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Nitration of Some 2-Iodo-1,3,5-trialkylbenzenes. Competition between Nitrodeprotonation and Nitrodeiodination. Discussion of Steric Effects

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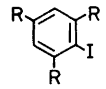
The nitration of some 2-iodo-1,3,5-trialkylbenzenes in a nitric acid–nitromethane medium has been investigated. The nitronium ion is found to replace three different substituents competitively, hydrogen, iodine or, to a smaller extent, an alkyl group. The expelled iodonium ion forms some iodo electrophile, which attacks the substrate in a secondary reaction and gives rise to a 2,4-diiodo-1,3,5-trialkylbenzene, which is then nitrodeiodinated. The product of this last reaction and that of the primary nitrodeprotonation are identical, which makes a careful kinetic analysis necessary. The true ratio between the nitrodeiodination and the nitrodeprotonation rate constants is determined *via* a simulation of the course of the total reaction. The rate ratios have been determined for eight iodotrialkylbenzenes with different steric properties and found to vary with the degree of branching in the alkyl substituents. The nitrodeiodination is favoured when the branching is in the α-position of each chain and disfavoured when the branching is in the β-position. The nitrodeiodination–nitrodeprotonation rate ratio is invariant with the medium, and the product-determining transition states are thus similar for the two reactions.

There has been a growing interest in aromatic nitration lately,[1] especially concerning *ipso*-attack and the medium-dependent consequences thereof.[2] It has been shown that possible fates of *ipso* Wheland intermediates are *e.g.*

1. capture by a nucleophile
2. rearrangement by 1,2-migration of the nitro group with loss of a proton
3. loss of the attacked group, *i.e.*, *ipso* substitution.[3]

In this laboratory an interest has been taken in type 3 as manifested in attack on an iodine-substituted position. The present work deals mainly with the steric effects on nitrodeiodination compared to nitrodeprotonation. These effects are expected to be different as the iodine is exchanged for a smaller substituent and the hydrogen for a larger one. Earlier investigations have ended in a somewhat vague picture, since only 2-iodomesitylene and 2-iodo-1,3,5-trineopentylbenzene have been compared.[4] In order to enhance the insight into the effects of different alkyl groups on the choice between nitrodeprotonation and nitrodeiodination, a series of 2-iodo-1,3,5-trialkylbenzenes, *1a–1h*, has been synthesized and the rate ratios



1a: R = $-CH_3$ *1e*: R = $-CH_2CH(CH_3)_2$
1b: R = $-CH_2CH_3$ *1f*: R = $-CH(CH_3)CH_2CH_3$
1c: R = $-CH_2CH_2CH_3$ *1g*: R = $-CH_2C(CH_3)_3$
1d: R = $-CH(CH_3)_2$ *1h*: R = $-C(CH_3)_3$

nitrodeiodination–nitrodeprotonation have been investigated. These substrates offer electronically equal attack positions (hydrogen- or iodine-substituted) for the nitronium ion apart from the difference in *ipso* and *meta* effects of the substituents in question, which, of course, is impossible to evade. Moreover, *ipso*-attacks on the alkyl-substituted positions, C–1, C–3, C–5, are less likely to occur since these positions are not as activated as C–2

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$$HNO_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2^+ \xrightarrow[ArHI\ k_C]{k_B} \begin{matrix} ArHNO_2 + I^+ \\ ArINO_2 + H^+ \end{matrix}$$

$$I^+ \overset{k_I}{\rightarrow} \text{“}I^+ \text{ electrophile”} \xrightarrow[ArHI]{k_D} ArI_2 \xrightarrow[NO_2^+]{k_E} ArINO_2 + I^+$$

Scheme 1.

and C−4 (*cf.* no methyl attack is found in nitration of mesitylene,[5] in 2-chloro-1,3,5-trimethylbenzene traces of attack are found at C−5 and only to an extent of 6 % at C−1[6]). Consequently, the rate constant ratio should reflect the true activation energy difference for direct attack without larger disturbances from nitro group migrations. One substrate with less steric crowding, 1-iodo-2,4-dimethylbenzene, *2*, has been studied for comparison.

The nitration of the substrates *1a*, *1d*, *1e* and *1g* has been discussed from the kinetic point of view and a method to analyze the course of the reaction has been published.[7] This method is used in the present work to get reliable values of the ratio between the deiodination and the deprotonation rate constants in spite of interfering consecutive reactions.

RESULTS

The nitrations have been made in a nitric acid–nitromethane medium and followed by taking aliquots at proper time intervals. The previously published kinetic analysis method[7] can briefly be described as a simulation using numeric integration of the rate equations derived from the assumed reaction scheme, Scheme 1.

The nitronium ion is assumed to be present in a steady-state concentration. In certain cases the nitrodeiodination process is accompanied by iodination which gives rise to 2,4-diiodo-1,3,5-trialkylbenzene. The nitrodeiodination of this substrate gives the same product as the nitrodeprotonation of the 2-iodo-1,3,5-trialkylbenzene, *1*. It is thus important to make a careful analysis, based on kinetic data, to ensure that the rate ratio deiodination–deprotonation is based on the rate constants for the primary formation of the products. In the previous publication[7] an alternative iodination reaction path *via* I_2 and I_3^+ was suggested but here the above possibility is chosen for the sake of simplicity. Both alternatives give good reproduction of the results.

As the nitration medium is rather complicated, containing nitric acid, water, urea and nitromethane, it is hardly possible to reproduce all rate constants exactly from one experiment to another. Thus it is difficult to compare rate constants from different kinetic runs. A change in any of the ingredients above will lead to a change both in the pseudo first-order rate constant k_1 and in the equilibrium constant $K = k_1/k_{-1}$ which is

Table 1. Rate constants for the nitration of substrates *1a*–*1g*. Conditions: 4.94 M nitric acid, 1.32 M water and 0.028 M urea in nitromethane at 0 °C. The simulation acid parameters are: $k_1 = 6.0 \times 10^{-7}$ s^{-1} and $K = k_1/k_{-1} = 2.4 \times 10^{-14}$.

Substrate	$k_B \times 10^{-9}$/M^{-1} s^{-1} [b]		$k_C \times 10^{-9}$/M^{-1} s^{-1} [b]		$k_F \times 10^{-9}$/M^{-1} s^{-1} [c]
1a	1.50;	1.55 [a]	2.49;	2.42 [a]	
1b	0.86		1.04		
1c	0.71		0.92		
1d		0.56 [a]		0.29 [a]	0.052 [a]
1e		0.83 [a]		1.37 [a]	
1f	0.19		0.090		0.040
1g	0.31;	0.58 [a]	1.08;	2.14 [a]	

[a] Conditions see Ref. 7. [b] Definitions see Scheme 1. [c] The bimolecular rate constant for the nitrodealkylation.

impossible to measure. The starting value for K is an estimated one from the literature.[8a] As the method gives comparable rate constants only for those substrates which are nitrated in literally equal media, the following procedure was chosen to make possible a qualitative comparison with earlier measurements on *1a*, *1d*, *1e* and *1g*. The nitrations (followed in parallel runs with acid from the same batch. *i.e.* with the same acid parameters) of the substrates *1b*, *1c* and *1f* plus *1a* and *1g* as references are analyzed. When the initial slope and the form of the reaction curve for *1a* has given a value of k_1 (see Ref. 7), the equilibrium constant is varied until it gives approximately the same rate constants for *1a* as the previous measurement.[7] The same acid parameters are then used for the other substrates. The resulting rate constants are given in Table 1 together with those for *1a*, *1d*, *1e* and *1g* published earlier.

The kinetic analyses show that the rate constant ratio nitrodeiodination – nitrodeprotonation equals the initial product ratio. At least three kinetic runs have been made with substrates *1a*–*1g* with approximately 5 M nitric acid. The average values of these rate-constant ratios are accounted for in Table 2.

Substrate *1h* is a gift from Prof. P. C. Myhre. It arrived during the preparation of this manuscript and time has only allowed one preliminary experiment. No traces of nitrodeprotonated product could be detected. The dominating product was 2-nitro-1,3,5-tri-*tert*-butylbenzene. Two other products were found in smaller amounts; when 22% starting material was left there were 14 and 11% of these together with 53% of the nitrodeiodinated product. For the first-mentioned unknown product the yield curve showed a sigmoid form which points at an iodination process,[7] which, according to GLC/MS, might be iododealkylation giving 2,5-diiodo-1,3-di-*tert*-butylbenzene. GLC/MS results indicate that the other product may be 2-iodo-5-nitro-1,3-di-*tert*-butylbenzene resulting from nitrodealkylation.

Nitration of 1-iodo-2,4-dimethylbenzene, *2*, gives 2,4-dimethyl-1-nitrobenzene, 1-iodo-2,4-dimethyl-5-nitrobenzene, and a smaller amount of 1-iodo-2,4-dimethyl-3-nitrobenzene together with 1,5-diiodo-2,4-dimethylbenzene from a consecutive reaction. The yields from deiodination and deprotonation in the otherwise equivalent positions C–1 and C–5 have been used to calculate the product ratio. No kinetic analysis was made in this case and only the initial product ratio values are used. The average value of three measurements is given in Table 2.

The iodination process is found to be medium-dependent. The value of k_I varies from 0.95×10^{-3} s^{-1} to 5.3×10^{-3} s^{-1} when the nitric acid concentration is varied from 4.94 to 5.10 M. The k_D and k_I values for substrates *1a*, *1b*, *1c* and *1d* are given in Table 3. No traces of iodinated product have been detected with *1g* and *1f*. For *1e* slight iodination was observed in a preliminary experiment but not in those being analyzed kinetically.

Nitrodealkylation occurs with substrate *1f* as with *1d*[7] though to a somewhat larger extent. The ratio nitrodealkylation – total nitration is 0.125 compared to 0.058 for substrate *1d*. The kinetics of the nitrodealkylation seems to follow the same pattern

Table 2. Ratios between nitrodeiodination and nitrodeprotonation rate constants adjusted for the number of available positions. The values are the average of at least three measurements.

Substrate	n_α[a]	n_β[a]	ν[b]	Deiodination – deprotonation
2				0.80±0.04
1a	0	0	0.56	1.22±0.06
1b	1	0	0.68	1.60±0.05
1d	2	0	0.98	3.75±0.11
1h	3	0	1.34	no traces of nitrodeprotonation
1c	1	1	0.68	1.56±0.06
1e	1	2	0.68	1.24±0.04
1g	1	3	0.70	0.57±0.02
1f	2	1	1.00	4.18±0.20

[a] The number of carbons in the α- and β-positions, respectively. [b] The Charton ν-values[16] for R–CH_2- substituents corresponding to the 1,3,5-tri(R)-benzene derivatives *1a*–*1f*.

Table 3. Iodination parameters for substrates *1a*–*1d*. Conditions, see Table 1.

Substrate	$k_I \times 10^3/s^{-1}$		$k_D/M^{-1}\,s^{-1}$	
1a	0.95;	5.3[a]	40;	6.0[a]
1b	0.95		4.0×10^{-2}	
1c	0.95		2.0×10^{-2}	
1d		5.3[a]		4.9×10^{-3}[a]

[a] From Ref. 7.

$$HNO_3 \overset{1}{\rightleftharpoons} NO_2^+ \overset{2}{\underset{ArH}{\rightleftharpoons}} ArH \cdot NO_2^+ \overset{3}{\rightleftharpoons} Ar^+\!\!\diagup\!\!\diagdown \begin{matrix} NO_2 \\ H \end{matrix} \overset{4}{\rightarrow} \text{products}$$

Scheme 2.

as the other competing nitration reactions and the second-order rate constant, k_F, is given in Table 1.

Besides the three kinetic runs accounted for above, at least five different runs with varying concentrations of nitric acid in nitromethane were carried through with each of the substrates *1a–1g*. The half lives ranged from 5 to 60 min. The initial product ratios differed only within the experimental error.

A preliminary investigation[9] of the nitrode-iodination-nitrodeprotonation product ratio for *1g* in the following media has been carried out: nitroethane, 2-nitropropane and 1-nitropropane with nitric acid and catalytic amounts of sulfuric acid, *p*-fluoronitrobenzene and sulfolane with nitric acid only. The ratio had the same value as in nitromethane within an experimental accuracy of 5%. A similar test on *1d* in nitroethane and 1-nitropropane with nitric acid only gave the same result.

DISCUSSION

The most widely accepted mechanism for aromatic nitration is given in Scheme 2.[10]

Here one of the steps 1–3 is usually rate-limiting, depending upon the reactivity of the substrate. For a few sterically crowded molecules step 4 has been found to be rate-limiting.[11] As can be seen from the very small but chemically significant span in the rate constants as well as from the similarity of the reactivity to that of *m*-xylene,[12] the 2-iodo-1,3,5-trialkylbenzenes react with rates close to the encounter rate. The rate constant for the consumption of *1a* as measured by our method is 3.97×10^9 M^{-1} s^{-1} when K is assumed to be $10^{-13.7}$. The same assumption gives the value 1.02×10^{10} M^{-1} s^{-1} for mesitylene in a similar medium.[12] The relative rate of mesitylene to *1a* is then 2.6 which is close to the ratio of 2.7 between the rates for mesitylene and *m*-xylene earlier observed.[12] The kinetics also show that the production of NO_2^+ is partly rate-determining (zeroth- to somewhat less than first-order in the aromatics). Thus the product-determining step is often different from the rate-limiting step. As there seem to be no effects of the solvent on the product ratio, it can be assumed that the two product-determining transition states are similar. The course of the reaction can then be described as an intramolecular competition, where, once the encounter pair is established, the choice between the two positions (iodine- or hydrogen-substituted) comes out independent of the reaction medium.

The choice between the two positions may be expected to be governed by two main factors in the substrate, the electronic one and the steric one.

Taking the result in the nitration of 1-iodo-2,4-dimethylbenzene as a starting point, the amount of nitronium ion attack at C–5 exceeds the amount of attack at the iodine *ipso* position, C–1, giving the ratio 1.25. Apparently, iodine deactivates the *ipso* position slightly more than the position *meta* to iodine, C–5. Perrin has found partial rate factors[13] (relative to anisole) for nitration of *p*-iodoanisole of 0.18 for the iodo *ipso* position and 0.12 for the position *meta* to iodine. However, according to Bacciochi and Illuminati[14] the polar effect (which is the dominating one at the *ipso* and *meta* positions) should be stronger at the short distance of the *ipso* position, which is consistent with our results for *2*.

Comparing the deiodination–deprotonation ratio of 0.80 in *2* with the corresponding ratios for the various iodotrialkylbenzenes shows deviations in both directions, the reasons of which ought to be found in steric interactions. The van der Waals volumes[15] of the hydrogen atom, 3.45 cm^3/mol, the nitro group, 11.80 cm^3/mol, and the iodine atom, 19.93 cm^3/mol make these substituents quite different. The expected sensitivity for steric crowding will thus be different for the two reactions. The rate ratio, being the result of an intramolecular competition between the reactions, is a measure of the difference in free energy of activation between the two pathways. Fig. 1 shows a plot of the logarithm of the rate ratios *versus* v which is a steric parameter (developed by Charton[16]) based on the van der Waals volumes. The carbon atom in the benzene nucleus between the attacked position and the substituent is taken into consideration in the present choice of v value (see Table 2). From Fig. 1 it

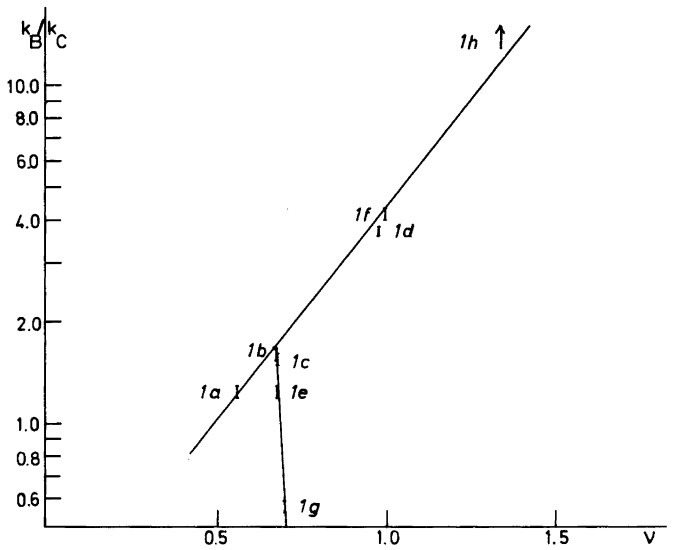

Fig. 1. Semilogarithmic plot of the nitrodeiodination–nitrodeprotonation rate constant ratio in the nitration of substrates *1a–1h versus* the Charton steric parameter ν[16] for $R-CH_2$ substituents corresponding to the 1,3,5-tri(R)-benzene derivatives.

is evident that the deiodination reaction is favoured (*i.e.* the ratio deiodination–deprotonation increases) when ν gets larger as long as the branching is in the α-position. In the extreme case, *1h*, the nitrodeprotonation is totally suppressed. When, on the other hand, the branching is in the β-position the deiodination seems to be disfavoured. In *1g*, which has a maximum of β-brancing, the ratio is even smaller than in *2*.

An inspection of the rate constants in Table 1 reveals that the differences in rate constants are somewhat larger for nitrodeprotonation than for nitrodeiodination, which might be due to the larger steric strain in the nitrodeprotonation product with its iodine retained. It also shows that the nitrodeiodination rate constants are of closely similar magnitude for *1d*, *1e*, *1f* and *1g*, which have at least two carbon atoms either at the α- or at the β-position. In the nitrodeprotonation reaction there seems to be a trend giving larger rate constants with more β-carbons and smaller with more α-carbons (*e.g.*, a factor of ten between *1f* and *1g*). Similar trends are documented in an elaborate investigation of the steric effects in the nitration of monoalkylbenzenes by Baas and Wepster.[17] The relative amount of *ortho* substitution decreases in the series methyl-, ethyl-, isopropyl- and *tert*-butylbenzene and increases going from ethyl-, propyl- and isobutyl- to neopentylbenzene. The last-mentioned result is explained by "the increase of the steric hindrance is compensated by the increase of the polarizability of the alkyl groups". The fact that the reactivity in the iodoposition, C–2, in *1g* seems to be depressed, compared to that of C–4, could be explained by the existence of attractive forces between the alkyl groups in trineopentylbenzene which make them interact outside the plane of the benzene ring. Apparently, the hindrance from these side chain interactions would make the departure of the iodonium ion more difficult than that of the proton. However, the differences are very small and the reactivity of these molecules depends upon a delicate balance between electronic effects from the alkyl substituents,[19] steric hindrance to solvation of the transition state and steric influences around the reaction centre, which makes an unambiguous interpretation of the relative rate constants rather unattainable.

The steric effects on the iodination reaction can be noted to be different from those on the nitration reaction. The suppression of the iodination reaction seems to increase as the steric crowding increases regardless of where the branching is. Further-

more, the differences are much larger and probably not diminished by encounter control.

There are also steric effects on the nitrodealkylation, as can be expected. The steric strain increases in the series *1d* < *1f* < *1h* and the ratio between the yield from the dealkylation reaction and the total nitration yield rises accordingly, being 0.058, 0.125 and 0.172, respectively.

EXPERIMENTAL

The method and equipment used in this investigation have been accounted for earlier.[7] In the case of substrate *2* the GLC analyses were made on 2 m × 3 mm OV-225 columns in order to get sufficient separation. All kinetic measurements were made with substrates of >99 % purity according to GLC.

The substrates *1a*, *1d*, *1e*, *1g* and their derivatives have been prepared for earlier investigations.[7] Substrate *1h* and 2-nitro-1,3,5-tri-*tert*-butylbenzene are a gift from Professor P. C. Myhre. All substrates used were identified by means of NMR and MS. Spectra are only given for the new compounds but are available on request.

1-Iodo-2,4-dimethylbenzene, *2*, and *1,5-diiodo-2,4-dimethylbenzene* were made *via* iodination according to Keefer and Andrews[20] of commercially available *m*-xylene. Substrate *2* was isolated from the mixture by distillation (46 °C, 20 Pa). The diiodo compound was recrystallized from hexane.

2,4-Dimethyl-1-nitrobenzene was obtained from nitration of *m*-xylene by nitric acid in nitromethane and was purified by crystallization from pentane, the m.p. was below room temperature.

1-Iodo-2,4-dimethyl-3-nitrobenzene was not isolated from the nitration mixture but identified by means of GLC/MS. The 5-nitro isomer has been identified (see below) and has a different retention time on GLC. When 1,3-dimethylbenzene is nitrated no trace of the 5-nitro isomer is detected.[8b] The fragment M − OH indicates that the nitro group is in a position next to an alkyl group.[21] MS: [IP 70 eV; *m/e* (% rel. int.)]: 277 (95, M), 260(100, M − OH), 232(11), 133(41), 105(32), 104(67), 103(35), 91(12), 78(33), 77(32).

1-Iodo-2,4-dimethyl-5-nitrobenzene was isolated from the nitration mixture by HPLC (on a 30 cm × 7.7 mm I.D. column packed with Polygosil 60-10, eluted with hexane/5 % ethyl acetate).

2-Iodo-1,3,5-triethylbenzene, *1b*, and *2,4-diiodo-1,3,5-triethylbenzene* were prepared from commercially available 1,3,5-triethylbenzene *via* iodination according to Marton and Martinsson.[22] Substrate *1b* was chromatographed on a silica gel column eluted with hexane. The diiodo compound was recrystallized from pentane, 98 % pure (GLC), m.p. 25 − 30 °C.

2-Nitro-1,3,5-triethylbenzene was obtained from commercial 1,3,5-triethylbenzene *via* nitration with nitric acid in nitromethane and chromatography on silica gel − hexane.

2-Iodo-4-nitro-1,3,5-triethylbenzene was made *via* preparative nitrodeiodination of 2,4-diiodo-1,3,5-triethylbenzene with nitric acid in nitromethane.[23] The product mixture was chromatographed on silica gel − hexane which gave the pure product in 60 % yield.

2-Iodo-1,3,5-tripropylbenzene, *1c*, was synthesized in five steps from mesitylene *via* a triple Wittig reaction with acetaldehyde, which gave the unsaturated product, 1,3,5-tris(1-propenyl)benzene, as an isomeric mixture in 31 % yield, followed by hydrogenation and iodination, all according to a procedure previously described.[7] MS [IP 50 eV; *m/e* (% rel. int.)]: 330 (79, M), 301(100, M − C_2H_5), 202(25), 175(63), 173(37), 159(22), 133(32), 131(35), 117(24). Mol. wt., obs. 330.0838 ± 0.005, calc. for $C_{15}H_{23}I$ 330.0846. ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.92 (3H,t,J = 8 Hz), 0.99(6H,t,J = 8 Hz), 1.61 (6H, double sextet, J = 8 Hz), 2.47(2H,t,J = 8 Hz), 2.71(4H,t,J = 8 Hz), 6.82(2H,s).

2-Nitro-1,3,5-tripropylbenzene, *2-iodo-4-nitro-1,3,5-tripropylbenzene* and *2,4-diiodo-1,3,5-tripropylbenzene* were isolated from the product mixture of the nitration of *1c* [according to the kinetic procedure described earlier[7] ($HNO_3 - CH_3NO_2$)] by means of HPLC (reverse phase column, RP-18 − acetonitrile). 2-Nitro-1,3,5-tripropylbenzene: MS [IP 70 eV; *m/e* (% rel. int.)] 249(1, M), 232(5, M − OH), 219(20), 217(38), 215(24), 190(85), 188(100), 186(62). ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.95(9H,t, J = 9 Hz), 1.63(6H, double sextet, J = 9 Hz), 2.50 (4H,t,J = 9 Hz), 2.57(2H,t,J = 9 Hz), 6.92(2H,s).

2-Iodo-4-nitro-1,3,5-tripropylbenzene: MS [IP 70 eV; *m/e* (% rel. int.)]: 375(76, M), 358(100, M − OH), 330(36), 302(36), 202(71). ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.93(3H,t,J = 8.5 Hz), 1.01(3H,t, J = 8.5 Hz), 1.03(3H,t,J = 8.5 Hz), 1.49 − 2.22(6H,m), 2.44 (2H,t,J = 8.5 Hz), 2.65(2H,t,J = 8.5 Hz), 2.75 (2H,t,J = 8.5 Hz), 6.99(1H,s).

2,4-Diiodo-1,3,5-tripropylbenzene: MS [IP 70 eV; *m/e* (% rel. int.)]: 456(100, M), 427(70, M − C_2H_5), 301(22), 173(75), 131(27), 129(25), 128(22). ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.98(6H,t,J = 8.5 Hz), 1.07(3H,t,J = 8.5 Hz), 1.60(6H, double sextet, J = 8.5 Hz), 2.70(4H,t,J = 8.5 Hz), 3.23(2H,t,J = 8.5 Hz), 6.86(1H,s).

2-Iodo-1,3,5-tris(1-methylpropyl)benzene, *1f*, was synthesized in four steps from 1,3,5-triacetylbenzene *via* a triple Wittig reaction with ethyltriphenylphosphonium bromide[24] in DMSO with butyl lithium as base, which gave the unsaturated product, 1,3,5-tris(1-methylpropenyl)benzene, as an

isomeric mixture in 72 % yield. The same procedure as for *1c* was then used.[7] MS [IP 50 eV; *m/e* (% rel. int.)]: 372(38, M), 343(100, M − C_2H_5). Mol. wt., obs. 372.1305 ± 0.005, calc. for $C_{18}H_{29}I$ 372.1315. ^1H NMR (270 MHz, $CDCl_3$): δ 0.82, 0.89, 0.90 (9H, 3 triplets, $J = 7.3$ Hz), 1.19. 1.22(9H, 2 doublets, $J = 7.3$ Hz), 1.44 − 1.75(6H, m, $J = 7.3$ Hz), 2.55(1H, sextet, $J = 7.3$ Hz); 3.20(2H, sextet, $J = 7.3$ Hz), 6.80(2H,s).

1,3,5-Tris(1-methylpropyl)-2-nitrobenzene and *2-iodo-1,3,5-tris(1-methylpropyl)-4-nitrobenzene* were isolated from the nitration mixture by means of HPLC (referse phase column, RP-18 − acetonitrile). The 1,3,5-tris(1-methylpropyl)-2-nitrobenzene fraction also contained the nitrodealkylated product, *2-iodo-1,3-bis(1-methylpropyl)-5-nitrobenzene*. This mixture was chromatographed once more with HPLC on a silica gel column (see above) eluted with hexane which gave a very good separation.

1,3,5-Tris(1-methylpropyl)-2-nitrobenzene: MS [IP 70 eV; *m/e* (% rel. int.)]: 291(7, M), 274(100, M − OH), 262(19), 244(38), 232(27), 218(22), 202(19), 174(20), 146(84), 117(21), 91(26). ^1H NMR (270 MHz, $CDCl_3$): δ 0.83(9H, three triplets, $J = 7.1$ Hz), 1.22, 1.23(9H, 2 doublets, $J = 7.1$ Hz), 1.61, (6H, m, $J = 7.1$ Hz), 2.51(2H, sextet, $J = 7.1$ Hz), 2.62(1H, sextet, $J = 7.1$ Hz), 6.94 (2H,s).

2-Iodo-1,3,5-tris(1-methylpropyl)-4-nitrobenzene: MS [IP 70 eV; *m/e* (% rel. int.)]: 417(69, M), 400(100, M − OH), 388(51), 370(34), 358(37), 214(51), 187(32), 128(31), 115(27), 91(27). ^1H NMR (270 MHz, $CDCl_3$, 60 °C): δ 0.83, 0.83, 0.90, 0.91(9H, 4 triplets, $J = 7.1$ Hz), 1.21(9H, d, $J = 7.1$ Hz), 1.44 − 1.77 (6H, m), 2.45(1H, sextet, $J = 7.1$ Hz), 3.32(1H, 2 sextets, $J = 7.1$ Hz), 3.46 − 3.60(1H, broad peak), 7.01(1H,s).

2-Iodo-1,3-bis(1-methylpropyl)-5-nitrobenzene: MS [IP 70 eV; *m/e* (% rel. int.)]: 361(42, M), 332(100, M − C_2H_5), 128(15), 115(15), 91(9). ^1H NMR (270 MHz, $CDCl_3$): δ 0.91(6H, 2 triplets, $J = 7.1$ Hz), 1.24(6H, d, $J = 7.1$ Hz), 1.53 − 1.76 (4H, m, $J = 7.1$ Hz), 3.33(2H, sextet, $J = 7.1$ Hz), 7.84(2H,s).

MS for the first eluted by-product from nitration of *1h*, which is assumed to be *2,5-diiodo-1,3-di-tert-butylbenzene:* [IP 70 eV; *m/e* (% rel. int.)]: 442(34, M), 427(37, M − CH_3), 399(17), 173(20), 143(21), 141(20), 128(31), 115(35), 91(37), 77(26), 65(26), 57(100).

MS for the assumed dealkylation product, *2-iodo-5-nitro-1,3-di-tert-butylbenzene*, [IP 70 eV; *m/e* (% rel. int.)]: 361(24 M), 346(27, M − CH_3), 331(16), 318(15), 192(26), 173(27), 148(40), 128(27), 115(29), 91(41), 77(27), 65(27), 57(100).

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