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Synthesis, Reactions and ^{1}H NMR Spectroscopic Studies of 1,4-Bis(1,1,2,2-tetramethylpropyl)benzene

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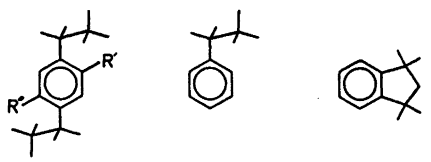
1,4-Bis(1,1,2,2-tetramethylpropyl)benzene has been prepared *via* Friedel-Crafts alkylation of benzene with 2,3,3-trimethyl-2-chlorobutane below −10 °C. In addition 1,1,3,3-tetramethylindane was formed. Nitration and bromination of the former yielded the mono- and 2,5-disubstituted derivatives, but more highly substituted derivatives were not obtained. Dynamic ^{1}H NMR studies on the parent compound have given $\Delta G^{\ddagger}_{298} = 38.9 \pm 0.4$ kJ mol^{-1}, $\Delta H^{\ddagger} = 35.2 \pm 0.4$ kJ mol^{-1} and $\Delta S^{\ddagger} = -11.7 \pm 2.9$ J mol^{-1} K^{-1} for the hindered rotation of the *tert*-butyl groups. In this paper is also included a study of the rotational isomerism of 2-acetylamino-1,4-bis(1,1,2,2-tetramethylpropyl)benzene. The ratio between the *E* and *Z* forms was found to be 35/65 at 243 K. The result is in accordance with other investigations which show that the *E* form increases as the size of the *ortho* substituent increases.

Following previous studies of the 1,3,5-trineopentylbenzene system,[1-3] we decided to study the bulkiness and mobility of the highly branched 1,1,2,2-tetramethylpropyl (triptyl) group – properties which are likely to be manifested in aromatic substitution reactions [4] as well as in studies on restricted rotation by the NMR kinetic method.[3,5] Since a symmetrically trisubstituted system has shown to have many merits for such studies, attempts were made to synthesize 1,3,5-tris(1,1,2,2-tetramethylpropyl)benzene. Since these attempts turned out to be unsuccessful our attention was turned towards the *p*-disubstituted system, 1,4-bis(1,1,2,2-tetramethylpropyl)benzene (*1a*).



1 *2* *3*

	R'	R''
1a	H	H
b	Br	H
c	Br	Br
d	NO_2	H
e	NO_2	NO_2
f	NH_2	H
g	NHAc	H

RESULTS and DISCUSSION

Syntheses

A theoretically possible route to 1,3,5-tritriptylbenzene is the Friedel-Crafts alkylation method. This method has been used by Huston and Barret [6] to prepare triptylbenzene in low yield from benzene and 2,3,3-trimethyl-2-butanol (or the corresponding chloro compound) in the presence of aluminium chloride. Efforts to improve the yield by variation of the reaction temperature (between 10 and 40 °C) were not successful but resulted instead in various amounts of additional *tert*-alkylbenzenes. However, it has later been shown that the triptyl cation is stable in highly acidic media at low temperatures (≤ -20 °C) contrary to its rapid decomposition above 0 °C.[7] In the present work

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benzene was reacted with a large excess of 2,3,3-trimethyl-2-chlorobutane at a temperature not exceeding −10 °C to yield 1,4-bis(1,1,2,2-tetramethylpropyl)benzene (*1a*) in 60 % yield with a minimum of by-products (see below). We were never able, however, to obtain any 1,3,5-tritriptylbenzene, although under very similar reaction conditions, *tert*-butylation of benzene is reported to give 1,3,5-tri-*tert*-butylbenzene in 83 % yield.[6]

One explanation of our results could be that the steric requirement of the triptyl group is too large to allow 1,3 or 1,3,5 substitution. Perhaps a more plausible explanation is that the *tert*-butyl cation is more stable than the triptyl cation [9] so that *tert*-butylbenzenes will be more prone to undergo dealkylation-alkylation reactions. Attempts to disubstitute toluene with triptyl groups by the same procedure as described above resulted in a mixture of *o*- and *p*-triptyltoluene. No evidence for a toluene derivative with two triptyl groups was found.

Another possible method to synthesize 1,3,5-trialkylated benzene derivatives involves base catalyzed cyclotrimerization of methyl ketones.[1] Numerous efforts were made with 3,3,4,4-tetramethyl-2-pentanone but failed to give the desired 1,3,5-tritriptylbenzene (see Experimental).

In the preferred method of synthesis of *1a* the product consisted of three major components in the ratio 65:17:18 according to GLC. After separation and purification the components were identified by MS and ^{1}H NMR as *1a*, triptylbenzene (*2*) and 1,1,3,3-tetramethylindane (*3*). Longer reaction times and/or higher temperatures did not improve the yield of *1a*, neither did solvents like carbon disulfide or pentane/nitromethane have any positive effect. When these solvents were used in the reaction a further major component appeared which was identified as *tert*-butylbenzene.

The formation of *3* can be due to isomerisation of the triptyl cation to the 2,4-dimethyl-2-pentyl cation [10] with subsequent cycloalkylation by the latter, as it is known that 1,1,3,3-tetramethylindane is formed through cycloalkylation by 2-chloro-2,4-dimethylpentane of benzene in the presence of aluminium chloride.[11]

Derivatives of *1a*

One of the main objectives of the present work was to study the internal rotation around the C(sp^2)−C(sp^3) bond as a function of one or two *ortho* substituents. This could have been achieved in a mono- or disubstituted 1,3,5-tritriptylbenzene. However, the same pattern of substitution *ortho* to a triptyl group would be obtained in a tri- or tetrasubstituted derivative of *1a*. Therefore *1a* was subjected to some halogenation and nitration reactions. By using forcing conditions it was hoped to get tri- or tetrasubstitution. However, we were only able to get mono- and disubstitution.

Halogenation. Several powerful electrophilic halogenating species were examined in attempts to halogenate *1a*. Bromination with molecular bromine and sodium persulfate in acetic acid [12] after 40 h at 70 °C yielded 2-bromo-1,4-bis-(1,1,2,2-tetramethylpropyl)benzene (*1b*). Silver ion induced bromination [13] of *1a* during 24 h at room temperature yielded 2,5-dibromo-1,4-bis(1,1,2,2-tetramethylpropyl)benzene (*1c*) as the only product. *N*,*N*-Dibromoisocyanuric acid in concentrated sulfuric acid has been described [14] as a very potent brominating agent. Attempts to brominate *1a* as well as *1c* with this reagent failed, probably due to the low solubility of *1a* and *1c* in concentrated sulfuric acid. The structures of *1b* and *1c* are confirmed by the respective ^{1}H NMR spectra (see Experimental).

An attempt to chlorinate *1a* with *tert*-butyl hypochlorite in acetic acid yielded a complex mixture of products which were difficult to separate and were not further investigated.

Nitration. Nitration of *1a* was performed with nitric acid in acetic acid at 50 °C. The reaction was followed by GLC and was found to be complete after 4 days. 2-Nitro-1,4-bis(1,1,2,2-tetramethylpropyl)benzene (*1d*) was the only product formed. This result can be compared with the high yield of nitrodealkylation when 1,4-di-*tert*-butylbenzene is nitrated with nitric acid in acetic acid [15] or with nitronium tetrafluoroborate in sulfolane.[16] In both cases 20 % nitrodealkylation and 80 % nitrodeprotonation were reported. This probably reflects both the greater leaving ability of the *tert*-butyl cation compared to the triptyl cation and the larger steric hindrance of the nitronium ion to

approach the triptyl-carrying carbon atom in *1a*. The structure of *1d* is confirmed by its ^{1}H NMR spectrum (see Experimental).

In addition, *1a* was nitrated with nitric acid in sulfuric acid. The reaction was considered less satisfactory for preparative purposes as it yielded a mixture of several components according to GLC. A mixture of the two major components was separated from the crude product by column chromatography. These two components were further separated by recrystallization and identified as *1d* and 2,5-dinitro-1,4-bis(1,1,2,2-tetramethylpropyl)benzene (*1e*). This is in contrast with the reported [15] high yield (53 %) of 2,6-dinitro-1,4-di-*tert*-butylbenzene when 1,4-di-*tert*-butylbenzene is nitrated under similar conditions. No further effort was made to identify the remaining mixture. The structure of *1e* is confirmed by its ^{1}H NMR spectrum (see Experimental).

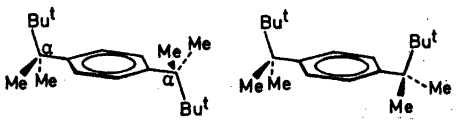
Reactions with 1d. The mononitro compound *1d* was reduced to the corresponding amine (2-amino-1,4-bis(1,1,2,2-tetramethylpropyl)benzene (*1f*)) by catalytic hydrogenation (10 % Pd/C) in ethanol. The ^{1}H NMR spectrum of *1f* showed the expected *tert*-butyl singlets and the characteristic pattern for the aromatic protons. The amino protons showed a broad resonance band at 3.63 ppm. The amine *1f* was acetylated to 2-acetylamino-1,4-bis(1,1,2,2-tetramethylpropyl)benzene (*1g*) with acetic anhydride in acetic acid.

Variable-temperature ^{1}H NMR studies of *1a* and *1g*

Compound 1a. Hindered rotation of *tert*-butyl groups attached to sp^3-hybridized carbons is a matter of current interest.[17,18] We have investigated the temperature-dependence of the methyl proton peaks in the ^{1}H NMR spectrum of *1a* by the complete band shape method. The activation parameters at 298 K for the restricted rotation around the *t*-Bu – C(Ph,Me,Me) bonds extracted from these spectra are: $\Delta G^{\ddagger}_{298} = 38.9 \pm 0.4$ kJ mol^{-1}, $\Delta H^{\ddagger} = 35.2 \pm 0.4$ kJ mol^{-1} and $\Delta S^{\ddagger} = -11.7 \pm 2.9$ J mol^{-1} K^{-1}.

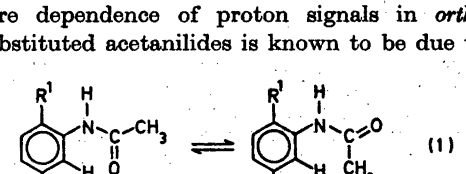
A comparison between the barrier height for this compound and those for compounds with the general structure: *t*-Bu – C(X,Y,Z) (X,Y,Z = hydrogen, alkyl, aryl or halogen) shows that the origin of the barrier to a large extent is steric. $\Delta G^{\ddagger}$ values between 20.5 kJ mol^{-1} (X = Y = H, Z = CH_3) and 43.5 kJ mol^{-1} (X = Y = CH_3, Z = Cl) have been reported.[19,20] Unfortunately, $\Delta S^{\ddagger}$ values for most of these compounds are unknown and the barriers have been obtained from rate constants close to the coalescence of these peaks. A detailed comparison is thus not meaningful.

Restricted rotation around the phenyl-carbon bond in *1a* could not be visualized in the NMR spectra at temperatures down to – 150 °C. This may depend on a too low population of one of the two possible conformers (A and B) or an accidental shift equivalence of the considered protons, *i.e.* α-methyl and *tert*-butyl protons. A low population of one conformer seems to be a more reasonable explanation than an accidental shift equivalence since the methyl proton NMR spectrum of the corresponding dibromo compound *1c* showed only general T_2 broadening down to – 120 °C. The initial state for the rotation of the triptyl groups is (in analogy with the 1,3,5-trineopentylbenzene system[3]) assumed to be the conformation where these groups are perpendicular to the aromatic ring.



A B

Compound 1g. At ambient temperature the ^{1}H NMR spectrum of *1g* showed two singlets of unequal intensity for the methyl protons of the acetyl group. These bands were broadened and collapsed when the temperature was increased (~ 70 °C, $\Delta G^{\ddagger}_c = 69.9$ kJ mol^{-1}) and appeared as a new singlet when the temperature was further increased (100 °C). At low temperatures (≤ 20 °C) an additional splitting of the *tert*-butyl singlet (at 0.91 ppm) and the α,α-dimethyl singlet (at 1.46 ppm) occurred. Such a temperature dependence of proton signals in *ortho* substituted acetanilides is known to be due to



(1)

Z E

the partial double-bond character of the amide bond which enables the observation of *E* and *Z* rotational isomers (eqn. 1) by NMR. Kessler and Rieker[21] have investigated some *ortho*-alkyl substituted acetanilides ranging from the methyl to the *tert*-butyl derivative. They found that the *Z* isomer has a lower ground-state energy due to the smaller non-bonded interaction between the carbonyl oxygen atom and the *ortho* hydrogen in the aromatic ring than between the methyl protons and the aromatic proton in the *E* form. In unsubstituted acetanilide the *Z* form is predominating by more than 99 %. However, an *ortho* substituent forces the acetylamino group out of coplanarity with the aromatic ring, thus weakening the interaction between the methyl and the *ortho* hydrogen in the *E* form. The equilibrium is affected and the *E* fraction increases as the steric requirement of the *ortho* substituent increases. Thus the *E*/*Z* ratio can be taken as a rough measure of the size of alkyl groups. In the investigation by Kessler and Rieker the *E*/*Z* ratio ranged from 6:94 ($R^1 = CH_3$, $R^2 = H$, $T = 243$ K) to 25:75 ($R^1 = t$-Bu, $R^2 = H$, $T = 253$ K), while in our investigation an *E*/*Z* ratio equal to 35:65 was found in *1g* ($R^1 = R^2 =$ triptyl, $T = 243$ K). In this situation the steric size of a triptyl group is obviously larger than that of a *tert*-butyl group.

The *E*/*Z* equilibrium ratio was measured by integration of the peak areas (for the acetyl group) at 4 different temperatures down to −30 °C and was found to vary by less than ± 6 %. The same ratio was found from measurements on the α,α-dimethyl group and the *tert*-butyl group. In this context it may be pointed out that for 2-acetylaminoneopentylbenzene an *E*/*Z* ratio of 12/88 ($R^1 =$ neopentyl, $R^2 = H$, $T = 253$ K) has been found.[22] The assignment of *E* and *Z* forms was based on the same arguments as stated by Kessler and Rieker.[21]

EXPERIMENTAL

Measurements. GLC analyses were carried out on either a Perkin-Elmer 900 or a Perkin-Elmer 3920 gas chromatograph, both equipped with flame ionization detectors and 2 m columns with an inner diameter of 2 mm. The stationary phase was 3 % of SE-30 silicon gum rubber on Gas-Chrom Q, 100 − 120 mesh. Percentage composition refers to relative areas as measured by a Hewlett-Packard 3380 A integrating recorder.

The IR spectra were recorded on a Beckman IR 9 spectrophotometer using potassium bromide pellets or a potassium bromide cell with CCl_4 as solvent.

The mass spectra (MS) were determined at 70 eV on an AEI 902 mass spectrometer or on a LKB 9000 mass spectrometer connected to a gas chromatograph.

Melting points were determined on a Kofler micro hot stage.

The ^1H NMR spectra were recorded on a Varian A 60, a Varian XL-100-15 or a Bruker WH 270 instrument. For routine spectra, about 5 % solutions in $CDCl_3$ were used and they were run at probe temperature (308 K) unless otherwise stated. Variable-temperature measurements were made on either a Varian XI-100-15 (compound *1a*) or a Bruker WH 270 (compound *1g*) instrument. Compound *1a* was dissolved in $CHCl_2F$ and compound *1g* in $CDCl_3$, both in concentrations of about 5 mol-%. TMS was used as an internal resolution reference. Temperatures were measured either with a copper-constantan thermocouple (compound *1a*) inserted in the probe or by a Bruker B-ST 100/700 temperature control unit (compound *1g*). For compound *1a* spectra were obtained with a scale expansion of 2 Hz cm^{-1}. and a scan rate of 0.1 cm s^{-1}. The Bloch equations describing the two site-exchanges of the methyl proton bands were programmed on an HP 9820 desk calculator equipped with an XY plotter. The shift between the two methyl proton bands and values for the T_2 parameter were iterated from spectra, run at approximately 10 − 30 degrees below the coalescence temperature. Rate constants for the rotation of one methyl group $2\pi/3$ rad were then obtained from visual comparison between calculated and experimental spectra.

Materials. All chemicals used were of the reagent grade and were used without further purification unless otherwise stated.

1,4-Bis(1,1,2,2-tetramethylpropyl)benzene (1a). To 67 g (0.5 mol) of 2,3,3-trimethyl-2-chlorobutane [6] was added 3.9 g (0.05 mol) of benzene, dried over sodium chips, and the resulting semi-solid mixture was cooled to −40 °C with a dry ice/acetone bath. Freshly sublimed aluminium chloride (3.3 g, 0.025 mol) was added to the mixture in small portions over a 10 min period. The reaction was held under nitrogen atmosphere and the mixture, which liquified during the reaction, was stirred for 20 min at −40 °C and thereafter at −10 °C for a further 2 h and then hydrolyzed with crushed ice. The aqueous layer was extracted three times with hexane and the combined hexane extracts were washed with water until neutral and dried over magnesium sulfate. Evaporation of the solvent left a crude product which was recrystallized twice from methanol to yield 8.2 g (60 %, based on benzene) of white crystals that were pure according to GLC. M.p. 185 − 186 °C. MS: 274(0.2), 218(9.5), 217(49),

162(14), 161(100), 160(12), 159(11.5), 146(8.5), 91(4.5), 57(18.5), 43(5), 41(14), 29(5). Mol. wt., obs. 274.264, calc. for $C_{20}H_{34}$ 274.266. NMR: δ 0.83(18 H, s, *tert*-butyl), 1.33(12 H, s, α,α-dimethyl), 7.22(4 H, s, aromatic). IR: 3090(w), 2980(vs), 2955(vs), 2910(s), 2875(s), 1920(w), 1670(w), 1510(m), 1475(m), 1460(s), 1400(m), 1375(s), 1365(s), 1220(m), 1160(s), 1115(m), 1015(m), 835(s).

2,3,3-Trimethyl-2-phenylbutane (2) and 1,1,3,3-tetramethylindane (3). The combined methanolic mother liquors from the recrystallization of *1a* were evaporated and the resulting oil was distilled on a spinning-band column. Four fractions were taken at 0.67 kPa: fraction 1, 12.2 g, b.p. 36–62 °C, fraction 2, 1.4 g, b.p. 62–64 °C, fraction 3, 0.6 g, b.p. 64–76 °C, fraction 4, 1.1 g, 76–78 °C. Fraction 2, which consisted of a colourless oil was identified as *3*. It was 97 % pure according to GLC and had the following characteristics: n_D^{20} 1.5015, lit.[24] 1.5020. MS: 174(14), 160(13), 159(100), 144(5), 143(6), 141(5), 131(17), 128(22), 118(5), 117(49), 115(15), 105(5), 91(11), 77(8), 71(6), 51(6), 43(9), 41(7), 39(8), 27(5). NMR: δ 1.30 (12 H, s, methyl), 1.90 (2 H, s, methylene), 7.13 (4 H, m, aromatic).

A GLC analysis of fraction 4 showed one main component of 95 % purity, the remaining 5 % being largely composed of *3*. The former was identified as *2* by MS and NMR and had physical properties in accordance with those previously reported.[25]

Friedel-Crafts alkylation of toluene. The same reaction as described for the preparation of *1a* was carried out with toluene instead of benzene. The reaction mixture was worked up and the resulting yellow oil was shown by GLC to consist of two major components in a ratio of about 1:3. After careful separation on a spinning-band column these two components were identified as 1-methyl-2-(1,1,2,2-tetramethylpropyl)benzene (the smaller peak) and 1-methyl-4-(1,1,2,2-tetramethylpropyl)benzene.

1-Methyl-2-(1,1,2,2-tetramethylpropyl)benzene. MS: 190(3), 175(1.5), 134(24), 133(100), 132(18), 119(18), 117(5), 105(20), 93(7), 91(6.5), 77(3), 57(5), 41(9), 40(5), 39(2). NMR: δ 0.83 (9 H, s, *tert*-butyl), 1.33 (6 H, s, α,α-dimethyl), 2.31 (3 H, s, methyl), 7.14 (4 H, m, aromatic).

1-Methyl-4-(1,1,2,2-tetramethylpropyl)benzene. MS: 190(3), 175(3), 134(32), 133(100), 132(32), 119(21), 117(10), 115(6), 105(38), 93(13), 91(12), 77(5), 57(6), 41(18), 40(5), 39(4). NMR: δ 0.83 (9 H, s, *tert*-butyl), 1.32 (6 H, s, α,α-dimethyl), 2.27 (3 H, s, methyl), 7.04 (2 H, d, J 8.3 Hz, aromatic), 7.23 (2 H, d, J 8.3 Hz: aromatic).

2-Bromo-1,4-bis(1,1,2,2-tetramethylpropyl)-benzene (1b). To a stirred suspension of 1.1 g (4 mmol) of *1a* and 9.52 g (40 mmol) of sodium persulfate in 30 ml of acetic acid, molecular bromine (3.2 g, 20 mmol) was added dropwise over a 10 min period. The temperature was raised to 70 °C and the mixture was stirred for 40 h. Then the mixture was poured onto crushed ice and the aqueous layer extracted several times with hexane. The combined hexane extracts were washed with water, 5 % aqueous sodium hydroxide and then water again until neutral before drying over calcium sulfate. The solvent was evaporated and the remaining crystalline product was shown by GLC to consist of one product and unreacted starting material (10 %). The product was separated from the starting material by elution with hexane from a column of alumina and identified as 2-bromo-1,4-bis(1,1,2,2-tetramethylpropyl)-benzene. Yield 0.82 g (58 %), m.p. 81–82 °C. MS: 354(0.1), 352(0.1), 298(9), 297(40), 296(10), 295(40), 242(14), 241(88), 240(26), 239(100), 238(14), 237(13), 225(10), 211(6), 160(8), 159(7), 91(5), 57(61), 43(12). NMR: δ 0.85 (9 H, s, *tert*-butyl), 0.94 (9 H, s, *tert*-butyl), 1.30 (6 H, s, α,α-dimethyl), 1.58 (6 H, s, α,α-dimethyl), 7.12 (1 H, dd, J 2.3 and 8.6 Hz, aromatic), 7.31 (1 H, d, J 8.6 Hz, aromatic), 7.55 (1 H, d, J 2.3 Hz, aromatic). IR: 3030(w), 2980(vs), 2910(s), 2880(s), 1600(m), 1530(m), 1480(s), 1470(s), 1400(w), 1380(vs), 1360(s), 1255(m), 1220(m), 1205(m), 1160(s), 1125(s), 1030(vs), 920(w), 890(m), 830(s).

2,5-Dibromo-1,4-bis(1,1,2,2-tetramethylpropyl) benzene (1c). Silver perchlorate (3.75 g, 18 mmol) was dissolved in 150 ml of acetic acid. A solution of 1.0 g (3.6 mmol) of *1a* in 40 ml of dioxane was added under stirring. To this mixture bromine (2.85 g, 18 mmol), dissolved in 10 ml of acetic acid/dioxane 4:1, was added dropwise. The reaction mixture was stirred in darkness for 24 h at room temperature. Precipitated silver bromide was then filtered off, and 10 % aqueous sodium hydroxide was added to the filtrate until it became slightly basic, and this solution was extracted three times with hexane. The combined hexane extracts were decolourized by shaking with 5 % aqueous sodium hydroxide, washed with water and then finally dried over calcium sulfate. The solvent was evaporated and the remaining light yellow crystals were shown by GLC to consist of two components in a ratio of 9:1. The smaller component was unreacted starting material and the other one was identified as 2,5-dibromo-1,4-bis(1,1,2,2-tetramethylpropyl)benzene after separation on a column of alumina with hexane as eluent. Yield 1.0 g (64 %), m.p. 176–177 °C. MS: 434(0.2), 432(0.4), 430(0.2), 419(0.6), 417 (1.2), 415(0.7), 378(6), 377(19), 376(10), 375(37), 374(7), 373(19), 322(17), 321(59), 320(46), 319(100), 318(43), 317(71), 316(15), 306(4), 304(9), 302(6), 292(7), 290(13), 288(8), 276(3), 274(6), 272(3), 240(6), 238(7), 115(5), 91(2), 57(76), 41(15), 40(8), 29(9). NMR: δ 0.94 (18 H, s, *tert*-butyl), 1.56 (12 H, s, α,α-dimethyl), 7.57 (2 H, s, aromatic). IR: 3020(m), 2980(vs), 2960(vs), 2900(s), 2870(m), 1465(s), 1405(m), 1380(m), 1370(m), 1310(m), 1240(w), 1220(m), 1205(w), 1160(m), 1140(s), 1030(vs), 915(w), 890(m).

Attempts to brominate 1a *and* 1c *with* N,N-*dibromoisocyanuric acid.* To a stirred suspension

of 1.35 g (5 mmol) of *1a* in 25 ml of concentrated sulfuric acid, *N,N*-dibromoisocyanuric acid [23] (1.45 g, 5 mmol) dissolved in 30 ml of concentrated sulfuric acid was added rapidly at 25 °C. After 3 h, the mixture was poured onto crushed ice and extracted three times with cyclohexane. The organic extracts were combined and washed with 5 % aqueous sodium hydroxide and water and then dried over calcium sulfate. Evaporation of the solvent yielded only starting material according to GLC and NMR analyses. When *1c* was reacted in the same manner as described above only starting material was collected in the reaction mixture.

2-Nitro-1,4-bis(1,1,2,2-tetramethylpropyl)benzene (1d). A solution of 4.4 g (16 mmol) of *1a* in 125 ml of acetic anhydride and 50 ml of acetic acid was stirred at 50 °C while 10 ml of nitric acid ($d = 1.52$) in 50 ml of acetic anhydride was added dropwise. The progress of the reaction was followed by GLC and it was found to be complete after 4 days of stirring at 50 °C. The solution was then cooled and poured onto crushed ice and carefully neutralized with solid sodium carbonate. The aqueous layer was extracted several times with cyclohexane, the combined cyclohexane extracts washed with water and then dried over calcium sulfate. The yellow solution was decolourized with charcoal and the solvent was evaporated. The remaining oil was crystallized in methanol and after one recrystallization 2.7 g (56 %) of faint yellow crystals were collected. M.p. 79–80 °C. MS: 319(0.2), 304(5), 262(21.5), 246(23), 206(31.5), 190(44.5), 189(41), 188(13.5), 174(13.5), 173(10), 172(12), 164(23), 163(10), 147(12), 146(18), 132 (12.5), 117(12), 115(8.5), 96(39), 91(10), 57(100), 43(16), 41(45), 29(22). NMR: δ 0.83 (9 H, s, *tert*-butyl), 0.94 (9 H, s, *tert*-butyl), 1.32 (6 H, s, α,α-dimethyl), 1.36 (6 H, s, α,α-dimethyl), 7.08 (1 H, d, J 2.23 Hz, aromatic), 7.34 (1 H, dd, J 2.23 and 8.58 Hz, aromatic), 7.40 (1 H, d, J 8.58 Hz, aromatic). IR: 3090(w), 2980(vs), 2910(s), 2880(s), 1610(w), 1530(vs), 1475(s), 1455(s), 1400(m), 1375(vs), 1220(m), 1155(m), 1125(m), 1055(m), 840(s).

2,5-Dinitro-1,4-bis(1,1,2,2-tetramethylpropyl)benzene (1e). In a flask equipped with a magnetic stirring bar, 1.35 g (5 mmol) of *1a* was dissolved in 10 ml of chloroform. A solution of 0.4 ml of nitric acid ($d = 1.40$) in 0.6 ml of concentrated sulfuric acid was added rapidly and the mixture was stirred at room temperature. After 12 h practically no reaction had occurred according to GLC, and more nitrating mixture (16 ml of nitric acid in 24 ml of sulfuric acid) was added. After a total reaction time of 4 days the mixture was poured onto crushed ice and extracted three times with dichloromethane. The combined organic extracts were washed with 5 % aqueous sodium hydroxide and water and then dried over calcium sulfate. Evaporation of the solvent yielded 1.2 g of crude product. This crude product was shown by GLC to consist of a mixture of two main products and several other compounds with lower retention times. Partial separation was performed on a column of silica gel. With toluene as eluent, the two main products were eluted together. Separation of these two products could be achieved by recrystallization twice in cyclohexane which gave 100 mg of white crystals, 95 % pure according to GLC. Identification by MS and NMR proved it to be 2,5-dinitro-1,4-bis(1,1,2,2-tetramethylpropyl)-benzene (*1e*) M.p. 208–209 °C. MS: 364(0.1), 349(3.5), 308(6), 291(5), 262(7), 246(7), 236(5), 235(36), 219(8), 207(6), 206(9), 205(8), 190(11.5), 189(10), 164(6), 96(8), 77(2), 57(100), 43(10), 41(24.5), 40(52), 29(28). NMR: δ 0.93 (18 H, s, *tert*-butyl), 1.35 (12 H, s, α,α-dimethyl), 7.27 (2 H, s, aromatic).

Evaporation of the combined filtrate solution gave 600 mg of faint yellow crystals with the same physical and spectral properties as *1d*.

2-Amino-1,4-bis(1,1,2,2-tetramethylpropyl)-benzene (1f). 2-Nitro-1,4-bis-(1,1,2,2-tetramethylpropyl)benzene (2.6 g, 8 mmol) was dissolved in 100 ml of 99.5 % ethanol under warming. This solution was added to 150 mg of 10 % palladium on charcoal and hydrogenation was carried out in a Parr low-pressure hydrogenator at about 50 °C. After 4 days the theoretical amount of hydrogen had been adsorbed. The catalyst was filtered off, washed twice with warm ethanol and the combined ethanol solution was evaporated, yielding a crystalline solid that was identified as 2-amino-1,4-bis(1,1,2,2-tetramethylpropyl)benzene (*1f*). This solid was purified *via* the amine hydrochloride, yielding, after decomposition of the salt, 1.9 g (83 %) of white crystals which were 99.5 % pure according to GLC. M.p. 155–156 °C. MS: 289(4), 274(3), 233(16), 232(85), 202(6), 177(14.5), 176 (100), 175(27.5), 174(9.5), 161(6), 160(16), 134 (7), 57(10), 41(11), 29(5). NMR: δ 0.84 (9 H, s. *tert*-butyl), 0.93 (9 H, s, *tert*-butyl), 1.29 (6 H, s, α,α-dimethyl), 1.47 (6 H, s, α,α-dimethyl), 3.63 (2 H, s, amino), 6.53 (1 H, d, J 2.45 Hz, aromatic), 6.70 (1, H, dd, J 2.45 and 8.75 Hz, aromatic), 7.07 (1 H, d, J 8.75 Hz, aromatic). IR: 3480(m), 3400(m), 2980(vs), 2950(vs), 2900(s), 2860(s), 1620(s), 1550(m), 1510(m), 1480(m), 1460(s), 1405(s), 1375(s), 1305(m), 1200(w), 1160(m), 1100(w), 810(m).

2-Acetylamino-1,4-bis(1,1,2,2-tetramethylpropyl)benzene (1g). 2-Amino-1,4-bis(1,1,2,2-tetramethylpropyl)benzene (0.29 g, 1.0 mmol) was dissolved in 10 ml of acetic acid and 5 ml of acetic anhydride. This solution was stirred at room temperature and the reaction progress was followed by GLC. After 4 days of stirring, the reaction was complete and the solution was poured onto crushed ice and extracted twice with ether. The combined ether extracts were washed with water, 5 % aqueous sodium carbonate and water, in that order, and then dried over calcium sulfate. Evaporation of the ether yielded a solid that was recrystallized in cyclohexane. The dried product was more than 99 % pure according to GLC. Yield 0.23 g

(70 %), m.p. 161–162 °C. MS: 331(0.3), 316 (3.5), 274(84), 232(11.5), 219(47), 218(100), 202(15), 200(27), 199(14), 178(17), 177(89), 176 (86), 174(34), 160(21), 159(32), 158(16), 134(48), 132(16), 94(15), 91(15), 57(88), 56(43), 43(78), 41(93), 39(51), 29(52). NMR (100 °C): δ 0.84 (9 H, s, *tert*-butyl), 0.91 (9 H, s, *tert*-butyl), 1.32 (6 H, s, α,α-dimethyl), 1.46 (6 H, s, α,α-dimethyl), 1.51 (1 H, s, amide), 2.01 (3 H, s, acetyl), 7.15 (3 H, m, aromatic). IR: 3560(m), 3420(m), 3320(m), 2980(vs), 2920(s), 2880(s), 1685(s), 1660(vs), 1640(s), 1555(m), 1525(s), 1475(s), 1400(s), 1380(s), 1300(w), 1155(m), 1125(m), 830(m).

Attempts to cyclotrimetize 3,3,4,4-tetramethyl-2-pentanone. 3,3,4,4-Tetramethyl-2-pentanone (2.3 g, 16 mmol) was reacted with sodium hydride (0.78 g, of 50 % suspension in mineral oil, 16 mmol) in the same way as described for the synthesis of 1,3,5-trineopentylbenzene.[1] After a second addition of 1.15 g (8 mmol) of ketone, the temperature was raised to 200 °C and maintained at this temperature for 24 h. After the usual work-up procedure the resulting oil was shown, by GLC, to consist of about 50 % of unreacted 3,3,4.4-tetramethyl-2-pentanone and about 50 % of a complex mixture of compounds. After the unreacted starting material had been separated off, an NMR spectrum of the complex mixture showed no bands in the aromatic region.

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