

1,3,5-Trineopentylbenzene. VII.* Friedel-Crafts Reactions of 1,3,5-Trineopentylbenzene with Acyl Chlorides and Preparations of Some Chloro Derivatives of 1,3,5-Trineopentylbenzene

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2-Acetyl-1,3,5-trineopentylbenzene, 2-propanoyl-1,3,5-trineopentylbenzene, 2-benzoyl-1,3,5-trineopentylbenzene, 2-(2-methylpropanoyl)-1,3,5-trineopentylbenzene, and 2,4,6-trineopentylbenzenecarboxylic acid have been prepared by Friedel-Crafts acylation of 1,3,5-trineopentylbenzene with acyl chlorides and aluminum chloride in carbon disulfide. NMR, IR, and mass spectra are reported for these novel compounds.

Ring-chlorinated products were formed when 1,3,5-trineopentylbenzene was treated with antimony(V) chloride in carbon disulfide, and thus 1,3,5-trichloro-2,4,6-trineopentylbenzene could be prepared in good yield.

In the present investigation, larger and larger acyl groups were introduced into the ring of 1,3,5-trineopentylbenzene. In some cases, introduction of such groups into polyalkylbenzenes brings about migration³⁻⁵ or removal⁶ of alkyl groups, possibly due to steric strain,⁷ and it was considered of interest to study acylation reactions of the sterically hindered 1,3,5-trineopentylbenzene.

RESULTS

Dermer *et al.*⁸ have examined a series of metal chlorides to determine their relative efficiencies as Friedel-Crafts catalysts. For the acetylation of toluene, the efficiency was found to decrease in the series: aluminum chloride > antimony(V)

chloride > iron(III) chloride > tellurium(II) chloride > tin(IV) chloride. For the preparation of 2-acetyl, 2-propanoyl, 2-benzoyl, and 2-(2-methylpropanoyl)-1,3,5-trineopentylbenzene, and 2,4,6-trineopentylbenzenecarboxylic acid (I)–(V) in the present work, aluminum chloride, iron(III) chloride, and tin(IV) chloride were employed as catalysts, and carbon disulfide, dichloromethane, and nitrobenzene as solvents.

Freshly sublimed aluminum chloride caused dealkylation of 1,3,5-trineopentylbenzene to form 1,3-dineopentylbenzene, neopentylbenzene, and 2-methylbutane. The latter product was probably formed by rearrangement of neopentyl groups which had been removed from the 1,3,5-trineopentylbenzene. 1,3-Dineopentylbenzene was formed as the major product by treating 1,3,5-trineopentylbenzene with freshly sublimed aluminum chloride in carbon disulfide for 24 h at room temperature.

It has been reported that the use of acyl halides as acylating agents causes some complications. Acyl halides often decarbonylate in the presence of Friedel-Crafts catalysts, and alkyl cations are formed, which, in some cases, act as alkylating agents.^{9,10} In the present case, freshly sublimed aluminum chloride caused

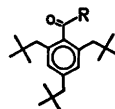


Fig. 1. R = methyl (I), ethyl (II), phenyl (III), isopropyl (IV), or hydroxyl (V).

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decomposition of the acyl chlorides. This reaction was most significant when 2-methylpropanoyl chloride was used.

The dealkylation of 1,3,5-trieneopentylbenzene and the decomposition of the acyl chlorides were minimized when commercial aluminum chloride was used without further sublimation. As has been reported for similar reactions, the improvement of the acylation reaction when commercial aluminum chloride was used may be due to trace amounts of iron(III) chloride^{11,12} or products of hydrolysis.¹³

It has been demonstrated¹⁴ that the yield of product often decreases rapidly when the amount of catalyst exceeds the molar amount of the aromatic substrate. In the present case, however, an excess of catalyst improved the acylation reaction in accordance with what was reported by Dermer *et al.*⁸

When 1,3,5-trieneopentylbenzene was treated with acetyl chloride and iron(III) chloride in carbon disulfide, 2-chloro-1,3,5-trieneopentylbenzene was formed as the major product. Treatment of 1,3,5-trieneopentylbenzene with iron(III) chloride in carbon disulfide for 20 h at room temperature gave 40 % of 2-chloro-1,3,5-trieneopentylbenzene as the only product.

This can be compared with the report that mesitylene was found to react with iron(III) chloride at room temperature in an aromatic solvent to yield 12–19 % of 2,2',4,4',6,6'-hexamethylbiphenyl in addition to 24–36 % of 2-chloromesitylene.¹⁵ Moreover, an increase in yield of biaryl-type product was found in the order toluene < *m*-xylene < mesitylene, which was correlated with an increase in steric hindrance, basicity, and opportunity for hyperconjugative stabilization of the σ -complex.¹⁶ However, recent studies by Nyberg indicate that the biaryl formation is a cation radical reaction.¹⁷ The absence of biaryl products in the case of 1,3,5-trieneopentylbenzene may be explained by the much larger steric demands of *tert*-butyl groups. It can be noted that in the treatment of 1,3,5-trieneopentylbenzene with freshly sublimed aluminum chloride (see above) no biaryl or chloro-substituted compounds were formed.

When tin(IV) chloride was used, no acetylation or chlorination took place.

Carbon disulfide was preferred to dichloromethane and nitrobenzene as solvent in the

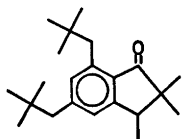
acylation reaction. When 1,3,5-trieneopentylbenzene was treated with acetyl chloride and aluminum chloride for 20 h at room temperature in carbon disulfide, dichloromethane, or nitrobenzene, the yields of 2-acetyl-1,3,5-trieneopentylbenzene were 80, 30, and 5 %, respectively.

With commercial aluminum chloride as catalyst and carbon disulfide as solvent, compounds (I), (II), and (III) could be prepared in good yields without any side reactions. In the preparation of (IV), under the same conditions, some minor side reactions occurred. If the 2,2-dimethylpropanoylation reaction was interrupted before completion, the only side reaction was the formation of a small amount of 2-chloro-1,3,5-trieneopentylbenzene. Attempts to force the reaction toward completion failed because of decomposition of the product (IV).

Compound (V) could be prepared by treating 1,3,5-trieneopentylbenzene with oxalyl chloride and aluminum chloride in carbon disulfide.

Attempts to prepare 2-(2,2-dimethylpropanoyl)-1,3,5-trieneopentylbenzene *via* acylation failed. The above-mentioned solvents and catalysts, including antimony(V) chloride, were employed. The combination commercial aluminum chloride-dichloromethane was preferred since the main product [*i.e.* (VI)] was formed in the highest yield with this combination. The decomposition of 2,2-dimethylpropanoyl chloride was considerable. The main product was formed in about 40 % yield in addition to about 30 different by-products. When the reaction was carried out in carbon disulfide instead of dichloromethane, the yield of the main product decreased and the number of by-products increased. The main product was not 2-(2,2-dimethylpropanoyl)-1,3,5-trieneopentylbenzene, however, and none of the other products observed on the gas chromatograms had the same retention time as this compound, which has recently been prepared¹⁸ by a lithium organic reaction. The main product has been identified as 2,2,3-trimethyl-5,7-dieneopentyl-1-indanone (VI).¹⁹ In this connection, it is interesting to note that successful introduction of the 2,2-dimethylpropanoyl group in mesitylene and a number of polymethylbenzenes has been reported.⁷

It has been reported that aromatic compounds can be chlorinated by antimony(V) chloride,¹⁶ and that chlorinated compounds are formed as by-products when antimony(V) chloride is used



VI

as a Friedel-Crafts catalyst.⁹ In the present case, only chlorinated compounds were formed when antimony(V) chloride was used in the presence or absence of an acyl component. 1,3,5-Trineopentylbenzene thus yielded mono-, di- and trichloro-1,3,5-trineopentylbenzene with antimony(V) chloride, paralleling the behavior of mesitylene.¹⁰

2-Chloro-1,3,5-trineopentylbenzene, 2,4-dichloro-1,3,5-trineopentylbenzene, and 1,3,5-trichloro-2,4,6-trineopentylbenzene were originally prepared by Márton and Martinson²¹ using chlorine gas and iron as a catalyst. In their preparation of 1,3,5-trichloro-2,4,6-trineopentylbenzene, chloroalkylation occurred and a complex mixture of compounds was formed. In the present case, no side reactions took place, and 1,3,5-trichloro-2,4,6-trineopentylbenzene could be prepared in good yield with antimony(V) chloride as the chlorinating agent.

EXPERIMENTAL

Measurements. Gas chromatographic (GLC) analyses were carried out on a Perkin-Elmer 900 gas chromatograph fitted with a flame ionization detector. The inner diameter of the columns used was 2 mm and the length 2 m. The stationary phase was 3 % of SE-30 silicon gum rubber on Gaschrom Q 100–200 mesh. The areas of the peaks on the gas chromatograms were measured by triangulation.

The IR spectra were recorded on a Beckman IR 9 spectrophotometer using potassium bromide pellets. The absorption maxima are reported in cm^{-1} and the intensities are characterized as weak (w), medium (m), strong (s), or very strong (vs).

The NMR spectra were recorded on a Varian A 60 spectrometer. About 10 % by weight solutions in carbon tetrachloride were used. The probe temperature was 35 °C. The chemical shifts are reported in ppm downfield from tetramethylsilane as internal standard. The multiplicities of the peaks are reported as singlet (s), doublet (d), triplet (t), quartet (q), heptet (h) and multiplet (m).

The mass spectra (MS) were determined (at the Department of Medical Biochemistry, University of Göteborg) on an AEI MS 902 mass

spectrometer under the following conditions: electron energy 70 eV, accelerating voltage 8 kV and emission 100 μA , or (at the Department of Medical Chemistry, University of Göteborg) on an LKB 9000 mass spectrometer with an electron energy of 70 eV. The latter mass spectrometer was connected to a gas chromatograph with a column containing 3 % of OV-1. The intensities of the peaks are reported in parenthesis as percentages of the base peak. Only the most abundant peaks are reported, together with the parent peaks and the isotope peaks corresponding to the latter.

The melting points were determined on a Kofler micro hot stage.

Materials. Acyl chlorides: Fluka (*purum*). Aluminum chloride: Kistner (*puriss.*). Antimony(V) chloride: Riedel-De Haën (anhydrous, fuming). Silica gel; Merck (neutral, less than 0.08 mm, for column chromatography). Carbon disulfide: Kistner (*purum*). Dichloromethane: Fisher (*p.a.*). The above chemicals were used without further purification, with the exception of aluminum chloride which was sublimed before it was used in some reactions. 1,3,5-Trineopentylbenzene was prepared as described by Martinson and Márton.²²

Acylation s

2-Acetyl-1,3,5-trineopentylbenzene (I). a. *With aluminum chloride as catalyst and carbon disulfide as solvent.* In a two-necked flask equipped with a magnetic stirrer, a drying tube, and a dropping funnel, 13.9 g (104.1 mmol) of finely powdered aluminum chloride was covered with 50 ml of carbon disulfide, and the flask was then cooled with ice water. The mixture was magnetically stirred and 7.4 ml (104.1 mmol) of acetyl chloride was added. After 15 min 10.0 g (34.7 mmol) of 1,3,5-trineopentylbenzene, dissolved in 20 ml of carbon disulfide, was added dropwise over a period of 30 min. After this addition, the mixture was stirred at room temperature. At regular time intervals small aliquots were withdrawn and analyzed by GLC. The reaction was found to be complete after 15 h, and the flask was then cooled with ice water and the excess of aluminum chloride and acetyl chloride was destroyed with crushed ice. The organic and aqueous layers did not separate well, and therefore the carbon disulfide was evaporated and the aqueous layer was extracted five times with 20 ml portions of hexane. The combined hexane extracts were dried over magnesium sulfate. After evaporation of the solvent, the product was decolorized by adsorption chromatography (alumina, hexane). Recrystallization several times from ethanol (water was cautiously added to the hot solution until turbidity appeared) gave 10.2 g (89 %) of a white crystalline product. *M.p.*: 63–65 °C. *IR*: 2962vs, 2910m, 2870m, 1694vs, 1604m, 1565w, 1481s, 1427w, 1396w, 1366s, 1352m, 1280w,

1245s, 1204w, 1148m, 1054m, 980m, 882m, 874m, 780w, 756w, 700w, 607w, 584w, 546w. MS: *m/e* (%) MS: 29(13), 41(15), 43(12), 57(41), 147(15), 162(100), 163(13), 219(9), 247(8), 315(20), 330(6.9), 331(1.8), 332(0.2). NMR: δ 0.88 (s, 18 H, *tert*-butyl), 0.93 (s, 9 H, *tert*-butyl) 2.28 (s, 3 H, methyl), 2.38 (s, 4 H, methylene), 2.43 (s, 2 H, methylene), 6.75 (s, 2 H, aromatic).

When the acetylation reaction was carried out in 10 ml of carbon disulfide with 1 % of the above-mentioned molar amounts, 2-acetyl-1,3,5-trineopentylbenzene was formed in about 80 % yield after 20 h.

b. With iron(III) chloride as catalyst. The reaction was carried out in 10 ml of carbon disulfide at room temperature with the same molar amounts as in the last experiment described under *a*, but the aluminum chloride was exchanged for iron(III) chloride. A GLC analysis of the mixture after 20 h showed that two products had been formed. 2-Acetyl-1,3,5-trineopentylbenzene had been formed in about 10 % yield, and the other product, which was formed in about 22 % yield, was identified as 2-chloro-1,3,5-trineopentylbenzene.

c. With tin(V) chloride as catalyst. The reaction was carried out at room temperature with the same molar amounts as in *b* but the iron(III) chloride was exchanged for tin(IV) chloride. No products could be detected in the mixture after 20 h (GLC).

d. With dichloromethane as solvent. The reaction was carried out in 10 ml of dichloromethane at room temperature with the same molar amounts as in the last experiment described under *a*. After 20 h, 2-acetyl-1,3,5-trineopentylbenzene had been formed in about 30 % yield (GLC).

e. With nitrobenzene as solvent. The reaction was carried out in 10 ml of nitrobenzene at room temperature with the same amounts of reactants as in *d*. After 20 h, 2-acetyl-1,3,5-trineopentylbenzene had been formed in about 5 % yield (GLC).

2-Propanoyl-1,3,5-trineopentylbenzene (II). The same molar amounts as in the first experiment described under *a* were used, but the acetyl chloride was exchanged for propanoyl chloride. The reaction, which was carried out at room temperature, was found to be complete after 34 h (GLC), and the final yield was 10.1 g (85 %) of white crystals. *M.p.*: 42–44 °C. IR: 2960vs, 2910m, 2868m, 1705vs, 1609m, 1569w, 1478s, 1465w, 1428w, 1413w, 1395m, 1367s, 1340m, 1228w, 1238s, 1223m, 1202m, 1166w, 1142m, 1076m, 1008w, 948s, 932w, 924w, 882s, 872w, 799w, 790m, 753w, 731w, 656w, 523w. MS: 29(19), 41(21), 43(15), 57(49), 71(8), 147(9), 176(13), 204(100), 205(16), 233(18), 260(47), 261(9), 290(6), 315(84), 316(22), 330(27), 331(6), 344(14.6), 345(3.8), 346(0.5). NMR: 0.87 (s, 18 H, *tert*-butyl), 0.93 (s, 9 H, *tert*-butyl), 1.11 (t, 3 H, methyl, *J* = 7 Hz), 2.30 (s, 4 H, methylene),

2.43 (s, 2 H, methylene), 2.45 (q, 2 H, methylene, *J* = 7 Hz), 6.76 (s, 2 H, aromatic).

2-Benzoyl-1,3,5-trineopentylbenzene (III). The same molar amounts as in the first experiment described under *a* were used, but the acetyl chloride was exchanged for benzoyl chloride. The reaction, which was carried out at room temperature, was found to be complete after 20 h (GLC). A hexane solution of the crude product was washed several times with 10 % aqueous sodium hydroxide solution to remove the benzoic acid from the organic layer. The organic layer was then washed with water, with dilute hydrochloric acid, and finally again with water. After the solution was dried over magnesium sulfate, the hexane was evaporated, and the product was decolorized by adsorption chromatography (alumina, hexane). Several recrystallizations (ethanol–water) gave 9.2 g (69 %) of crystalline product. *M.p.*: 90–92 °C. IR: 3062w, 2970vs, 2910m, 2859s, 1675vs, 1603m, 1582w, 1567w, 1477s, 1448m, 1424w, 1393m, 1362s, 1312m, 1288m, 1264s, 1236m, 1199w, 1170m, 1156w, 1116w, 1070w, 1024w, 926s, 897w, 879m, 870w, 797w, 790w, 750w, 706vs, 683m, 648w, 550w. MS: 29(39), 39(12), 41(59) 43(26), 57(100), 71(14), 77(14), 91(11), 105(39), 149(18), 209(13), 224(16), 262(16), 265(13), 279(26), 280(33), 335(61), 336(72), 337(18), 377(16), 392(0.9), 393(0.3). NMR: 0.82 (s, 18 H, *tert*-butyl), 0.97 (s, 9 H, *tert*-butyl), 2.27 (s, 4 H, methylene), 2.50 (s, 2 H, methylene), 6.87 (s, 2 H, aromatic), 7.1–7.7 (m, 5 H, aromatic).

2-(2-Methylpropanoyl)-1,3,5-trineopentylbenzene (IV). The same molar amounts as in the first experiment described under *a* were used, but the acetyl chloride was exchanged for 2-methylpropanoyl chloride. To minimize the decomposition of this acyl chloride, the flask was cooled to –10 °C before the acyl chloride was added. After this addition and the addition of 1,3,5-trineopentylbenzene, the temperature of the flask was slowly raised to room temperature and the acylation reaction begun. A small amount of gas evolved during the reaction. After 15 h a main product, which was later identified as 2-(2-methylpropanoyl)-1,3,5-trineopentylbenzene, had been formed in about 91 % yield (GLC), and a by-product, which was later identified as 2-chloro-1,3,5-trineopentylbenzene, had been formed in about 1 % yield (GLC). The work-up procedure described for 2-benzoyl-1,3,5-trineopentylbenzene was then applied. The two products and the unreacted 1,3,5-trineopentylbenzene were separated on a column of silica gel. With hexane as eluent, 1,3,5-trineopentylbenzene was eluted, followed by 2-chloro-1,3,5-trineopentylbenzene. 2-(2-Methylpropanoyl)-1,3,5-trineopentylbenzene was eluted with diethyl ether. Several recrystallizations (ethanol–water) of 2-(2-methylpropanoyl)-1,3,5-trineopentylbenzene gave 9.4 g (76 %) of white crystals. *M.p.*: 56–58 °C. IR: 2968vs, 2910m,

2868m, 1700vs, 1605m, 1567w, 1480s, 1470w, 1426w, 1396m, 1384w, 1366s, 1332w, 1289w, 1239s, 1221m, 1202w, 1135m, 1085w, 990w, 972s, 961w, 917w, 885m, 862w, 796m, 756w, 713w, 647w, 528w. *MS*: 29(6), 41(10), 43(14), 57(19), 71(7), 259(11), 315(100), 316(25), 343(10), 358(0.7), 359(0.2). *NMR*: 0.86 (s, 18 H, *tert*-butyl), 0.93 (s, 9 H, *tert*-butyl), 1.05 (d, 6 H, methyl, $J = 7$ Hz), 2.30 (s, 4 H, methylene), 2.44 (s, 2 H, methylene), 2.64 (h, 1 H, methine, $J = 7$ Hz), 6.77 (s, 2 H, aromatic).

2,4,6-Trineopentylbenzenecarboxylic acid (V). Aluminum chloride (2.53 g, 19.0 mmol) was covered with 20 ml of carbon disulfide and the flask cooled in an ice bath. Oxalyl chloride (1.62 ml, 19.0 mmol) was slowly added, and the mixture was stirred for 15 min before a solution of 4.9 g (17.0 mmol) of 1,3,5-trineopentylbenzene in 10 ml of carbon disulfide was added dropwise over a period of 30 min with continued stirring. The mixture was then reflux for 7 h before being poured into a mixture of 35 g of ice and 5 ml of concentrated hydrochloric acid. The organic layer was separated off, and the aqueous layer was extracted with three 10 ml portions of carbon disulfide. The combined organic layers were washed with two 10 ml portions of water and were then extracted with 20 ml of ice-cold 10 % sodium hydroxide solution. Acidification of the extract with 6 M hydrochloric acid liberated the 2,4,6-trineopentylbenzenecarboxylic acid which soon precipitated. The precipitate was collected and washed with water on a filter and was then dried in a desiccator. The tan-colored crude product (2.3 g) was recrystallized first from acetone and then from carbon tetrachloride to yield 1.9 g (34 %) of white crystals. *M.p.*: 164.5–165.5 °C. *IR*: 2955vs, 2907s, 2870s, 2655m, 2550m, 1688vs, 1606m, 1561w, 1480s, 1451m, 1427m, 1393m, 1364s, 1298s, 1279m, 1261m, 1237m, 1202w, 1182w, 1153w, 1094m, 930w(broad), 879w, 779w, 749w. *MS*: 29(20), 41(25), 43(9), 57(84), 71(5), 164(100), 165(11), 220(38), 221(6), 276(6), 317(10), 332(2.4), 333(0.7). *NMR*: 0.94 (s, 27 H, *tert*-butyl), 2.48 (s, 2 H, methylene), 2.81 (s, 4 H, methylene), 6.87 (s, 2 H, aromatic), 12.27 s, 1 H, carboxylic).

Attempts to prepare 2-(2,2-dimethylpropanoyl)-1,3,5-trineopentylbenzene. 1. With aluminum chloride as catalyst. The reaction was carried out in 30 ml of dichloromethane using 50 % of the molar amounts used in the first experiment described in *a* under the heading 2-acetyl-1,3,5-trineopentylbenzene, but the acetyl chloride was exchanged for 2,2-dimethylpropanoyl chloride. To minimize the decomposition of this acyl chloride, the flask was cooled to -35 °C before the acyl chloride was added. After this addition and the addition of 1,3,5-trineopentylbenzene the temperature of the flask was slowly raised to room temperature, and products started to form. Gases evolved during the reaction. After 10 h the mixture was worked up as described

for 2-benzoyl-1,3,5-trineopentylbenzene. The resulting oil was shown by GLC to consist of about 40 % of a main product and about 60 % of a complex mixture of about 30 compounds. The main product has been identified as 2,2,3-trimethyl-5,7-dineopentyl-1-indanone.¹⁹

2. With antimony(V) chloride as catalyst. A solution of antimony(V) chloride (1.33 ml, 10.41 mmol) in 20 ml of carbon disulfide was cooled with ice water, and 2,2-dimethylpropanoyl chloride (1.28 ml, 10.41 mmol) was added. After 15 min 1,3,5-trineopentylbenzene (1.0 g, 3.47 mmol), dissolved in 10 ml of carbon disulfide, was added over a period of 30 min. The reaction mixture was then stirred at room temperature. After 12 h the reaction mixture was worked up as described for 2-benzoyl-1,3,5-trineopentylbenzene. The crystalline product was shown by GLC to consist of two products. The minor product (3 %) was identified as 2-chloro-1,3,5-trineopentylbenzene and the other one as 2,4-dichloro-1,3,5-trineopentylbenzene. The products were separated on a column of silica gel. With hexane as eluent, 2,4-dichloro-1,3,5-trineopentylbenzene was eluted, followed by 2-chloro-1,3,5-trineopentylbenzene. Yields: 2-chloro-1,3,5-trineopentylbenzene, 12 mg (1 %), 2,4-dichloro-1,3,5-trineopentylbenzene, 1.0 g (80 %). *MS*: The masses of the molecules were determined by high-resolution mass spectrometry. For 2-chloro-1,3,5-trineopentylbenzene the value 322.243 ± 0.005 u was found. The value²³ for $C_{21}H_{35}^{35}Cl$ is 322.243 u. 29(15), 41(23), 43(15), 57(100), 71(8), 154(42), 155(6), 156(17), 210(31), 211(6), 212(10), 265(13), 266(10), 307(8), 322(8.5), 323(2.1), 324(3.1), 325(0.8). For 2,4-dichloro-1,3,5-trineopentylbenzene the value 356.202 ± 0.005 u was found for the mass of the molecule. The value²³ for $C_{21}H_{34}^{35}Cl_2$ is 356.204 u. 29(10), 41(24), 43(12), 57(100), 71(7), 188(34), 190(22), 244(16), 246(10), 299(10), 300(7), 301(7), 341(4), 356(2.9), 357(0.7), 358(1.9), 359(0.5), 360(0.4). The m.p. and NMR and IR spectra were identical with those reported²¹ for the two compounds.

Treatments of 1,3,5-trineopentylbenzene with Friedel-Crafts catalysts. a. With freshly sublimed aluminum chloride. Freshly sublimed aluminum chloride (0.69 g, 5.19 mmol) was covered with 15 ml of carbon disulfide, and a solution of 0.50 g (1.73 mmol) of 1,3,5-trineopentylbenzene in 5 ml of carbon disulfide was added. The mixture was then stirred at room temperature, and after 24 h the composition of the mixture was determined by GLC. Three products were detected, in addition to unreacted 1,3,5-trineopentylbenzene. The mixture was investigated with an LKB 9000 mass spectrometer which was connected to a gas chromatograph, before it was worked up as described for 2-acetyl-1,3,5-trineopentylbenzene. The total yield, including the remaining reactant was 0.40 g, and the products were separated on a column of silica gel with hexane as eluent. The products were identified as 1,3-dineopentylbenzene, neo-

pentylbenzene, and 2-methylbutane. The ratios of the amounts of 1,3,5-trineopentylbenzene, 1,3-dineopentylbenzene, and neopentylbenzene were 0.5:1:0.6, as estimated from the gas chromatogram. *MS*: 1,3-Dineopentylbenzene. 29(16), 41(23), 57(99), 71(5), 77(5), 91(14), 103(5), 104(7), 105(17), 106(100), 107(86), 115(5), 131(5), 161(13), 162(13), 203(14), 218(13.6), 219(2.6), 220(0.1). *NMR*: 1,3-Dineopentylbenzene. 0.92 (s, 18 H, *tert*-butyl), 2.44 (s, 4 H, methylene), 6.6–7.2 (m, 4 H, aromatic). The aromatic part of the spectrum clearly indicated that the compound was the *meta* isomer. *MS*: Neopentylbenzene. 29(12), 39(11), 41(24), 51(6), 57(85), 65(15), 91(64), 92(100), 93(7), 105(8), 115(5), 133(12), 148(18.3), 149(2.3), 150(0.1). These values are in accordance with those reported for neopentylbenzene.^{24a} *MS*: 2-Methylbutane. 27(25), 29(30), 39(19), 41(73), 42(95), 43(100), 55(7), 56(25), 57(73), 72(11), 73(0.5). These values are in accordance with those reported for 2-methylbutane.^{24b}

b. With commercial aluminum chloride. Commercial aluminum chloride (0.28 g, 2.07 mmol) was covered with 10 ml of carbon disulfide. A solution of 0.20 g (0.69 mmol) of 1,3,5-trineopentylbenzene in 5 ml of carbon disulfide was then added dropwise and the mixture was stirred at room temperature. A GLC analysis of the mixture after 20 h showed that only small amounts (altogether < 1 % of the above-mentioned aromatic substrate) of dealkylated products had been formed. No other products could be detected.

c. With iron(III) chloride. The reaction was carried out at room temperature with the same molar amounts as in *b*, but the aluminum chloride was exchanged for iron(III) chloride. A GLC analysis of the mixture after 20 h showed that one product had been formed in about 40 % yield. This product was identified as 2-chloro-1,3,5-trineopentylbenzene. No other products could be detected.

d. With tin(IV) chloride. The same molar amounts as in *b* were used. A GLC analysis of the mixture after 20 h at room temperature showed only starting material.

e. With antimony(V) chloride. The reaction was carried out at room temperature in 30 ml of carbon disulfide with twice the molar amounts used in *a*, but the aluminum chloride was exchanged for antimony(V) chloride. Two products which were later identified as 2,4-dichloro-1,3,5-trineopentylbenzene and 1,3,5-trichloro-2,4,6-trineopentylbenzene were formed. The composition of the mixture changed as follows (GLC): 1 h, 94 % of 2,4-dichloro-1,3,5-trineopentylbenzene and 6 % of 1,3,5-trichloro-2,4,6-trineopentylbenzene; 2 h, 40 and 60 %, respectively; 4 h, 20 and 80 %, respectively. After 4 h the reaction mixture was worked up as described for 2-acetyl-1,3,5-trineopentylbenzene. The two products were separated on a column of silica gel. With hexane as eluent, 1,3,5-tri-

chloro-2,4,6-trineopentylbenzene was eluted, followed by 2,4-dichloro-1,3,5-trineopentylbenzene. Yields: 2,4-dichloro-1,3,5-trineopentylbenzene 0.15 g (13 %), 1,3,5-trichloro-2,4,6-trineopentylbenzene 0.95 g (70 %). The physical properties of the products were in accordance with those reported.²⁰

Acknowledgements. We thank Professor Lars Melander for his interest in this work and for his constructive criticism during the course of preparation of the manuscript. We also thank Dr. Johanna Andersson for her linguistic corrections. This work has been supported by the Swedish Natural Science Research Council.

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Received May 6, 1974.