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1,3,5-Trineopentylbenzene

III.* The Halogenation of 1,3,5-Trineopentylbenzene and Some of Its Derivatives

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The halogenation of a series of 2-X-1,3,5-trineopentylbenzenes (X=H, Cl, Br, I, CH_3) with molecular halogens (Cl_2, Br_2, ICl, I_2) and positive halogenating species ("Br^+", "I^+") has been investigated. A series of new mono- and dihalogenated trineopentylbenzenes as well as polychlorinated neopentylbenzene derivatives have been prepared. The reactivity observed for both molecular and "positive halogens" as well as for different 2-X-1,3,5-trineopentylbenzenes varied as expected for electrophilic halogenations. NMR and IR data for these hitherto unknown 2-X-1,3,5-trineopentylbenzenes and 2-X-4-Y-1,3,5-trineopentylbenzenes (X=H, Cl, Br, I, CH_3, Y=Cl, Br) are reported. Strong temperature dependence of the NMR spectra of all the 2-X-4-Y-1,3,5-trineopentylbenzenes was observed.

The recent preparation of 1,3,5-trineopentylbenzene[1,2] (TNB, I) and some of its derivatives[3] made these highly substituted benzenes available for studying the influence of steric factors on the mechanism of electrophilic aromatic halogenations. This work, using the isotope-effect technique, is published in the subsequent two papers of this series. Prior to isotope-effect investigations, however, it was of interest to study the halogenation of (I) and its derivatives in some detail.

The halogenation of aromatic compounds with electrophilic halogenating species has been extensively reviewed.[4–6] Polyalkylbenzenes were found to be, in general, suitable substrates for halogenations. However, there seem to be only a few investigations dealing systematically with the halogenation of

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1,3,5-trialkylbenzenes and their derivatives. These investigations may briefly be summarized as follows.

The chlorination of mesitylene, with or without a catalyst, proceeds smoothly, yielding mono-,[7,8] di-,[8] or tri-[8,9] chloromesitylene. During iron-catalysed chlorination, polyalkylbenzenes containing alkyl side-chains higher than methyl suffer chlorodealkylation, yielding hexachlorobenzene as the final product,[9] but with care the reactions may be controlled and in some cases polychlorobenzenes were isolated.

Similarly, mesitylene [10] and 1,3,5-triethylbenzene [11–13] undergo stepwise nuclear bromination under mild conditions yielding the corresponding tribromoderivatives as end-products. Hennion and Anderson [13] have found that in the iron-catalysed polybromination of higher polyalkylbenzenes, only the primary alkyl groups are retained, whereas secondary and tertiary alkyl groups are displaced, yielding hexabromobenzene as the final product. The authors concluded that both steric and electron-releasing properties of the alkyl groups may contribute to the ease of bromo-dealkylation reactions. It seems probable that the relative stability of the carbonium ions as leaving groups is one of the decisive factors, although the effect of the electrophilic power of the reagent should not be underestimated, as shown by the chlorodealkylation [9] (*vide supra*) or by the enhanced bromo-dealkylating power of the bromine-aluminium tribromide reagent.[12] Nevertheless, under mild conditions the monobromination of 1,3,5-triisopropylbenzene with molecular bromine in the presence of an iron catalyst [14,15] and a slow bromination of 1,3,5-tri-*t*-butylbenzene with molecular bromine in the presence of zinc chloride as catalyst [16] has been reported. In the latter case, however, silver ion-induced bromination [17,18] has been recommended for preparative purposes, although the method is again accompanied by undesired bromo-dealkylation [17–19] and in acetic acid solution by acetoxylation,[18] as well. Recently it was found that these side-reactions may be general for this type of halogenation.[18]

Molecular iodine is unreactive compared with chlorine or bromine. Therefore, polyalkylbenzenes can only be iodinated under special conditions, mainly in the presence of strong oxidizing agents such as nitric acid, sulphuric acid, *etc.* These reagents are, however, reactive electrophiles, and they often induce nitration or sulphonation and sometimes undesired oxidation of the alkyl side-chain as well. Nevertheless, molecular iodine and nitrosylsulphuric acid,[20] and molecular iodine and iodic acid [21,22] bring about iodination of mesitylene and of 1,3,5-triethylbenzene, respectively. More recently, a crossed Jacobsen reaction with *o*-iodoanisole in the presence of concentrated sulphuric acid has been reported [23] as a general method for the iodination of polyalkylbenzenes. The method was found to be effective for the monoiodination of 1,3,5-triethylbenzene and 1,3,5-triisopropylbenzene. Silver ion-induced iodination has also been recommended [24,25] as a valuable method for a variety of cases. But neither of these methods gives rise to complete nuclear iodination of the more branched symmetrical trialkylbenzenes.

1,3,5-Trineopentylbenzene (I), when prepared, was expected to be a moderately reactive aromatic exhibiting some steric effect in aromatic substitution reactions. Therefore, the main objectives of the present investigations

were the study of the reactivity of (I) and of its substituted derivatives towards electrophilic halogenating reagents, and the elaboration of the proper conditions for both the preparation of halogenated trineopentylbenzenes and isotope-effect investigations.

RESULTS AND DISCUSSION

Uncatalysed halogenations with molecular species

Chlorination of (I) with two moles of chlorine * in dimethylformamide (DMF) at room temperature yields 2-chloro-1,3,5-trineopentylbenzene (ClTNB, II) in nearly quantitative yield.

Under similar conditions molecular bromine converts (I) into 2-bromo-1,3,5-trineopentylbenzene (BrTNB, III), but at least a 100 % excess of bromine should be used to compensate for tribromide formation through the equilibrium

$$Br^- + Br_2 \rightleftharpoons Br_3^-$$

because tribromide ion is not a brominating species for (I). For preparative purposes a 4—5 fold excess of bromine is desirable to avoid unnecessarily long reaction times.

On the other hand, molecular iodine or iodine monochloride fail to yield 2-iodo-1,3,5-trineopentylbenzene (ITNB, IV) in DMF solution even at elevated temperatures.

Molecular chlorine, if present in large excess in DMF solution, converts the 2-X-1,3,5-trineopentylbenzenes (II—IV) to 2,4-dichloro-1,3,5-trineopentylbenzene (Cl_2TNB, V), 2-bromo-4-chloro-1,3,5-trineopentylbenzene (ClBrTNB, VI) and 2-chloro-4-iodo-1,3,5-trineopentylbenzene (ClITNB, VII), respectively.

On the contrary, molecular bromine seems to be completely unreactive towards (II—IV) in DMF solution, because no evidence for the formation of di- or higher halogenated products, within the limits of the analytical methods used, was observed, but it easily brominates 2-methyl-1,3,5-trineopentylbenzene (MeTNB, VIII)[3] yielding 2-bromo-4-methyl-1,3,5-trineopentylbenzene (BrMeTNB, IX) in very high yield.

These halogenation reactions (Chart I) were found to be complete within a few minutes, but they were still slow enough to be followed in their initial stages. Gas chromatographic (GLC) analyses of the reaction mixtures and the products showed almost complete purity. Some minor impurities hidden under the tails of the product peaks could be detected, but their quantity was estimated as less than 1 % based on results obtained by using different types of chromatographic columns. The single exception was the chlorination of (IV). In this case several impurities were observed in small but varying amounts on the gas chromatograms recorded during the reaction and on those

* The chlorination of TNB with less than 2 moles of chlorine gas in DMF certainly proceeds but, in order to cover losses in the semi-micro scale used, a 100 % excess of chlorine is rather safe without any dichlorination. For larger scale synthesis a smaller excess of chlorine could well be satisfactory.

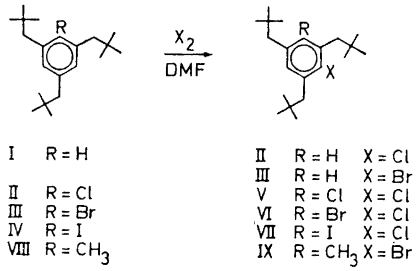


Chart I. Molecular halogenation of TNB derivatives in dimethylformamide. $X_2 = Cl_2$ or Br_2.

of the product mixture. Two of these impurities had the same retention time as authentic samples of (II) and (V), respectively. But even in this case (VII) could be isolated in better than 99 % purity after two recrystallizations.

Uncatalysed halogenations of TNB (I) in other solvents were found to be less favourable. TNB (I) is poorly soluble in acetic acid and in trifluoroacetic acid, and brominations in dilute solutions are rather slow compared to those in DMF. Trifluoroacetic acid was also found to be effective in inducing a hydrogen-exchange reaction with the aromatic hydrogens of (I). This exchange reaction might interfere with isotope effect investigations, and therefore halogenations with molecular species in these solvents have not been investigated in detail.

It should be mentioned, however, that iodine monochloride in trifluoroacetic acid solution at moderately elevated temperatures reacts with TNB (I) yielding a complex mixture of products identified by GLC as unreacted (I), a large quantity of (II) and some (IV), (V), (VII), as well as 2,4,6-trichloro-1,3,5-trineopentylbenzene (Cl_3TNB, XII). From this complex mixture only (XII) has been isolated in pure form. The complexity of the mixture formed shows that under these conditions chlorination is favourably competing with iodination. This is not at all surprising, as it has been pointed out [26] that iodine monochloride also acts as a chlorinating agent by the formation of chlorine through the equilibrium

$$2\ ICl \rightleftharpoons I_2 + Cl_2$$

if the reactive positions of the aromatic compound are sterically hindered. In addition, the quantity of iodinated products originally formed might be reduced further by a protodeiodination reaction in this highly acidic solvent.*

Uncatalysed chlorination or bromination of TNB (I) in carbon tetrachloride solution also gives a complex mixture of products, containing unreacted starting material and at least four different chlorinated or brominated compounds, among which some (II) or (III), respectively, were indicated by GLC, but neither of them has been identified in purified form.

* ITNB, when heated in trifluoroacetic acid solution at 100—110°C in a sealed tube, underwent complete protodeiodination within a few hours.

In conclusion, uncatalysed halogenations with molecular species in DMF were found to be the most favourable, for both preparative purposes and mechanistic investigations.

Mechanistic aspects of halogenations in DMF solution have not been investigated. It has been previously pointed out that the bromination of 1,3,5-trimethoxybenzene [27] and its bromo-[28] and methyl-[29] substituted derivatives, as well as that of 1,3,5-triethylbenzene and its bromo-[30] and methyl-[31] substituted derivatives follows the generally accepted two-step mechanism under these conditions.

$$ArH + Br_2 \underset{-1}{\overset{1}{\rightleftharpoons}} ArHBr^+ + Br^- \xrightarrow[base]{2} ArBr + H^+ + Br^-$$

The analogy between trineopentyl- and trimethoxybenzene and, in particular, triethylbenzene is quite close. In addition, the observed reactivity of molecular halogens ($Cl_2 > Br_2 > ICl > I_2$) as well as of trineopentylbenzenes (VIII > I > II—IV) follows the same order as expected for electrophilic halogenations, and therefore the mechanism seems consistent with the one depicted above. Consequently, there seems to be no reason to question the validity of the two-step model in DMF solution. The somewhat lowered reactivity of (I) and its derivatives (II—IV, VIII), compared to those of other aromatics more thoroughly investigated,[4-6,27-31] is believed to be the most pronounced deviation in the details of the mechanism. Therefore, these preparative results led to the conclusion that, with the exception of the chlorination of (IV), halogenations of trineopentylbenzenes (I—III) in DMF solution are favourable for isotope-effect investigations as well.

Catalysed halogenations

Catalysed reactions are also widely used for the preparative halogenation of polyalkylbenzenes.

Chlorination of TNB (I) in carbon tetrachloride solution, in the presence of an iron catalyst (Friedel-Crafts conditions), at 0—10°C, gives a complex mixture as the result of nuclear chlorination and chlorodealkylation reactions (Chart II). Repeated GLC analyses of the reaction mixtures during the course of the reaction showed a continuous formation followed by a gradual consumption of the more chlorinated products with intact carbon skeleton. This suggests that nuclear chlorination precedes chlorodealkylation. Despite this general trend the reaction does not proceed by cleanly separated steps. For example, GLC analyses of the reaction mixtures clearly showed substantial formation of Cl_3TNB (XII) before appreciable decrease in concentration of (II), the initial product of the chlorination reaction. The peak of the compound identified as 1,2,3,5-tetrachloro-4,6-dineopentylbenzene (Cl_4DNP, XIII) also appeared much before the disappearance of (V). Consequently, the chlorine-ferric chloride reagent should be regarded as a rather strong electrophile, exhibiting low substrate selectivity.

The complexity of the reaction makes it unfavourable for preparative purposes, but Cl_3TNB (XII), Cl_4DNB (XIII), and pentachloroneopentylbenzene (Cl_5NB, XIV) have been isolated from different batches in the follow-

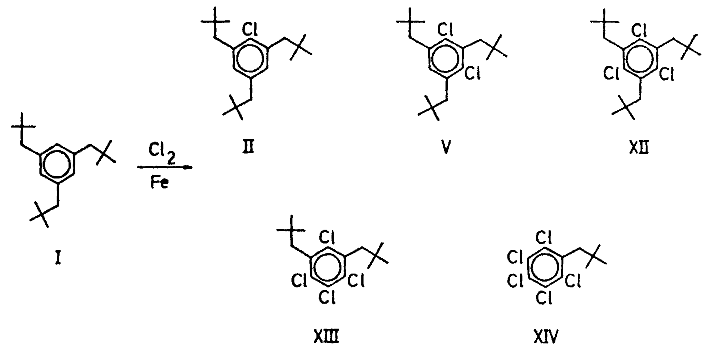


Chart II. Chlorination of TNB under Friedel-Crafts conditions.

ing way. Cautiously conducted reactions were followed with GLC and interrupted at the proper time. After the usual work-up procedure the reaction mixtures were subjected to preparative GLC.

An attempt to isolate hexachlorobenzene from the reaction mixture, when the reaction was run at room temperature or below, was unsuccessful, but in accordance with the findings reported by Harvey *et al.*[9] concerning mesitylene, it appeared in boiling carbon tetrachloride.

Iodine-catalysed bromination of TNB (I) with 2 moles of bromine in carbon tetrachloride yields (III) with a minor amount of Br_2TNB (X) as impurity. When iron catalyst and two moles of bromine are used (X) is the product, but one mole of bromine results in a high yield of (III). In the presence of a large excess of bromine, prolonged reaction time results in a small extra peak with a rather long retention time in the gas chromatograms. It might probably be 2,4,6-tribromo-1,3,5-trineopentylbenzene, but its quantity was too small and it could not be identified in pure form. These results also provide further support for the observations of Hennion and Anderson,[13] as no bromodealkylation was observed within the limits of the GLC analyses.

Molecular iodine in carbon tetrachloride with an iron catalyst was found to be unreactive. On the other hand, iodine monochloride reacts with (I) in carbon tetrachloride solution in the presence of an iron catalyst, resulting in a mixture of products (II, IV, V, VII, XII, and unreacted I) similar to the one found in trifluoroacetic acid solution (*vide supra*), *i.e.* iodine monochloride acts again as a chlorinating as well as an iodinating agent. As iodine monochloride, in accordance to the expected polarization within the molecule, usually gives only iodinated products, the diminished iodinating power of iodine monochloride in this case may be taken as an indication of a definite steric retardation of iodination of (I) caused by the bulky neopentyl substituents.

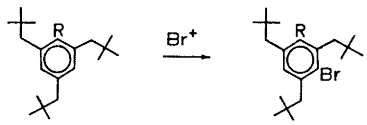
Silver ion-induced halogenations

As molecular bromine is fairly unreactive towards monohalogenated 1,3,5-trineopentylbenzenes (II—IV) and no iodination of (I) takes place with molecular iodine, reactions with the more reactive "positive" bromine and iodine have also been investigated.

From the mechanistic point of view the most extensively investigated positive halogenating species are the protonated hypohalous acids,[4-6] but the insolubility of TNB (I) in solvent systems containing appreciable amounts of water ruled out the use of these reagents. Therefore the silver ion-induced halogenations[32] have been investigated.

Silver and other metal salts of carboxylic acids form acyl hypohalites when treated with an equivalent amount or excess of halogen.[33] These compounds are considered to be effective halogenating agents for aromatics. Thus, in mixtures of bromine and silver acetate,[54-36] bromine or iodine and silver trifluoroacetate,[37,38] chlorine and mercuric acetate [39] as well as bromine and mercuric acetate [40] the acyl hypohalites have repeatedly been shown to be the active halogenating species. Even more powerful "positive halogens" are formed from the silver salts of mineral acids and molecular halogens, the most reactive reagents being the silver perchlorate-halogen systems,[23] originally introduced by Birkenbach and Goubeau.[24]

TNB (I) and its derivatives (II—IV) undergo rapid nuclear bromination with "positive bromine" formed either from silver trifluoroacetate or silver perchlorate and molecular bromine. Silver perchlorate and iodine was also found to be an energetic iodinating reagent for TNB (I). All of these reactions were carried out in aqueous acetic acid-dioxane (the addition of different amounts of water was made to get a suitable reaction rate for kinetic studies).



I R H
II R = Cl
III R = Br
IV R = I

III R H
VI R = Cl
X R = Br
XI R = I

Chart III. "Positive bromination" of TNB derivatives.

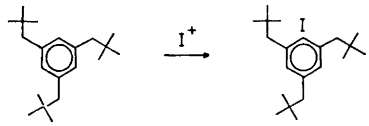
Thus, trifluoroacetyl hypobromite brominates (I), (II), and (III) to the corresponding bromo derivatives (III), (VI), and (X), respectively, in 50—80 % yields, but ITNB (IV) reacts rather slowly with this reagent. GLC analyses of the product mixtures in the first three cases showed only trace amounts of impurities (besides unreacted starting material), indicating that the extent of undesired side-reactions accompanying the substitutions is negligible.

Trifluoroacetyl hypoiodite was found to be unreactive towards TNB (I) and its monohalogenated derivatives (II—IV).

"Positive halogens" derived from silver perchlorate were found to be still more reactive. Thus, bromination of (I) under these conditions resulted in a mixture of BrTNB (III) and Br_2TNB (VIII). Also, ClTNB (II), BrTNB (III) and ITNB (IV) underwent rapid nuclear substitutions yielding the corresponding bromo derivatives (VI, VIII and IX), in yields greater than 90 %.

The silver perchlorate-induced reaction was also found to be successful for the iodination of (I), but the halogenated derivatives of TNB (II—IV)

failed to react with "positive iodine" formed from silver perchlorate and molecular iodine.



GLC analyses of the reaction mixtures as well as products again showed rather high chemical purities, leading to the conclusion that the extent of side-reactions is again unimportant.

For a better characterization of the relative reactivities of TNB derivatives (I—IV) towards trifluoroacetyl hypobromite as well as bromine perchlorate and iodine perchlorate reagents the progress of the reactions was followed at room temperature in dilute solutions containing both reagents in equimolar initial concentrations (0.005—0.04 M in aqueous acetic acid-dioxane (5:1 v/v) with definite amounts of added water (Table 1)). In all these runs the whole reaction mixture was quenched at different time intervals (generally after 5, 10, 15, 30, and 60 sec) by adding sodium carbonate-sodium sulphite solutions followed by work-up and GLC analyses of the resulting mixtures. Calculated approximate rate constants are tabulated in Table 1.

Table 1. Approximate rate constants for the "positive" halogenation of TNB derivatives at room temperature.

Reagent	Substrate	Product	Solvent	Approximate rate constants (M^{-1} sec^{-1})
CF_3COOBr	TNB	BrTNB	A	50
CF_3COOBr	ClTNB	BrClTNB	A	0.25
CF_3COOBr	BrTNB	Br_2TNB	A	0.24
$BrClO_4$	TNB	BrTNB + Br_2TNB	A	10^3
$BrClO_4$	ClTNB	BrClTNB	A	4.75
$BrClO_4$	BrTNB	Br_2TNB	A	4.68
$BrClO_4$	ITNB	BrITNB	B	0.25
$IClO_4$	TNB	ITNB	C	0.05

A: Acetic acid-dioxane-water (73.5:16.5:10.0 v/v)
B: Acetic acid-dioxane-water (78.5:16.5:5.0 v/v)
C: Acetic acid-dioxane-water (81.0:16.5:2.5 v/v)

It should be stressed that the method applied was a rather approximate one. The evaluation of more precise kinetic data, however, seemed to be doubtful as these reactions were extremely rapid. Repeated runs gave a reproducibility of better than ±20 %. The absolute precision should further be limited by the omission of temperature regulation and by the fact that

the solvents were purified only by a single distillation. Therefore, data are presented as approximate, but it is believed that the reliability is better than one order of magnitude and the data are still informative.

For the trifluoroacetyl hypobromite reagent a plot of $1/c$ *versus* reaction time for (II) and (III) gives a straight line only in the initial stage of the reaction, approximately up to 30—40 % conversion (corresponding to 2—3 min reaction), and then the consumption of the acetyl hypobromite is more rapid than that of the aromatic. Under these conditions the reactions generally stop at 45—50 % conversion. This has never been observed for the bromination of TNB (I), a substrate which gives practically complete bromination within this period. In addition, in more concentrated solutions, the same 1:1 molar ratio of the aromatics and of trifluoroacetyl hypobromite gave much higher conversion, generally 75—80 % as shown by GLC. Moreover, all the substrates gave straight lines up to 80—90 % conversion when the more reactive bromine perchlorate reagent was used. Therefore, it is believed that the more rapid consumption of the trifluoroacetyl hypobromite reagent could be due to some oxidative side-reaction with some reducing impurity in the solvent. The consumption of the reagent by the well-known Hunsdiecker decarboxylation seems to be less probable due to the small amount of water added to the solvent.

The rates of brominations are highly sensitive to the composition of the solvent system. Addition of a small amount of magnesium perchlorate (in concentrations comparable to those of the reagents) gives a practically negligible salt effect, but a large quantity (5—10 %) of added salt increases the rate of the reaction appreciably (Fig. 1).

On the other hand addition of water reduces the rate of the reactions (Fig. 2).

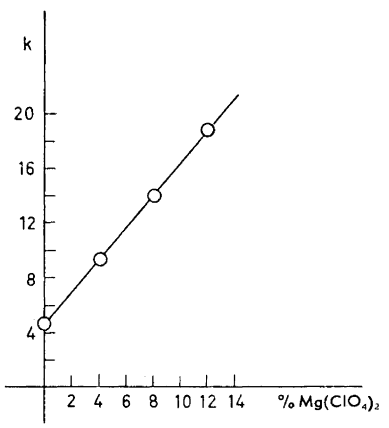


Fig. 1. Dependence of the rate constant k (M^{-1} sec^{-1}) for the bromination of BrTNB with $BrClO_4$ on the concentration of added magnesium perchlorate in acetic acid-dioxane-water (78.5:16.5:5.0 v/v) at room temperature.

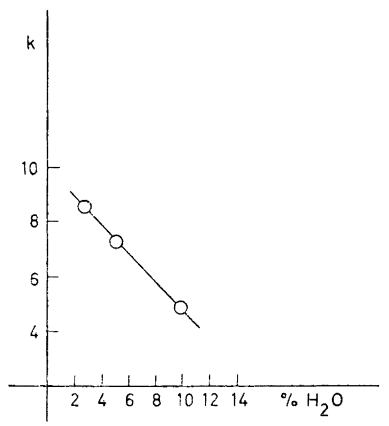


Fig. 2. The effect of added water on the rate constant k (M^{-1} sec^{-1}) of the bromination of BrTNB with $BrClO_4$ in the media A, B, and C (Table 1) at room temperature.

The observed relative rates, for the bromination of (I—IV) with trifluoroacetyl hypobromite and with bromine perchlorate, need some discussion. Partial rate factors for the bromination of monohalogenated symmetrical trialkylbenzenes are available only for the bromination of halogenated mesitylenes with molecular bromine in nitromethane.[41] These are summarized in Table 2 together with the corresponding values for the monosubstituted TNB

Table 2. Partial rate factors relative to the parent hydrocarbon in the bromination of monosubstituted mesitylenes with molecular bromine (A) and of TNB's with CF_3COOBr (B) and $BrClO_4$) (C).

Substituent	Partial rate factors (k/k_0) for brominations		
	A [a]	B [b]	C [b]
H	1	1	1
F	8.6×10^{-4}	—	—
Cl	4.9×10^{-4}	7.6×10^{-3}	7.1×10^{-3}
Br	4.3×10^{-4}	7.1×10^{-3}	7.0×10^{-3}
I	1.1×10^{-3}	$<10^{-4}$	3.8×10^{-4} *

[a] Reported by Illuminati and Marino.[41] Determined in nitromethane.
[b] Present investigation. Determined in acetic acid-dioxane-water (73.5:16.5:10.0), except in the starred case, which was determined with the solvent proportions (78.5:16.5:5.0).

derivatives relative to TNB (I) (k/k_0 values) for brominations with positive entities. If only the inductive effect were operative in the reaction a relative reactivity order of I>Br>Cl>F might be expected. The observed relative *meta*-reactivities for substituted mesitylenes is H>I>F>Cl≳Br and this suggests that resonance effects are also transmitted to the *meta* position, but the steric effect of the halogens seems to be less important as the most bulky iodine compound reacts most rapidly. For a similar series of 2-X-1,3,5-trineopentylbenzenes, however, the order of relative rates (H>Cl≳Br>I) is different both for bromination with trifluoroacetyl hypobromite and bromine perchlorate. This order does not exclude the possible operation of both inductive and resonance effects, but the relative reactivity of the *meta* positions seems to be controlled mainly by steric effects of the X substituents. In addition, the spread of the relative rates is not the same for the two series of brominations. Although the differences are not too great, they still seem to be significant, because the separation of the values is greater than the relative uncertainty of the method used. The higher relative rates for ClTNB (II) and BrTNB (III) as compared to the corresponding mesitylenes should be due to the enhanced reactivity of the "positive bromines", used in this investigation. This suggests a rather "early" transition state for the reaction, the transition state being more displaced towards the reactants as their reactivity increases. This should lead to a decrease in selectivity of the reac-

Table 3. Characteristic NMR shifts of TNB derivatives and some related compounds in CCl_4 solution (determined on 500 Hz sweep width at 40°C).

Compounds	Chemical shifts in ppm and the number of corresponding protons											
	Aromatic		Methylene				*t*-Butyl					
I TNB	6.65, s, 3H				2.42, s, 6H					0.90, s, 27H		
II ClTNB	6.81, s, 2H			2.73, s, 4H	2.41, s, 2H			0.97, s, 18H		0.92, s, 9H		
III BrTNB	6.75, s, 2H			2.79, s, 4H	2.38, s, 2H			0.97, s, 18H		0.92, s, 9H		
IV ITNB	6.82, s, 2H			2.92, s, 4H	2.41, s, 2H			0.99, s, 18H		0.92, s, 9H		
V Cl_3TNB	6.91, s, 1H	3.11, s, 2H	2.72, s, 4H[a]				1.02, s, 9H	0.98, s, 18H				
X Br_2TNB	6.90, s, 1H	3.33, s, 2H	2.79, q, 4H[b]				1.05, s, 9H	0.99, s, 18H				
VI ClBrTNB	6.93, s, 1H	3.23, s, 2H	2.81, s, 2H[a]		2.72, s, 2H[a]		1.04, s, 9H	0.99, s, 18H				
VII ClITNB	6.93, s, 1H	3.38, s, 2H	2.92, s, 2H[a]		2.72, s, 2H[a]		1.06, s, 9H	1.01, s, 9H		0.98, s, 9H		
XI BrITNB	6.93, s, 1H	3.53, q, 2H[c]	2.97, q, 2H[b]		2.76, q, 2H[b]		1.08, s, 9H	1.02, s, 9H		1.01, s, 9H		
IX $BrCH_3$TNB[d]	6.79, s, 1H	3.05, s, 2H[e]	2.78, s, 2H[e]		2.53, s, 2H[e]		0.97, s, 9H	0.96, s, 9H		0.94, s, 9H		
XII Cl_3TNB	—	3.13, s, 6H					1.06, s, 27H					
XIII Cl_4DNB	—	3.12, s, 4H					1.05, s, 18H					
XIV Cl_5NB	—	3.12, s, 2H					1.05, s, 9H					

[a] Broad singlet at 40°C, but an AB quartet appears at lower temperatures, centered around the same ppm value.
[b] Center of a broad AB quartet.
[c] Center of what is tentatively assigned a strongly coupled AB quartet.
[d] Methyl absorption at 2.30 ppm.
[e] Broad absorption between 2.4 and 3.3 ppm at 40°C. Reported values originates from three singlets resulting at 70°C.

tion * and lower the reactivity differences. Results of an isotope-effect study of these reactions are also consistent with an "early" transition-state model.[42]

Spectra

The NMR spectra of all the TNB derivatives are remarkably regular, giving unequivocal proof of the chemical constitution. The characteristic chemical shifts for the aromatic, methylene, and *t*-butyl protons in carbon tetrachloride solution are tabulated in Table 3. All data are reported in ppm downfield from TMS as internal standard.

The peaks from the three chemically different types of protons in TNB (I) appear as singlets.[1] The introduction of one halogen atom results in a characteristic downfield shift of the aromatic as well as the *ortho* methylene and *ortho* *t*-butyl peaks. The most characteristic shifts are those of the *ortho* methylene hydrogens, the magnitude of the shifts being 0.31, 0.37, and 0.50 ppm for Cl, Br, and I, respectively, from the original position in TNB. The positions of the peaks of the methylene protons *para* to the halogens (determined on 500 Hz sweep width) are nearly constant but they all seem to be shifted upfield a few Hz, if at all.

The introduction of a second halogen atom results in a further downfield shift. The aromatic and *t*-butyl protons again appear as singlets. The peaks corresponding to the methylene protons between the two halogens (deduced from the size of the integrals) appear as singlets for Cl_2TNB (V), Br_2TNB (X), ClBrTNB (VI), and ClITNB (VII), but the corresponding methylene peak is split for BrITNB (XI) at 40°C. This splitting is tentatively assigned a strongly coupled AB-system. Temperature dependence of this part of the spectrum has only been observed for BrITNB (XI) (at about 60—70°C the methylene peak appears as a sharp singlet).

Methylene protons which are *ortho* both to the remaining aromatic proton and the halogens appear as AB quartets at some temperatures due to the fact that they can become magnetically nonequivalent in a frozen nonplanar conformation. For Cl_2TNB this appears below 0°C, but for Br_2TNB it is observable at room temperature. The rate of the rotation about the Ar—CH_2 bonds has been measured by the NMR kinetic method. These investigations will be published in a separate paper.[43] For the unsymmetrical compounds ClBrTNB, ClITNB, and BrITNB (VI, VII, and XI) the situation is more complex, as this magnetic nonequivalence results in two AB systems superimposed onto one another. A quantitative study of these spectra is now under way. The data presented in Table 3 give only the most probable values of these AB systems.

On further nuclear substitution, as in Cl_3TNB (XII), only two sharp singlets appear, one for the methylene and one for the *t*-butyl protons. The position of the latter is very similar to that of the corresponding protons in Cl_2TNB (V). This pattern did not change on further chlorodealkylation,

* The decrease in selectivity of the more powerful reagents is clearly indicated by the present preparative results, *i.e.* molecular bromine does not react with compounds (II—IV), but both CF_3COOBr and $BrClO_4$ do. $BrClO_4$ gives a mixture of BrTNB (III) and Br_2TNB (X) when TNB is brominated, but CF_3COOBr gives only BrTNB (III).

resulting in practically identical spectra from Cl_4DNB (XIII) and Cl_5NB (XIV).

The IR spectra were also consistent with the structures of these new compounds. They are, however, less straightforward than the NMR spectra. Therefore, the detailed interpretation is omitted for the present, although characteristic IR bands are given in the experimental section.

The mass spectra of compounds (XII—XIV) have been recorded. They also support the structures indicated. The parent peaks appeared at *m/e* values of 390, 354, and 318, respectively. These values are identical with the molecular weights calculated for the isotopically pure compounds (XII—XIV). The intensities of the isotope peaks, relative to the parent peaks, were those expected for the tri-, tetra-, and pentachloro compounds. In addition, the degradation pattern (although it became more complex with increasing chlorine substitution) clearly indicated a step-wise cleavage of the required number of *t*-butyl groups (accompanied by hydrogen rearrangement). This fragmentation pattern was found to be characteristic for TNB [1] and for some of the monohalogenated trineopentylbenzenes as well.

EXPERIMENTAL

The NMR spectra were recorded on a Varian A-60 spectrometer equipped with a V 6040 variable temperature controller. Peaks are reported in ppm downfield from TMS as internal standard.

The infrared spectra were recorded on a Beckman IR-9 spectrophotometer, with potassium bromide pellets. The positions of the absorption maxima are expressed in wave numbers (cm^{-1}). Band intensities are indicated as weak (w), medium (m), strong (s), and very strong (vs).

Mass spectra were obtained at 70 eV on the LKB A 9000 mass spectrometer at the Department of Organic Chemistry of the University of Lund. Only the most abundant ions are tabulated.

Analytical GLC was carried out with a Perkin-Elmer F11 gas chromatograph equipped with a flame ionisation detector. For the analyses the following columns were used: 6 ft × 0.125 in. 15 % SE-30 silicone gum rubber on 80—100 Chromosorb W and 2 m × 0.125 in. 5 % Carbowax 20 M TPA on AW DMCS Chromosorb G 80—100 mesh. Percentage composition refers to the relative areas (planimeter integration) observed for the different compounds.

Preparative GLC was carried out with an Autoprep A 700 gas chromatograph on a 4 m × 0.25 in. column of 4 % silicone gum rubber on Chromosorb W 60—80 mesh.

The elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Melting points were determined on a Kofler micro hot stage.

1,3,5-Trineopentylbenzene (TNB, I) was prepared as reported previously.[2]

2-Methyl-1,3,5-trineopentylbenzene (MeTNB, VIII) was prepared by reduction of 2-chloromethyl-1,3,5-trineopentylbenzene with lithium aluminium hydride.[3]

2-Chloro-1,3,5-trineopentylbenzene (ClTNB, II)

Chlorination of TNB (I). Chlorine gas (1.75 g, 25.0 mmoles) was dissolved in 5 ml of dimethylformamide (DMF) and a solution of 3.6 g (12.5 mmoles) of TNB (I), dissolved in 40 ml of DMF, was added in one portion. The mixture was allowed to react at room temperature in the dark for about one hour. After this time GLC analysis of the reaction mixture showed complete conversion. The mixture was diluted with 500 ml of water and extracted with four 25 ml portions of carbon tetrachloride. The combined organic layers were washed, first with saturated sodium carbonate solution, then with water

until neutral. The solution was dried over Sikkon (Fluka, anhydrous calcium sulphate) overnight. Evaporation of the solvent gave 4.2 g (104 %) of crude oil which crystallized on standing. Recrystallization from ethanol (water was cautiously added to the hot solution until turbidity appeared) gave 3.9 g (95 %) of white crystalline product. GLC showed better than 99 % purity. M.p. 64.0—65.0°C. After several recrystallizations from ethanol-water the compound melted at 65.5—66.0°C. (Found: C 78.02; H 10.73; Cl 11.00. Calc. for $C_{21}H_{35}Cl$: C 78.10; H 10.92; Cl 10.98). *NMR spectrum* is given in Table 3. *IR spectrum:* 3050w, 2965vs, 2910s, 2864s, 1598w, 1580w, 1478s, 1432m, 1392m, 1367s, 1237m, 1202w, 1151w, 1046s, 881m, 872m.

2,4-Dichloro-1,3,5-trineopentylbenzene (Cl_2TNB, V)

a) Chlorination of ClTNB (II). A solution of 650 mg (2.0 mmoles) of (II) in 30 ml of DMF was cooled to 0°C in an ice-bath, protected from light and stirred magnetically. A slow chlorine-gas stream was bubbled into the mixture for about 30—40 min. The mixture was worked up as described in the preparation of (II) to yield 0.7 g of crude crystalline product (97 %). Recrystallization from abs. ethanol gave 0.62 g (87 %) of white crystals. After several recrystallizations the product melted at 83.0—83.5°C. (Found: C 70.98; H 9.31; Cl 19.62. Calc. for $C_{21}H_{34}Cl_2$: C 70.57; H 9.59; Cl 19.84). *NMR spectrum* is given in Table 3. *IR spectrum:* 3040w, 2960vs, 2910s, 2865s, 1582w, 1478s, 1467m, 1448m, 1420s, 1392s, 1365s, 1233s, 1201m, 1150m, 1068s, 1032w, 1000m, 878m.

b) Dichlorination of TNB (I). A solution of 578 mg (2.0 mmoles) of TNB (I) in 20 ml of DMF was chlorinated under the same conditions as (II) for 40—50 min. The work-up of the reaction product was also identical, and yielded 0.7 g of crude crystalline material. Recrystallization from abs. ethanol gave 0.6 g (84 %) of (V).

2-Bromo-4-chloro-1,3,5-trineopentylbenzene (ClBrTNB, VI)

Chlorination of BrTNB (III). A solution of 735 mg (2.0 mmoles) of BrTNB (III) in 20 ml of DMF was chlorinated under conditions identical to those used for (II) (see above) for 50 min. The work-up procedure was also similar, and yielded 0.8 g (99 %) of crude crystalline material. Recrystallization from abs. ethanol gave 0.72 g (87 %) of white crystals. After several recrystallizations from the same solvent the product melted at 80.0—80.5°C. (Found: C 63.06; H 8.54; Cl 8.76; Br 19.69. Calc. for $C_{21}H_{34}ClBr$: C 62.77; H 8.53; Cl 8.82; Br 19.88). *NMR spectrum* is given in Table 3. *IR spectrum:* 3044w, 2965vs, 2910m, 2870m, 1575w, 1479s, 1466m, 1459m, 1417m, 1395m, 1368s, 1235m, 1205w, 1155m, 1055m, 998m, 874m.

2-Chloro-4-iodo-1,3,5-trineopentylbenzene (ClITNB, VII)

Chlorination of ITNB (IV). A solution of 1.24 g (3.0 mmoles) of ITNB (IV) in 25 ml of DMF was chlorinated at room temperature with a slow chlorine-gas stream. The reaction mixture was protected from light and when necessary external water-cooling was also applied. After chlorination for 3 h the reaction was practically complete, but the reaction mixture contained a few percent of impurities (indicated by GLC to be (II) and (V) among others). The work-up procedure was identical with that in the preparation of (II), and yielded 1.35 g (100 %) of a crude yellow oil which crystallized on standing. Recrystallization from abs. ethanol gave 0.95 g (71 %) of white crystalline product. The purity of the recrystallized compound was better than 99 %. After several recrystallizations the compound melted at 67.5—68.0°C. (Found: C 56.02; H 7.54; Cl 8.08; I 28.58. Calc. for $C_{21}H_{34}ClI$: C 56.19; H 7.64; Cl 7.90; I 28.27). *NMR spectrum* is given in Table 3. *IR spectrum:* 3035w, 2955vs, 2905m, 2862m, 1570w, 1498s, 1463m; 1407m, 1392m, 1363s, 1230m, 1201w, 1150w, 1042m, 990m, 868m.

Polychlorinated neopentylbenzene derivatives

Chlorination of TNB (I) under Friedel-Crafts conditions (typical experiment). A solution of 870 mg (3.0 mmoles) of TNB (I) in 15 ml of carbon tetrachloride was cooled to 0°C, approximately 50 mg of iron powder was added as a catalyst and the reaction mixture was protected from light. A slow stream of chlorine gas was introduced into the well-stirred solution. At different time intervals small aliquots were withdrawn, the excess of chlorine was destroyed with sodium sulphite solution and the organic phase was washed until neutral. The composition of the reaction mixture (determined by GLC) at different times changed as follows:

30—40 min: ClTNB 20 %, Cl_2TNB 50 %, Cl_3TNB 30 %, other compounds 10 %.

80—90 min: ClTNB 0 %, Cl_2TNB 2—5 %, Cl_3TNB 70 %, Cl_4DNB 25 %; trace amounts of some other impurities were also observed.

150—180 min: Cl_3TNB 10 %, Cl_4DNB 55—60 %, Cl_5NB 25 %, and some other impurities 5 %.

After longer reaction times the quantity of Cl_5NB increased, but its formation was never complete.

Parallel experiments gave similar results, but the progress of the reaction is highly dependent on the rate of introduction of chlorine gas.

Isolation of 2,4,6-trichloro-1,3,5-trineopentylbenzene (XII). The chlorination was interrupted after 80—90 min reaction. The carbon tetrachloride solution was washed several times with dilute sodium hydroxide solution, washed with water, then with sodium sulphite solution, finally again with water. After drying (Sikkon, Fluka) the organic phase was evaporated to dryness. Preparative GLC of the white crystalline residue afforded an analytical sample of Cl_3TNB (XII), m.p. 132.5—133.5°C. (Can be recrystallized from abs. ethanol/petroleum ether.) *NMR spectrum* is given in Table 3. *IR spectrum:* 2950vs, 2900s, 2862s, 1533m, 1475s, 1460s, 1445m, 1392m, 1375m, 1365s, 1228s, 1200m, 1152s, 1032m, 990m, 874s, 730s. *Mass spectrum:* Intensities of isotope peaks relative to the parent peak (100), found: P+2 99.1; P+4 31.8; P+6 3.7, calculated for Cl_3-compounds:[44] P+2 99.8; P+4 31.9; P+6 3.47. Degradation pattern (isotope peaks are omitted): 390 (parent peak), 375, 333, 278, 222, 57 (base peak).

Isolation of 1,2,3,5-tetrachloro-4,6-dineopentylbenzene (XIII). The chlorination was interrupted after 2.5 h reaction and then the reaction mixture was worked up as in the isolation of (XII). The white crystalline compound obtained from the preparative GLC melted at 65—70°C, and consequently did not seem totally pure although no impurity could be detected by analytical GLC. *NMR spectrum* is given in Table 3. *IR spectrum:* 2962s, 2864m, 1540m, 1472m, 1464m, 1450m, 1368vs, 1228m, 1202w, 1152m, 1109m, 1038m, 995w, 876m, 760m. *Mass spectrum:* Intensities of isotope peaks relative to the parent peak (100), found: P+2 131.3; P+4 63.8; P+6 13.4; P+8 1, calculated for Cl_4-compounds:[44] P+2 131.0; P+4 63.9; P+6 14.0; P+8 1.15. Degradation pattern (isotope peaks are omitted): 354 (parent peak), 339, 297, 242, 57 (base peak).

Isolation of pentachloroneopentylbenzene (XIV). The reaction was interrupted after 5 h chlorination. The mixture was worked up as in the isolation of (XIII). Analytical GLC of the purified Cl_5NB showed about 5 % Cl_4DNB (XIII) impurity. *NMR spectrum* is given in Table 3. *IR spectrum:* 2970s, 1540w, 1475m, 1465m, 1445w, 1397w, 1370vs, 1354s, 1230m, 1152m, 1110m, 1138m, 889m, 778m, 765m, 680s. *Mass spectrum:* Intensities of isotope peaks relative to the parent peak (100), found: P+2 162.4; P+4 105.8; P+6 34.4; P+8 6.0, calculated for Cl_5-compounds:[44] P+2 163.0; P+4 106.0 P+6 34.7; P+8 5.66. Degradation pattern (isotope peaks are omitted): 318 (parent peak), 303, 261, 226, 191, 156, 149, 121, 57 (base peak).

2-Bromo-1,3,5-trineopentylbenzene (BrTNB, III)

a) Bromination of TNB (I) in DMF. To a solution of 2.9 g (10.0 mmoles) of (I) in 40 ml of DMF 8.0 g (50.0 mmoles) of bromine in 10 ml of DMF was added in small portions. The mixture was kept in the dark during the bromine addition and the subsequent 30 min reaction time. Then the reaction mixture was worked up as in the synthesis of (II). The yield was 3.4 g (93 %) of crude yellow product (generally an oil which crystallized slowly on standing). Recrystallization from abs. ethanol gave 3.2 g (87 %) of white

crystals, m.p. 48.0—49.0°C. After several recrystallizations from the same solvent the melting point rose to 50.0—50.5°C. (Found: C 68.31; H 9.68; Br 21.71. Calc. for $C_{21}H_{35}Br$: C 68.65; H 9.60; Br 21.75). *NMR spectrum* is given in Table 3. *IR spectrum:* 3050w, 2960vs, 2910s, 2860s, 1578w, 1479s, 1468m, 1429m, 1392m, 1365s, 1273m, 1201w, 1151w, 1019s, 882m, 872w.

b) Iodine-catalysed bromination of TNB (I) in carbon tetrachloride. To a solution of 289 mg (1.0 mmole) of (I) in 10 ml of carbon tetrachloride a few crystals of iodine and 0.32 g (2.0 mmoles) of bromine, in 2 ml of carbon tetrachloride, were added. The mixture was allowed to stand overnight in the dark at room temperature. The solution was then washed first with a 10 % sodium sulphite solution, then several times with water and finally dried over Sikkon (Fluka). The evaporation of the solvent gave a pale yellow oily residue (0.34 g). Recrystallization from abs. ethanol gave 0.32 g (87 %) of pure (III).

c) Iron-catalysed bromination of TNB (I) in carbon tetrachloride. To a solution of 3.6 g (12.5 mmoles) of (I) in 5 ml of carbon tetrachloride 100 mg of iron powder was added and the mixture cooled to 0°C. The reaction mixture was protected from the light and 2.0 g (12.5 mmoles) of bromine in 5 ml of carbon tetrachloride was added in two portions. The temperature was allowed to rise to room temperature overnight. The reaction mixture was poured into water, separated, and the organic phase was washed with 20 ml of 10 % sodium hydroxide solution followed by two 20 ml portions of saturated sodium chloride solution. After drying over anhydrous magnesium sulphate and evaporation of the solvent there remained 4.20 g (92 %) of (III).

2,4-Dibromo-1,3,5-trineopentylbenzene (Br_2TNB, X)

a) Iron-catalysed bromination of TNB (I) in carbon tetrachloride. Bromine (960 mg, 6.0 mmoles) was dissolved in 5 ml of carbon tetrachloride and added in one portion to a solution of 870 mg (3.0 mmoles) of TNB (I) in 20 ml of carbon tetrachloride containing 50 mg of iron powder as a catalyst. The reaction mixture was protected from light and left overnight at room temperature with stirring. The completion of the reaction was indicated by the (almost complete) disappearance of the bromine color. The reaction mixture was washed with 5×50 ml of sodium hydroxide solution (10 %) and then with distilled water until neutral. Evaporation to dryness afforded 1.24 g (92 %) of crude crystalline material. Recrystallization from abs. ethanol gave 1.1 g (82 %) of (X). After several recrystallizations from the same solvent the compound melted at 80.5—81.0°C. (Found: C 56.13; H 7.53; Br 34.60. Calc. for $C_{21}H_{34}Br_2$: C 56.51; H 7.68; Br 35.81). *NMR spectrum* is given in Table 3. *IR spectrum:* 3050w, 2970vs, 2910s, 2870s, 1570w, 1478s, 1468m, 1450m, 1422m, 1396m, 1369s, 1238m, 1206m, 1153w, 1141w, 1037m, 998w, 872m.

b) Silver perchlorate-induced bromination of BrTNB (III) in acetic acid-dioxane. BrTNB (III, 1.1 g, 3.0 mmoles) and 0.7 g (3.38 mmoles) of silver perchlorate, previously dried over P_2O_5 for 4—5 days, was dissolved in 20 ml of acetic acid-dioxane (5:1 v/v) under stirring. (In some cases 0.42 ml, 3.4 mmoles, of 70 % perchloric acid was also added, but this is not a necessary condition). To the vigorously stirred solution 5.5 g (3.4 mmoles) of bromine dissolved in 5 ml of acetic acid-dioxane (5:1 v/v) was added in one portion. Silver bromide precipitated immediately and the characteristic colour of bromine disappeared. The mixture was allowed to react for 15—20 min, then the silver bromide was filtered off and washed with several small portions of carbon tetrachloride. The filtrate was diluted with 200 ml of water, and extracted with 4×15 ml of carbon tetrachloride. The combined CCl_4 layers were washed first with dilute sodium hydroxide solution and then with water until neutral. If the removal of the bromine was not complete, an additional extraction with sodium sulphite solution was also made. After drying over Sikkon (Fluka) the solvent was distilled off. The remaining thick oil (1.3 g, 97 %) crystallized rapidly. Recrystallization from abs. ethanol yielded 1.15 g (86 %) of white crystalline product. Physical properties were identical with those of the compound prepared according to method *a*).

2-Bromo-4-iodo-1,3,5-trineopentylbenzene (BrITNB, XI)

Bromination of ITNB (IV). ITNB (IV, 1.24 g, 3.0 mmoles), 0.7 g (3.38 mmoles) of silver perchlorate and 0.42 ml (3.4 mmoles) of 70 % perchloric acid were dissolved in 20 ml of acetic acid-dioxane (5:1 v/v) whereupon 5.5 g (3.4 mmoles) of bromine in 5 ml of the same solvent was added. The reaction and work-up procedure were carried out as described for the preparation of (X). The yield of crude product was 1.35 g (93 %), and after recrystallization from abs. ethanol 1.1 g (75 %) of pure (XI) was obtained. Several recrystallizations from the same solvent raised the melting point to 73.0–73.5°C. (Found: C 51.26; H 6.89; Br 16.57; I 25.43. Calc. for $C_{21}H_{34}BrI$: C 51.13; H 6.95; Br 16.20; I 25.72). *NMR spectrum* is given in Table 3. *IR spectrum:* 3040w, 2960vs, 2905m, 2865s, 1770w, 1565w, 1478s, 1465m, 1448m, 1402m, 1394m, 1367m, 1230m, 1200m, 1149w, 1135w, 1030w, 1017m, 989w, 864m, 679m.

2-Iodo-1,3,5-trineopentylbenzene (ITNB, IV)

Iodination of TNB (I). TNB (I, 2.9 g, 10.0 mmoles), 2.6 g (12.5 mmoles) of silver perchlorate, previously dried over P_2O_5 for a few days, and 0.5 ml (3.5 mmoles) of 70 % perchloric acid were dissolved in a mixture of 10 ml of dioxane and 50 ml of acetic acid. Iodine (3.3 g, 13.0 mmoles) was added to 40 ml of acetic acid. Some iodine remained undissolved, but the saturated solution was added by decantation to the vigorously stirred reaction mixture. The rest of the iodine was dissolved by repeated addition of 5 ml portions of acetic acid and the solutions were added to the reaction mixture. This was repeated until the characteristic colour of iodine in the reaction mixture did not disappear. Then the reaction was completed by stirring for an additional 15 min. The mixture was worked up as described for the preparation of (X) to yield 4.0 g (97 %) of a yellow oil. Crystallization from abs. ethanol gave 3.7 g (89 %) of white crystalline compound. After several recrystallizations (IV) melted at 63.0–63.5°C. (Found: C 61.01; H 8.49; I 30.39. Calc. for $C_{21}H_{35}I$: C 60.87; H 8.51; I 30.62). *NMR spectrum* is given in Table 3. *IR spectrum:* 3050w, 2970vs, 2910s, 2870s, 1590w, 1565w, 1478s, 1468m, 1420m, 1396m, 1368s, 1238m, 1202m, 1004s, 881m, 869m.

Miscellaneous halogenations

Attempted iodination of ITNB (IV). ITNB (IV, 415 mg, 1.0 mmole), 420 mg (2.0 mmoles) of silver perchlorate and 0.1 ml (0.7 mmole) of 70 % perchloric acid in 10 ml of acetic acid-dioxane (4:1 v/v) were allowed to react for one hour with 500 mg (2.0 mmoles) of iodine dissolved in about 20 ml of acetic acid as described for the iodination of TNB. During the course of the reaction small aliquots were withdrawn, and GLC analyses of these aliquots as well as of the product resulting from the final work-up indicated only ITNB (IV). No diiodinated product could be detected.

Reaction of TNB (I) with iodine monochloride in carbon tetrachloride. TNB (I, 1.45 g, 5.0 mmoles) and 0.82 g (5.0 mmoles) of iodine monochloride were dissolved in 40 ml of carbon tetrachloride. To this solution 50 mg of iron powder was added and the reaction mixture was protected from light and allowed to react with moderate stirring for 24 h. The mixture was transferred to a separatory funnel and washed with 3×20 ml of 10 % sodium hydroxide solution, then with distilled water until neutral. After drying the solvent was evaporated. GLC analysis of the residual oily mixture indicated unreacted TNB, ClTNB, Cl_2TNB, ITNB, Cl_3TNB, ClITNB (as indicated by the relative retention times) and two other unidentified impurities in small amounts. No attempt has been made to isolate any of the compounds from this mixture.

Reaction of TNB (I) with iodine monochloride in trifluoroacetic acid. TNB (I, 2.40 g, 8.3 mmoles) was dissolved in 80 ml of trifluoroacetic acid by gentle heating. After cooling to room temperature 3.50 g (21.6 mmoles) of iodine monochloride was added, and the reaction mixture was protected from light. The temperature rose spontaneously to 70°C (slowly) and was maintained at this temperature by external heating for 10 h. The iodine

monochloride that sublimed into the condenser was now and then shaken down into the reaction flask. While still hot the solution was poured into 300 ml of an aqueous solution of sodium thiosulphate. Extraction with ether, drying of the organic phase over anhydrous magnesium sulphate and evaporation left a faintly brown residue. According to GLC this seemed very similar to the mixture resulting from the reaction in carbon tetrachloride. By four recrystallizations from abs. ethanol-petroleum ether (10:1) it was possible to isolate a pure sample of the compound with longest retention time, 2,4,6-trichloro-1,3,5-trineopentylbenzene (XII), m.p. 132.5–133.5°C.

2-Bromo-4-methyl-1,3,5-trineopentylbenzene (BrMeTNB, IX)

Bromination of MeTNB (VIII). To a solution of 303 mg (1.0 mmole) of MeTNB (VIII) in 5 ml of DMF, 0.8 g (5.0 mmoles) of bromine in 1 ml of DMF was added. The mixture was kept in the dark at room temperature overnight. Then the reaction mixture was worked up as in the synthesis of (II). The yield was 360 mg (95 %) of crystalline crude product. Recrystallization from abs. ethanol and from DMF gave 305 mg (80 %) of white crystals, m.p. 75.0–76.0°C. (Found: C 69.45; H 9.82; Br 20.73. Calc. for $C_{22}H_{37}Br$: C 69.27; H 9.78; Br 20.95). *NMR spectrum* is given in Table 3. *IR spectrum:* 3040w, 2960vs, 2906m, 2865s, 1478s, 1466m, 1439m, 1393m, 1365s, 1236m, 1204w, 1177w, 1153w, 1122m, 1033w, 994w, 884m.

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