.

Purification by recrystallization from benzene and by chromatography on alumina with benzene-ligroin (b. p. 80～100°C) gave pale yellow needles (m. p. 290～292°C). The molecular weight of this product was determined by the Rast method.

Found: C, 64.27; H, 8.42; N, 8.58%; mol. wt., 324.1. Calcd. for $C_{18}H_{28}O_4N_2$: C, 64.26; H, 8.39; N, 8.33%; mol. wt., 336.4.

The Reduction of I at a High Pressure: 2, 4, 6-Tri-*t*-butylaniline (III).—A suspension of 30 g. of I and a catalyst prepared from 20 g. of Raney-nickel-alloy in 300 ml. of ethanol was reduced with hydrogen (60 kg./cm^2) at 50～80°C for 3.5 hr. in a 500 ml. autoclave. After the catalyst had been filtered off, the solvent was distilled off; 22 g. of practically pure III with a m. p. of 143～145°C was thus obtained. One recrystallization from ethanol gave a sample melting at 145°C.

Found: C, 82.65; H, 11.79; N, 5.61%. Calcd. for $C_{18}H_{31}N$: C, 82.69; H, 11.95; N, 5.36%.

The Nitration of III: 2, 6-Di-*t*-butyl-4-nitroaniline (IV).—This was prepared in essentially the manner described in the literature,6) except that the reaction was carried out at 40°C, because most of the starting material (about 70%) was recovered at −10～−12°C, as is mentioned in the literature.

To a solution of 5.2 g. of III in a mixture of 40 ml. of acetic anhydride and 20 ml. of glacial acetic acid, 22 ml. of a mixture of 1 vol. of nitric acid ($d=1.52$) and 19 vol. of glacial acetic acid was added drop by drop at 40°C; hereupon III crystallized out in yellow needles. While the stirring was continued, the crystals of III disappeared and other crystalline material IV was obtained in the reaction mixture. After a total reaction time of 4.5 hr., the product was collected and dried; 1.9 g. Upon treatment with water, the filtrate gave further crops; 0.1 g.

The recrystallization of this product (m. p. 240～247°C) from benzene-ethanol (10 : 1) gave IV as pale yellow leaf crystals; m. p. 256°C.

Found: C, 66.92; H, 9.00; N, 10.92%. Calcd. for $C_{14}H_{22}N_2O_2$: C, 67.17; H, 8.86; N, 11.69%.

2, 6-Di-*t*-butyl-*p*-diaminobenzene (V).—A suspension of 3.0 g. of IV in 100 ml. of ethanol was shaken with hydrogen at room temperature under atmospheric pressure over Raney nickel for 6 hr. The catalyst was then filtered off under a stream of nitrogen. After the filtrate had been saturated with dry hydrogen chloride, the solvent was distilled off under reduced pressure. The dihydrochloride of V separated in the crystalline state. This salt was collected, washed with dry ether, and dried; yield 3.4 g. (96%). Recrystallization from ethanol saturated with dry hydrogen chloride gave a colorless salt which melted at 204°C (decomp.).

Found: Cl, 23.42%. Calcd. for $C_{14}H_{26}N_2Cl_2$: Cl, 24.17%.

Through a treatment of the salt with a dilute alkali solution, the base was liberated; m. p. 94～95°C.

2, 6-Di-*t*-butyl-*p*-benzoquinone (VI).—A suspension of 1 g. of the above salt in a solution of 15 g. of ferric chloride crystals in a mixture of 7.6 ml. of water and 1 ml. of concentrated hydrochloric acid was stirred overnight at room temperature and was then heated on a water bath for 2 hr. The product was then collected through steam distillation. The yield was 0.6 g. of orange yellow crystals (VI); 80% of yield, m. p. 66.5～68.5°C. Recrystallization from aqueous ethanol gave a sample melting at 67.5°C; this sample showed no depression on admixture with an authentic sample synthesized from 2,6-di-*t*-butylphenol.10)

Found: C, 76.48; H, 9.12%. Calcd. for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15%.

The Preparation of Other *m*-Dinitrobenzenes.—IIa, IIb and IIc were prepared by the standard procedures.

IIa, m. p. 90°C; IIb, m. p. 61～63°C; IIc, 165～166°C.

The Reduction of Dinitro Derivatives (Fig. 1).—A mixture of the purified dinitro compound (0.005 mol.) in 50 ml. ethanol was shaken with hydrogen for several hours at room temperature under atmospheric pressure in the presence of a catalyst prepared from 5 g. of Raney-nickel-alloy (5 g. of alloy for 0.01 mol., of I in 100 ml. ethanol) until no more hydrogen was absorbed. About 10～13% more than the stoichiometric quantity cf hydrogen for the reduction of nitro groups was absorbed. II resisted hydrogenation very strongly; most of it was recovered.

Infrared Spectra.—The spectra of 0.02 M solutions in chloroform were measured in a 0.511 mm. cell on a Hitachi EPI-2 double-beam prism spectrometer (with a rock salt prism).

The frequencies (in wave numbers) and the transmittance (%) of the symmetric (ν_s) and antisymmetric (ν_a) stretching modes of the nitro-group are summarized in Table I.

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13) S. Watarai, This Bulletin, 36, 747 (1963).

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