

# Nitration of Some 2-Iodo-1,3,5-trialkylbenzenes. Simulation and Discussion of the Kinetics

INGEGÄRD JOHANSSON and THOMAS OLSSON

Department of Organic Chemistry, University of Göteborg and Chalmers University of Technology, S-412 96 Göteborg, Sweden

In the nitration of 2-iodomesitylene, 2-iodo-1,3,5-triisobutylbenzene, 2-iodo-1,3,5-trineophenylbenzene and 2-iodo-1,3,5-triisopropylbenzene three main reactions are observed, nitrodeprotonation, nitrodeiodination and – in the first case – iodination by some iodo electrophile emanating from the expelled iodonium ion. The kinetics are found to vary with the reactivity and initial concentration of the aromatic substrate from pseudo zeroth- to pseudo first-order in the latter. The true second-order rate constants for the nitration processes are determined by means of a simulation. The reactions are found to be sterically retarded and the differences in rate constants rather small. The diminished span might be due to the proximity to diffusion control.

Nitration of iodotrialkylbenzenes gives rise to two main products emanating from nitrodeiodination and nitrodeprotonation, respectively.<sup>1,2</sup> In certain cases an iodination process accompanies the nitration, *i.e.*, the expelled iodonium ion forms some electrophilic entity which then attacks the iodotrialkylbenzene.<sup>2–4</sup> Investigations have been made of the ratio deiodination–deprotonation for a series of iodotrialkylbenzenes.<sup>1,2,5</sup> This ratio gives a measure of the difference in free energy of activation for the two processes.

The present work has been carried through to find out what influences the absolute rates of the two processes, nitrodeprotonation and nitrodeiodination. A series of 2-iodo-1,3,5-trialkylbenzenes with different steric properties has been synthesized and the kinetics of the nitration of these substrates have been investigated. A direct comparison of the reactivities from the reaction rates is not possible as the substrates are reactive enough to make the

nitration processes of mixed- or zeroth-order in the aromatics, *i.e.* the production of the nitronium ion rate determining.<sup>6</sup> The common solution to this problem is to make competitive measurements, but, since the total amount of liberated iodonium ion would then be different and give another product composition, it cannot be applied here. A more complete kinetic analysis is therefore required.

## KINETIC TREATMENT AND RESULTS

The iodotrialkylbenzenes, 1, 2, 3 and 4 were nitrated with 5.1 M nitric acid (also 1.9 M water and



- 1 R = -CH<sub>3</sub>
- 2 R = -CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>
- 3 R = -CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>
- 4 R = -CH(CH<sub>3</sub>)<sub>2</sub>

0.03 M urea to prevent nitrosation) in nitromethane and the reaction was followed by taking aliquots at proper time intervals. The mol fractions of remaining starting material and the different products were plotted *versus* time. The true second-order rate constants were calculated using a simulation, starting from the assumed rate equations and replacing the differentials of concentration and time,  $dA, \dots, dt$  with finite differences,  $\Delta A, \dots, \Delta t$ , using sufficiently small time intervals.<sup>7</sup>

The reactions are assumed to follow the path shown in Scheme 1.



Table 1. Kinetic parameters for the nitration of substrates 1–4 in 5.1 M nitric acid, 0.9 M water and 0.03 M urea in nitromethane at 0 °C.

Substrate	Initial conc./M	$k_B/M^{-1} s^{-1}$	$k_C/M^{-1} s^{-1}$	$(k_B + k_C)[ArI]_0 K/k_1$	$k_F/M^{-1} s^{-1}$
				with exp. initial conc.	with initial conc. 0.00133 M
1	0.01370	$1.55 \times 10^9$	$2.42 \times 10^9$	2.47	0.24
2	0.00102	$0.83 \times 10^9$	$1.37 \times 10^9$	0.10	0.13
3	0.00133	$0.58 \times 10^9$	$2.14 \times 10^9$	0.16	0.16
4	0.00500	$0.56 \times 10^9$	$0.29 \times 10^9$	0.20	0.054
					$0.052 \times 10^9$

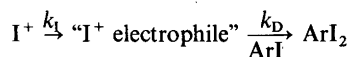
The concentration of nitric acid is considered to be constant.

The equilibrium constant  $K = k_1/k_{-1}$  is taken to be  $10^{-13.6}$ . As this value is approximate, no rate constants here are absolute but depend upon the value assigned to  $K$ . As the nitronium ion parameters (see below) are kept the same for all the substrates, however, the relative reactivities may be obtained from the rate constants given. An initial estimate of the  $k_1$  value is made from the initial rate of the nitration of substrate 1, which is the most reactive one, and consequently reacts to a large extent according to zeroth-order kinetics. The rate constants  $k_B$  and  $k_C$  are determined from the initial rate of consumption of the substrate, the deiodination–deprotonation ratio and the above estimated  $k_1$  value. The value of  $k_1$  is varied until a good agreement with the experimental data from substrate 1 is achieved. The final  $k_1$  value,  $2.2 \times 10^{-6} s^{-1}$ , is then used for all the substrates.

In the iodomesitylene case (and in the iodotriisopropylbenzene one, although the amounts of iodination are very small) the iodination process shows a time lag, probably due to the prior formation of the actual iodinating species from the liberated iodonium ion. It is impossible to simulate this behaviour assuming a direct attack by  $I^+$  on the aromatic substrate. The iodination path re-

corded in the Scheme, though, offers one model for this behaviour. The rate constants  $k_D$ ,  $k_2$  and  $k_3$  are varied until a perfect fit with experimental data is established. This set of parameters is not the only one to give this good agreement and their separate values are thus of no great significance. The rate constant for the nitrodeiodination of the diiodo compound,  $k_E$ , is determined in a separate experiment starting with diiodomesitylene. In Table 2 the above scheme for the iodine reactions is denoted pathway I.

It is also possible to simulate the iodination process by assuming a slow first step of pseudo first-order kinetics giving rise to an iodinating electrophile which then attacks the aromatic substrate,



This is called pathway II in Table 2.

The same iodination parameters  $k_2$  and  $k_3$  or  $k_1$  are used with substrate 4 and give a good fit.

All the iodination rate constants are given in Table 2.

In substrate 4 there is also a small amount of nitrodeisopropylation. This reaction is assumed to follow the same kinetic pattern as the two other nitration reactions and its kinetics are simulated in

Table 2. Iodination parameters for the substrates 1 and 4 according to the two assumed pathways, I and II and the nitration rate constants for the diiodo compounds.

Substrate	I			II		
	$k_E/M^{-1} s^{-1}$	$k_2/M^{-1} s^{-1}$	$k_3/M^{-1} s^{-1}$	$k_D/M^{-1} s^{-1}$	$k_1/s^{-1}$	$k_D/M^{-1} s^{-1}$
1	$5.8 \times 10^8$	12	38	65	$5.3 \times 10^{-3}$	6.0
4	$(1.5 \times 10^8)^a$	12	38	$1.1 \times 10^{-2}$	$5.3 \times 10^{-3}$	$4.9 \times 10^{-3}$

<sup>a</sup>This value is estimated and has little importance since the amounts of iodinated product are very small and the deiodination of the diiodo product is negligible during the part of the reaction studied here.

the same way. The additional second-order rate constant,  $k_F$ , is given in Table 1 together with all the other nitration rate constants. Simulated curves and experimental results are shown in Fig. 1. Pathway I was used in the case of 1 and 4, but pathway II gives no visible deviation.

To check whether the nitration mechanism is nitration *via* nitronium ion or nitrosation with subsequent oxidation, separate runs were made with substrate 1 (being the most reactive one and consequently the one most inclined to react through nitrosation<sup>9</sup>) with and without urea and sodium nitrite. The reaction rate is depressed by urea and even more so by nitrite, as is expected for nitration by nitronium ion.<sup>10,11</sup> Furthermore, the pseudo zeroth-order rate constant as calculated from  $k_1$  and the nitric acid concentration is  $1.1 \times 10^{-5}$  M/s, which is in good agreement with the literature value  $5.75 \times 10^{-5}$  M/s (5.0 M nitric acid in nitromethane)<sup>6</sup> when corrections are made for water and urea content. The water content is 0.9 M which would give a three- to fourfold depression of the rate,<sup>6</sup> and the added urea, 0.03 M, should further decrease the rate by a factor of two<sup>10,12</sup> assuming that urea has the same anticatalyzing effect in nitromethane as in sulpholane.

The rate of the iodination reaction is not influenced by nitrite and urea addition more than by the amount due to the decreased rate of consumption of the substrate by the nitration reactions. The initial time lag and the kinetic form is not influenced.

In order to see whether the nitrodeiodination could proceed *via* protodeiodination followed by a rapid nitrodeprotonation, the reaction was carried through with 3,5-dideuterio-1-iodo-2,4,6-triisopropylbenzene (this substrate being the most sterically strained and nitrodeiodinated one). The amount of aromatic protons was measured with NMR before the reaction and after 78% consumption of the substrate. The nuclear positions of the substrate were 96% deuterated before the reaction, and after the reaction the remaining substrate and the products were 96% deuterated in the benzene nucleus. This means that no proton attack takes place during the nitration reaction.

## DISCUSSION

As can be seen from the rate equations combined with the assumed steady-state expression for the  $\text{NO}_2^+$  concentration, the apparent order of the

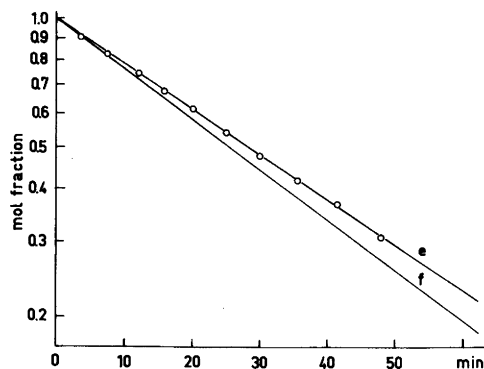


Fig. 2. A comparison between nitration reactions with different initial concentration of the aromatic substrate 4. Curve *e* shows log mol ratio (exp. dots and simulated curve) *versus* time for the consumption of 4 (initial conc. 0.00500 M) and *f* a simulated curve with a lower initial conc., 0.00133 M, which is the actual one of 3 in the kinetic measurement.

nitration reaction depends upon the value of the ratio  $(k_B + k_C)[\text{ArI}]/k_{-1}$  (if no allowance is made for the iodination reaction). The initial values of these ratios are given in Table 1. If this ratio is  $\gg 1$ , the kinetics will be of zeroth-order and if it is  $\ll 1$  of first-order in the substrate. This means that the concentration of the aromatics will influence the kinetics. If the reactivity of the substrate is such that the kinetics will be of mixed order (the ratio above having a value around 1) it can be deceptive to compare the reaction rates through some kind of pseudo first-order rate constants, as the kinetics may look like first-order, giving an apparently straight line in a logarithmic plot of mol ratios *versus* time but still be influenced by the initial concentration. Fig. 2 shows a comparison between experimental ( $\equiv$  simulated) kinetics for substrate 4 (which is the least reactive one and consequently most prone to react according to pseudo first-order kinetics) and a simulated curve which shows the probable course of the reaction with a lower initial concentration of the aromatic substrate ( $\equiv$  the actual concentration in the 3 case). Both curves seem to be straight lines but have different slopes. In our opinion the true second-order rate constants calculated as above give the best quantitative basis for comparison of the reactivities.

Most of the reported nitrodeisopropylations<sup>13</sup> occur in substrates where the isopropyl position is activated by another substituent in ortho or para

position. This is not the case in substrate 4. No nitrodeisopropylation in 1,3,5-triisopropylbenzene was found by Newton<sup>14</sup> in nitration with mixed acid, by us in the nitric acid–nitromethane medium (see Experimental) or by Myhre and Beug<sup>15</sup> using nitronium tetrafluoroborate as nitrating agent. The small amount of nitrodeisopropylation now found in substrate 4 can probably be understood in terms of favourable steric effects in the rather crowded molecule.

The iodination reaction path preferred by us is the one *via*  $I_3^+$ . This choice is supported by the visible formation of free iodine which mostly accompanies the nitrodeiodination reactions<sup>3,4,5</sup> and the fact that the time lag disappears partly when iodine is added to the reaction mixture (see Experimental section). We have no suggestion concerning the nature of the reducing agent inherent in  $k_2$ , however. Evidence for  $I_3^+$  as electrophile is also documented in the literature.<sup>16–18</sup> Butler and Sanderson<sup>3,19</sup> have suggested the possibility of a combination between nitrous acid and  $I^+$  as electrophile, but this can be ruled out here since the addition of nitrite or urea does not affect the iodination rate. It is also difficult to devise some other reaction *e.g.* with a nucleophile, which would be slow enough as to be rate determining and give the time delay reported above.

The steric strain as estimated from the rotational barriers in the 1-iodo-3-nitro derivatives<sup>20</sup> increases in the order  $1 < 2 < 3 < 4$ . The steric effects are expected to be larger in the nitrodeiodination reaction compared to the nitrodeprotonation, the iodine substituent being much larger. Inspection of the rate constants reveals the opposite trend. This might be due to the increased steric strain in the nitrodeprotonation product as compared to the decreased one in the nitrodeiodination product, a difference which might be qualitatively foreshadowed in the respective transition states. Both reactions seem to be retarded by steric strain with a minor deviation for 2/3. This could be explained by the following. According to Taylor<sup>21</sup> it can be assumed that activation through carbon–carbon hyperconjugation is larger than through carbon–hydrogen hyperconjugation, which would give the reversed reactivity order  $4 > 3 > 2 > 1$ . This activation is counteracted by the steric hindrance to solvation of the transition state.<sup>21</sup> For each molecule and each reaction (nitrodeprotonation and nitrodeiodination, respectively) the reaction rate will then be the result of the total effect of carbon–

carbon hyperconjugation, steric effects on solvation and steric effects around the reaction centre, the last mentioned being the reason for the most obvious trend and the minor deviation of 2/3 being the result of a somewhat different balance between the other two factors.

The differences in the rate constants are, on the whole, unexpectedly small. This might be due to the nearness to the encounter limit<sup>22</sup> which should influence the rates and diminish the differences. The rate constants will still fall in the order determined by the nitration reaction but the total reactivity span will appear to be smaller than expected.

## EXPERIMENTAL

The NMR analyses were performed on a Bruker WH 270 NMR spectrometer. The GLC analyses were made on a Perkin-Elmer 3920-B instrument fitted with 3 mm  $\times$  2 m SE-30 columns and flame ionization detector. The peak areas were determined with a Hewlett Packard 3380 A integrator. The mass spectra were recorded either on an LKB instrument (electron energy 70 eV) fitted with a gas chromatograph (at the Chemical Center, University of Lund), or an AEI 902 mass spectrometer (at the Department of Medical Biochemistry, University of Göteborg). Only major peaks are reported. The kinetic calculations were made on a CompuCorp 625 desktop computer. The time interval,  $\Delta t$ , was 2.5 s. Further reduction of the interval did not change the results of the numeric integrations. A Waters Model 201 (Waters Ass., Milford, Mass. USA) liquid chromatograph equipped with a Valco injector (Model CV-6-UHPa-N60, 50 MPa) and with a Refractive Index Detector was used for the HPLC separations. Acetonitrile (Rathburn Chemicals, HPLC grade) was used as the mobile phase. A stainless steel column (30 cm  $\times$  7.7 mm I.D.) packed with LiChrosorb RP-18, particle size 10  $\mu$ m (Merck) was used for the preparative scale separations.

The fuming nitric acid used was obtained according to Bennett *et al.*<sup>23</sup> The concentration was adjusted to 90 % by mixing with the proper amount of concentrated nitric acid of analytical grade.

The kinetic measurements were made in four parallel runs so as to keep the acid parameters and the temperature as equal as possible for all the substrates. Separate runs were made with substrate 1 in the same nitric acid–nitromethane medium without urea, with 0.03 M urea and with 0.027 M sodium nitrite. In the first case the half life as measured by the initial rate was 9.5 min, in the second 12 min and in the third 13.5 min. Separate runs were also made in the same medium to

determine  $k_E$  and compared to a parallel measurement with iodomesitylene to ensure that all the parameters were the same as in the main measurement (i.e. the reaction profile for iodomesitylene was identical). The kinetics for the nitration of 2,4-diiodomesitylene were considered to be of pseudo first-order and  $k_E$  was calculated as the pseudo first-order rate constant divided by the assumed equilibrium concentration of nitronium ion.

One comparative measurement was made with substrate 1 without and with added iodine (5.7 mM, dissolved in the substrate–nitromethane solution, see typical kinetic run below) which showed that the time lag in the iodination reaction was diminished when iodine was added but that the sigmoid form remained, though less marked.

One kinetic run with nitration of 1,3,5-triisopropylbenzene was made following the same procedure as described below. The reaction was complete after 8.5 min and gave 100% of mononitrated product. No traces of dealkylated product were observed in the GLC analyses.

#### Typical kinetic run

Nitromethane (5 ml) was thermostatted at 0 °C (the reaction vessels were kept, dark, in an ice water bath with efficient stirring). Nitric acid (3 ml, 22.1 M, 0.13 M in urea) at –30 °C was added and the mixture was allowed to warm up to 0 °C. A solution of the substrate in nitromethane (5 ml) at 0 °C was added. Aliquots (1 ml) were taken at proper time intervals and quenched in a mixture of 6 ml of ice water and 4 ml of methylene chloride. The mixture was shaken for 1 min and allowed to separate. The water layer was removed and the organic layer washed with 6 ml of cold water. The organic phase was concentrated (without drying, to prevent losses) and analyzed by GLC. Calibration with known amounts of the substrates was made.

The material balance was checked in separate experiments using added internal standards in the GLC determinations and showed no deficit with respect to the aromatic compounds within an accuracy of 5%.

#### Syntheses

The substrates 1 and 3 and all the derivatives thereof have been prepared for earlier investigations.<sup>24</sup>

2-Iodo-1,3,5-triisopropylbenzene, 4, was obtained from commercial 1,3,5-triisopropylbenzene via iodination according to Keefer and Andrews.<sup>25</sup> MS [IP 70 eV;  $m/e$  (% rel. int.)]: 330(79, M), 315(100,

M–CH<sub>3</sub>), 287(14), 188(12), 173(21), 145(19), 128(19), 117(19), 115(19), 91(33), 77(14). <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  1.23 (18 H, d,  $J=6.8$  Hz), 2.84 (1 H, septet,  $J=6.8$  Hz), 3.39 (2 H, septet,  $J=6.8$  Hz), 6.95 (2 H, s).

2-Nitro-1,3,5-triisopropylbenzene was prepared through nitration of commercial 1,3,5-triisopropylbenzene with 90% nitric acid in nitromethane. MS [IP 70 eV;  $m/e$  (% rel. int.)]: 249 (6, M), 232(100, M–OH), 216(14), 190(27), 174(14), 148(11), 132(26), 117(17), 115(14), 105(11), 91(27), 77(14). <sup>1</sup>H NMR (270 MHz, acetone):  $\delta$  1.26 (12 H, d,  $J=7$  Hz), 1.27 (6 H, d,  $J=7$  Hz), 2.77 (2 H, septet,  $J=7$  Hz), 3.01 (1 H, septet,  $J=7$  Hz), 7.28 (2 H, s).

2-Iodo-4-nitro-1,3,5-triisopropylbenzene was isolated from the product mixture of the nitration of 4 according to the kinetic procedure described above, through chromatography on silica gel/hexane. MS [IP 70 eV;  $m/e$  (% rel. int.)]: 375(66, M), 358(100, M–OH), 342(15), 316(16), 230(11), 216(57), 200(46), 188(24), 173(33), 158(28), 143(25), 128(47), 127(37), 117(30), 115(46), 91(49), 77(41). <sup>1</sup>H NMR (270 MHz, acetone, –5 °C):  $\delta$  1.21–1.32 (18 H, three d,  $J=7.0$  Hz), 2.69 (1 H, septet,  $J=7.0$  Hz), 3.51 (1 H, septet,  $J=7.0$  Hz), 3.80 (1 H, septet,  $J=7.0$  Hz), 7.44 (1 H, s).

2,4-Diiodo-1,3,5-triisopropylbenzene, a and the dealkylated product, 1,3-diisopropyl-2-iodo-5-nitrobenzene or 1,3-diisopropyl-4-iodo-5-nitrobenzene, b, were not possible to isolate from the product mixture above but were identified through GLC/MS. MS for a [IP 70 eV;  $m/e$  (% rel. int.)]: 456(100, M), 441(61, M–CH<sub>3</sub>), 314(16), 128(20), 91(14), 77(14). MS for b (as above): 333(73, M), 318(100, M–CH<sub>3</sub>), 272(13), 145(13), 130(15), 128(20), 115(23), 91(15), 77(14). The fragmentation is typical for the compounds in question. The diiodotrialkylbenzene first loses a methyl group and then iodine in analogy with the monoiodo compound. In the dealkylated product the nitro group must be in one of the two proposed positions (probably *para* to the iodine substituent) because the fragmentation shows no M–OH peak, which is typical for a nitro group adjacent to an isopropyl group.<sup>13</sup> The retention times in GLC are also the expected ones for molecules of the proposed type. The diiodo compound was impossible to synthesize through direct iodination of commercial triisopropylbenzene. Several methods were tried.<sup>25,26</sup>

1,3-Dideuterio-5-iodo-2,4,6-triisopropylbenzene was made in two steps from 1,3,5-triisopropylbenzene. The latter was equilibrated with deuterio-trifluoroacetic acid until NMR analysis showed 95% deuteration in nuclear position and then iodinated according to Marton and Martinsson,<sup>26</sup> which gave a 96% deuterated iodo product. This product was nitrated on a larger scale according to the kinetic procedure above. The reaction was

quenched in water when 22 % starting material remained in the mixture, extracted with methylene chloride, the extract dried, and the solvent evaporated. The resulting reaction mixture was analyzed by NMR. The amount of aromatic protons found corresponds to 96 % deuteration.

2-Iodo-1,3,5-triisobutylbenzene, 2, was synthesized in five steps from mesitylene through a triple Wittig reaction with acetone followed by hydrogenation and iodination.

1. 1,3,5-Tris(bromomethyl)benzene was made from mesitylene according to Offerman and Vögtle.<sup>27</sup>

2. Addition of triphenylphosphine in dry dimethylformamide gave the triphenylphosphonium salt, crystals of which precipitated. NMR showed a pure product, which was thoroughly dried and used in the Wittig reaction. <sup>1</sup>H NMR (270 MHz, CD<sub>3</sub>OD): δ 4.79 (6 H, s), 7.5–7.9 (48 H, m).

3. 1,3,5-Tris(2-methylpropenyl)benzene was obtained from the triphenylphosphonium salt of 1,3,5-tris(bromomethyl)benzene and acetone. The salt (11.6 g, 10.1 mmol) was suspended in 200 ml of dry benzene and 20 ml of 15 % butyl lithium solution in hexane (47 mmol) was mixed with the suspension under nitrogen. The dark red solution was held at a temperature of 60 °C and acetone was added until the colour disappeared. The reaction mixture was poured into water and extracted with benzene, the extract dried and the solvent evaporated. Chromatography of the crude product on silica gel–hexane gave 500 mg (2.1 mmol, yield 21 %) of pure product. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 1.87 (9 H, s), 1.88 (9 H, s), 6.23 (3 H, s), 6.89 (3 H, s).

4. The unsaturated product (see above) was reduced catalytically with H<sub>2</sub>–Pd in acetic acid (276 kPa, 100 °C) which gave a quantitative yield of 1,3,5-triisobutylbenzene. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 0.88 (18 H, d, *J* = 6.3 Hz), 1.83 (3 H, nine peaks, *J* = 6.3 Hz), 2.41 (6 H, d, *J* = 6.3 Hz), 6.73 (3 H, s).

5. This product was iodinated according to Marton and Martinsson<sup>26</sup> to give 2-iodo-1,3,5-triisobutylbenzene, 2. MS [IP 50 eV; *m/e* (% rel. int.)]: 372 (95, M), 329 (100), 245 (12), 203 (48), 149 (45), 128 (22), 91 (28). <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 0.90 (6 H, d, *J* = 7 Hz), 0.95 (12 H, d, *J* = 7 Hz), 1.83 (1 H, m, *J* = 7 Hz), 1.99 (2 H, m, *J* = 7 Hz), 2.39 (2 H, d, *J* = 7 Hz), 2.63 (4 H, d, *J* = 7 Hz), 6.76 (2 H, s).

2-Nitro-1,3,5-triisobutylbenzene, *c*, and 2-iodo-4-nitro-1,3,5-triisobutylbenzene, *d*, were isolated from the product mixture obtained by nitration of 2-iodo-1,3,5-triisobutylbenzene (nitric acid–nitromethane as in the kinetic procedure above) by means of high pressure liquid chromatography (reverse phase column, RP-18, –acetonitrile) and identified through MS and NMR.

*c*: MS [IP 55 eV; *m/e* (% rel. int.)]: 291 (14, M),

274 (78, M–OH), 232 (100). Mol. wt., obs. 291.2151 ± 0.005, calc. for C<sub>18</sub>H<sub>29</sub>NO<sub>2</sub> 291.2198. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 0.90 (12 H, d, *J* = 7.2 Hz), 0.91 (6 H, d, *J* = 7.2 Hz), 1.85 (3 H, m, *J* = 7.2 Hz), 2.41 (4 H, d, *J* = 7.2 Hz), 2.46 (2 H, d, *J* = 7.2 Hz), 6.87 (2 H, s). *d*: MS [IP 36 eV; *m/e* (% rel. int.)]: 417 (71, M), 400 (55, M–OH), 358 (100). Mol. wt., obs. 417.1140 ± 0.005 calc. for C<sub>18</sub>H<sub>28</sub>INO<sub>2</sub> 417.1167. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 0.88 (6 H, d, *J* = 7.2 Hz), 0.90 (6 H, d, *J* = 7.2 Hz), 0.95 (6 H, d, *J* = 7.2 Hz), 1.87 (1 H, m, *J* = 7.2 Hz), 2.02 (1 H, m, *J* = 7.2 Hz), 2.10 (1 H, m, *J* = 7.2 Hz), 2.34 (2 H, d, *J* = 7.2 Hz), 2.70 (2 H, d, *J* = 7.2 Hz), 2.71 (2 H, d, *J* = 7.2 Hz), 6.91 (1 H, s).

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