Anal. Calcd for $C_{14}H_{22}CuO_6$: C, 48.06; H, 6.34. Found: C, 47.80; H, 6.27.

Tris(*n*-propylacetoacetato)aluminum(III).—A solution of 41.4 g (0.1 mole) of tris(ethylacetoacetato)aluminum(III) in 36 g of *n*-propyl alcohol was subjected to similar transesterification. Nineteen fractions were taken in 16 hr, a trace of ethyl alcohol remaining in the last fraction. The product was purified by distillation through a 64-cm heated column. After a forerun of 12.2 g, bp 152–161° (0.35 mm), the *n*-propyl ester (21.8 g, 43%) was collected at 161–169° (0.5 mm). It was a colorless, slightly viscous oil of $n^{20}D$ 1.5030.

Anal. Calcd for $C_{21}H_{35}AlO_9$: C, 55.01; H, 7.26; Al, 5.89. Found: C, 54.57; H, 7.18; Al, 6.04.

Poly[2,2-dimethylpropane-1,3-bis(acetoacetato)]copper(II).—A solution of 28.056 g (0.09551 mole) of bis(methylacetoacetato)-copper(II) and 9.948 g (0.09552 mole) of 2,2-dimethylpropane-1,3-diol in 250 ml of benzene was subjected to very slow distillation at a reflux ratio of 30:1 through a 12-cm column. The volume was maintained by continuously adding benzene. After 4 days the benzene was replaced by toluene and the distillation was continued for 8 days. The product (30.5 g, 91%) was a green powder only slightly soluble in boiling toluene, crystalline by X-ray[15] and decomposing at 228–230°. It had no hydroxyl absorption in the infrared and analyzed satisfactorily for an infinite polymer.

Anal. Calcd for $C_{13}H_{18}CuO_6$: C, 46.77; H, 5.44; Cu, 19.03. Found: C, 46.84; H, 5.45; Cu, 18.84.

Poly[2,2-dimethylpropane-1,3-bis(acetoacetato)]beryllium(II).—A solution of 2.392 g (0.01 mole) of bis(methylacetoacetato)beryllium(II) and 1.0623 g (0.0102 mole) of 2,2-dimethylpropane-1,3-diol in 15 ml of benzene was subjected to slow distillation for 24 hr, while replacing the solvent which boiled off. The benzene was then replaced by toluene and the distillation was continued for 91 hr. The viscous reaction mixture was freed of solvent by the use of a nitrogen capillary under high vacuum at 110°. After cooling the product was a brittle, colorless glass, amorphous by X-ray,[15] of mol wt 1400 (benzene). No hydroxyl absorption was visible in the infrared spectrum. The product analyzed equally well for an infinite polymer or for a pentamer (mol wt 1428) with one methyl and one diol end group.

Anal. Calcd for $C_{13}H_{18}BeO_6$: C, 55.90; H, 6.50; Be, 3.23. Calcd. for $C_{66}H_{94}Be_5O_{31}$: C, 55.51; H, 6.64; Be, 3.16. Found: C, 55.65; H, 6.60; Be, 3.21.

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(15) We are grateful to Mr. R. Nilberg for the X-ray determinations.

Isomer Distributions in Electrophilic Substitution Reactions of Neopentylbenzene[1]

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In aromatic electrophilic substitution reactions of alkylbenzenes, it has been found that as the bulk of the alkyl substituent is increased the extent of *ortho* substitution is reduced and that of *para* substitution is increased.[2,3] It was therefore somewhat surprising to find that the nitration of neopentylbenzene gave only about 50% of *p*-nitroneopentylbenzene[4] and that another unidentified isomer was obtained in about equal amount.[5] This result prompted an investigation of the isomer distributions obtained in various electrophilic substitution reactions of neopentylbenzene. It was necessary first to characterize and identify the substitution products of neopentylbenzene, since the only previously identified substitution products were *p*-nitro-[4a] and *p*-bromoneopentylbenzene.[4b]

Isomer Distributions.—Analysis of the isomer distributions obtained in the substitution reactions of neopentylbenzene was made by vpc. The areas of the vpc peaks for the various isomers were determined by the triangulation method.[6,7] The results are listed in Table I together with previously reported values for toluene and *t*-butylbenzene under identical reaction conditions.

TABLE I

ISOMER DISTRIBUTIONS IN SUBSTITUTION REACTIONS OF TOLUENE, *t*-BUTYLBENZENE, AND NEOPENTYLBENZENE

Reaction	P_f^{Me}		Me	*t*-Bu	Neop[a]
Nitration, H_2SO_4[b] at 25°	*c*	*o*	58.5[d]	15.8[d]	44.9
		m	4.4	11.5	3.2
		p	37.2	72.7	51.8
Cl_2, HOAc at 25°	820[e]	*o*	59.8[e]	21.5[e]	25.5
		m	0.5	2.3	*f*
		p	39.7	76.2	74.5
Br_2, 85% HOAc at 25°	2420[e]	*o*	32.9[e]	1.2[e]	8.5
		m	0.3	1.5	*f*
		p	67.1	97.3	91.5
CH_3COCl, $AlCl_3$, CS_2 at room temp		*o,m*	*g*		5
		p	97.6[g]		95

[a] Average of several values obtained by vpc; maximum deviation in values is ±1.0. [b] Heterogeneous conditions of Brown and Bonner.[3] [c] The value of p_f^{Me} under these conditions is not known. For homogeneous nitration, p_f^{Me} is 48.5 in acetic anhydride at 25°, 58 in 90% acetic acid at 45°, and 45.8 in nitromethane at 25°.[2] [d] Data of Brown and Bonner.[3] For ethylbenzene, the percentages of *ortho*, *meta*, and *para* are 45.0, 6.5, and 48.5.[2] [e] Data from Tables II and XII of ref 2. [f] No *meta* isomer detected. [g] The *para* yield is reported on p 46 of ref 2; extent of *ortho* and *meta* substitution not reported.

Of much interest is the fact that the degree of *ortho* nitration of neopentylbenzene is considerably greater than that of *t*-butylbenzene, being comparable to that of ethylbenzene. Brown and Bonner found that the percentage of *ortho* substitution decreases markedly through the series toluene, ethylbenzene, isopropylbenzene, *t*-butylbenzene, and attributed this to classical steric hindrance to *ortho* substitution.[3] The relatively large *ortho*/*para* ratio for neopentylbenzene would appear to indicate that there is no great steric hindrance to *ortho* nitration of this hydrocarbon.

In chlorination in acetic acid, the degree of *ortho* substitution of neopentylbenzene is appreciably less than in nitration, becoming comparable to that of *t*-butylbenzene. Perhaps this could be attributed to greater steric hindrance to *ortho* chlorination as compared to *ortho* nitration of neopentylbenzene. Nowever, note that the *ortho*/*para* ratio for toluene and *t*-butylbenzene is comparable in chlorination and nitration. Furthermore, the *ortho*/*para* ratio in bromination in 85% acetic acid is much greater for neopentylbenzene than for *t*-butylbenzene. The product ratio is rate controlled and not equilibrium controlled, since *o*-bromoneopentylbenzene was found to be stable to treatment with excess hydrogen bromide under conditions identical with those used for bromination.

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(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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The *ortho/para* ratio of all the alkylbenzenes is lower in bromination than in nitration or chlorination. Also, the amount of *meta* substitution is less in bromination. Presumably the generally lower percentage of *ortho* and *meta* substitution is due at least in part to the greater selectivity of bromination, as reflected in the larger value of p_f^{Me}.[2] However, it is probable that factors other than reagent selectivity and classical steric hindrance play a significant role in governing the isomer distributions of Table I.

In a Friedel–Crafts acetylation of neopentylbenzene with acetyl chloride, only *p*-neopentylacetophenone was isolated. Analysis by vpc indicated that the *para* isomer constituted at least 95% of the acetylation product. The acetylation of toluene also is highly selective, being reported to yield 97.6% *p*-methylacetophenone (ref 2, p 46).

Identifications.—Previously, *p*-nitroneopenylbenzene had been identified by its elementary analysis, molecular weight, and oxidation with sodium dichromate–50% sulfuric acid to *p*-nitrobenzoic acid in 70% yield.[4] Attempts to apply this and other oxidation procedures to the more abundant of the remaining nitration products of neopentylbenzene failed to yield any nitrobenzoic acid, and only tars and ketonic materials were obtained. However *o*- and *m*-nitroneopentylbenzene were unambiguously identified by spectral methods, particularly by nmr.

The nmr spectra[8] of the isomeric nitroneopentylbenzenes had the following characteristics. The spectrum of the *para* isomer had an A_2B_2 pattern typical of the aromatic protons of unsymmetrically *para*-disubstituted benzenes[9] with single peaks at τ 1.85, 1.98, 2.66, and 2.79. The next most abundant isomer, labeled isomer A, showed a low-field multiplet of relative area one centered around τ 2.3 (about six peaks, nonsymmetric pattern)[10] and a separate more complex multiplet of relative area three centered around τ 2.65. The spectrum in the aromatic proton region was very similar, even in fine structure, to that of *o*-nitrotoluene. The spectrum of the least abundant isomer, labeled B, had an entirely different pattern in the aromatic proton region, consisting of a poorly resolved multiplet of relative area two centered around τ 2.1 and a multiplet also of relative area two centered around τ 2.6.[10] The aromatic proton spectrum of isomer B corresponded closely to that of *m*-nitrotoluene. The singlet signal for the methylene protons (relative area two) of isomer B, *p*-nitroneopentylbenzene, and isomer A occurred at τ 7.42, 7.38, and 7.06, respectively. This corresponds to the order of τ values for the methyl-proton signal of *m*-, *p*-, and *o*-nitrotoluene at τ 7.63, 7.57, and 7.44, respectively. The singlet signal for the terminal methyl groups (relative area nine) had practically the same τ value, $\backsim$9.10, for all three nitroneopentylbenzenes. The nmr spectral evidence clearly shows that isomer A is *o*-nitroneopentylbenzene and isomer B is *m*-nitroneopentylbenzene.

The infrared and ultraviolet spectra of the nitroneopentylbenzenes showed the expected behavior. According to Bellamy,[11] the infrared spectra of disubstituted benzenes in the 12–14-μ region show absorption in the μ order *ortho* > *meta* > *para*. For example, the infrared spectra of *o*-, *m*-, and *p*-nitrotoluene had strong bands at 13.75, 13.70, and 13.65 μ, respectively. In agreement with this, the corresponding bands for *o*-, *m*-, and *p*-nitroneopentylbenzene were found at 13.85, 13.80, and 13.75 μ. In a comparison of the ultraviolet spectra of a number of nitroalkylbenzenes in isooctane, Brown and Reagen noted that the order of $\lambda_{\max}$ and $\epsilon_{\max}$ of the principal electronic transition was *para* > *meta* > *ortho*. For example, the values reported for the nitrotoluenes are: *para*, 264 mμ (ϵ 10,250); *meta*, 256.5 (8160); *ortho*, 250 (5980).[12] The values obtained for the nitroneopentylbenzenes are: *para*, 267 mμ (ϵ 10,700); *meta*, 259 (7800); *ortho*, 250 (4100).

It is to be noted that the vpc retention times for the nitroneopentylbenzenes and nitrotoluenes have the same order, *para* > *meta* > *ortho*. The order of the retention times of haloneopentylbenzenes, *para* > *ortho*, also corresponded to that of the halotoluenes.

The two isomers obtained in the bromination of neopentylbenzene also were identified initially by nmr.[8] The nmr spectrum of the more abundant isomer had an A_2B_2 pattern centered at τ 2.85 in the aromatic proton region and resembled closely that of *p*-bromotoluene. The identity of the compound as *p*-bromoneopentylbenzene was verified by independent synthesis. A compound identical with the substitution product in index of refraction, vpc retention time, infrared spectrum, and nmr spectrum was obtained by reduction of *p*-nitroneopentylbenzene followed by a Sandmeyer reaction (cuprous bromide) on the diazotized amine. The less abundant bromoneopentylbenzene had an nm rspectrum, which was typical of that of an *ortho* isomer and closely resembled the spectrum of *o*-bromotoluene, but differed in a number of significant respects from the spectra of *m*- and *p*-bromotoluene. The compound was identical in index of refraction, vpc retention time, infrared spectrum, and nmr spectrum with *o*-bromoneopentylbenzene synthesized from *o*-nitroneopentylbenzene.

The more abundant of the two isomers obtained in the chlorination of neopentylbenzene was assigned the structure *p*-chloroneopentylbenzene on the basis of the characteristic pattern of the nmr spectrum and the similarity to the spectrum of *p*-chlorotoluene. The nmr spectrum of the less abundant isomer closely resembled that of *o*-chlorotoluene[13] and differed significantly from those of *m*- and *p*-chlorotoluene. The compound was identical in index of refraction, vpc retention time, infrared spectrum, and nmr spectrum with *o*-chloroneopentylbenzene synthesized from *o*-nitroneopentylbenzene by the Sandmeyer route.

The single isomer isolated in the acetylation of neopentylbenzene was identified as *p*-neopentylacetophenone by means of its nmr spectrum.[8] The nmr

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(8) The reputed τ values, obtained in a Varian A-60 instrument, are for 15–20% solutions in carbon tetrachloride and are not extrapolated to infinite dilution. Some medium dependence of the τ values, especially those for the aromatic protons, was noted.

(9) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 258–265.

(10) In benzenes substituted with an electron-withdrawing substituent, the signal of lowest field is usually that of the *ortho* protons.[9]

(11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 75–79.

(12) W. G. Brown and H. Reagen, *J. Am. Chem. Soc.*, **69**, 1032 (1947).

(13) The complex signal centered at about τ 2.9 was not clearly separated into two multiplets, as were the aromatic proton signals of *o*-bromo- and *o*-nitroneopentylbenzene.

spectrum had the following simple features: (1) a singlet of relative area nine at τ 9.11 (terminal methyl protons), (2) two close lying singlets at τ 7.52 and 7.48 of relative height 9 to 16 and total relative area 5.4 (methylene and acetyl methyl), and (3) an A_2B_2 pattern in the aromatic proton region,[9] with peaks at τ 2.13, 2.24, and 2.89.

Experimental Section

Nitration of Neopentylbenzene.—The heterogeneous conditions of Brown and Bonner were applied.[3] A mixture of sulfuric acid (29 ml, density 1.86 g/ml) and nitric acid (17 ml, density 1.42 g/ml) was added dropwise over a period of 3 hr to stirred neopentylbenzene (40 g, 0.27 mole) at 25°. The reaction mixture was maintained at 25° for an additional 6 hr, then poured onto ice and extracted with ether. The extract was dried over sodium sulfate and the ether removed by distillation. A small portion of the liquid residue was retained for vpc analysis (Aerograph Hy-Fi, cyanosilicone column). The residue was distilled, yielding 36.3 g (70%) of liquid, bp 83–105° (0.5 mm). A portion, 25 g, was purified by vpc (Aerograph A-700 Autoprep, silicone 710 column) yielding 8.8 g of isomer A, 0.2 g of isomer B, and 9.2 g of *p*-nitroneopentylbenzene, mp 29°.[2]

Isomer A, $n^{26}\text{D}$ 1.5150, was later identified as *o*-nitroneopentylbenzene.

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.36; H, 7.82; N, 7.25; mol wt, 193. Found: C, 68.28; H, 7.52; N, 7.42; mol wt (parent peak, mass spectrum), 193.

Isomer B, $n^{26}\text{D}$ 1.5193, was later identified as *m*-nitroneopentylbenzene.

Anal. Found: C, 68.38; H, 7.67; N, 7.39; mol wt (parent peak, mass spectrum), 193.

Bromination.—A solution of neopentylbenzene (2.0 g, 0.0135 mole) and bromine (0.0135 mole) in 30 ml of 85% acetic acid was maintained at 25° for 26 hr in the dark. Then the solution was poured into 50 ml of water and extracted with carbon disulfide. The extract was washed with water and then dried over barium oxide. In an analysis of the carbon disulfide solution in the Aerograph Hy-Fi (Carbowax 20 M, furnace temperature 130°) only two symmetrical peaks were obtained: isomer 1 had a retention time of 17 min (relative yield 91.5%), and isomer 2 had a retention time of 14 min (relative yield 8.5%). The carbon disulfide was removed by distillation and the residual oil purified by vpc in a preparative Aerograph A-90P (Carbowax 20 M column). A few drops were isolated of each of isomer 1, $n^{26}\text{D}$ 1.5228, and isomer 2, $n^{26^\circ}\text{D}$ 1.5265, and no other compounds were obtained. Isomer 1 later was shown to be *p*-bromoneopentylbenzene and isomer 2 was shown to be *o*-bromoneopentylbenzene.

Chlorination.—A solution of neopentylbenzene (2.0 g, 0.0135 mole) and chlorine (0.0135 mole) in 10 ml of glacial acetic acid was maintained at 25° for 26 hr in the dark. The acetic acid was removed by fractional distillation. Analysis by vpc (Aerograph Hy-Fi) showed only three compounds present: unchanged neopentylbenzene, chloro isomer 1 (relative yield, 74.5%), and chloro isomer 2 (relative yield 25.5%). The three compounds were separated on the Aerograph A-700 (Silicon 710 column). Chloro isomer 1, $n^{26}\text{D}$ 1.5033, later was shown to be *p*-chloroneopentylbenzene. Chloro isomer 2, $n^{26}\text{D}$ 1.5062, was shown to be *o*-chloroneopentylbenzene.

Acetylation.—Neopentylbenzene (0.0135 mole) was added over a period of 15 min to a solution of acetyl chloride (0.016 mole) and aluminum chloride (0.014 mole) in 15 ml of carbon disulfide. After 2 hr at room temperature, the reaction mixture was poured onto acidic ice water and extracted with carbon disulfide. The extract was washed and then dried over sodium sulfate. Analysis of the residual oil (2.26 g) on the Aerograph Hy-Fi gave two overlapping peaks (relative area, 5%) and a third separate peak (relative area, 95%) of greater retention time. The compound corresponding to the large peak was isolated by vpc on an Aerograph A-90P (silicone 710 column), 1.30 g, $n^{26}\text{D}$ 1.5140. It had a strong band in the carbonyl region of the infrared at 5.95 μ. Its nmr spectrum showed it to be *p*-acetylneopentylbenzene (see Discussion).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 81.42; H, 9.46.

***p*-Neopentylaniline.**—Reduction of *p*-nitroneopentylbenzene (10 g) with hydrazine and palladium on carbon according to the method of Pietra[14] gave *p*-neopentylaniline, which was recrystallized from methanol–water, 8.2 g (95%), mp 56–56.5°.

Anal. Calcd for $C_{11}H_{17}N$: C, 80.92; H, 10.50; N, 8.58. Found: C, 80.95; H, 10.41; N, 8.74.

The N-acetyl derivative melted at 165–165.5°.

***o*-Neopentylaniline.**—Reduction of *o*-nitroneopentylbenzene, isomer A, by the method of Pietra,[14] gave 1.25 g (71%) of liquid amine, $n^{26}\text{D}$ 1.5290. The parent peak in the mass spectrum, mass 163, corresponds to the molecular weight of *o*-neopentylaniline. The hydrochloride was prepared by bubbling hydrogen chloride into a solution of the amine (1.15 g) in 20 ml of absolute alcohol. The alcohol was evaporated and the residue recrystallized from ethanol–ether, yield 0.76 g, mp 105–106°.

Anal. Calcd for $C_{11}H_{18}ClN$: C, 66.18; H, 9.02; N, 7.01. Found: C, 66.11; H, 9.07; N, 7.17.

***p*-Bromoneopentylbenzene.**—The Sandmeyer procedure described by Fieser,[15] with bromides being used in place of chlorides and acetic acid as the solvent, was applied to 1.5 g of *p*-neopentylaniline and yielded 0.94 g of product. The bromide was further purified by vpc (Aerograph A-90P, Carbowax 20 M column) giving a colorless liquid, $n^{26}\text{D}$ 1.5227 (lit.[46] $n^{25}\text{D}$ 1.5240). It was identical with isomer 1 obtained in the bromination of neopentylbenzene.

Anal. Calcd for $C_{11}H_{15}Br$: C, 58.15; H, 6.66; Br, 35.18. Found: C, 58.18; H, 6.70; Br, 35.08.

***o*-Bromoneopentylbenzene.**—The procedure used above on *p*-neopentylaniline was applied to *o*-neopentylaniline (1.50 g) to yield 1.03 g of bromo compound. It was further purified by vpc, giving a colorless liquid, $n^{26}\text{D}$ 1.5268. The compound was identical with isomer 2 obtained in the bromination of neopentylbenzene.

Anal. Calcd for $C_{11}H_{15}Br$: C, 58.15; H, 6.66; Br, 35.18. Found: C, 58.01; H, 6.78; Br, 35.04.

***o*-Chloroneopentylbenzene.**—The procedure of Fieser,[15] modified by the use of acetic acid as the solvent, was applied to 4 g (0.025 mole) of *o*-neopentylaniline, yielding 1.90 g of *o*-chloroneopentylbenzene. Further purification in an Aerograph Autoprep Model A-700 (silicone 710 column) yielded 1.49 g (40%) of colorless liquid, $n^{26}\text{D}$ 1.5064. The compound was identical with isomer 2 obtained in the chlorination of neopentylbenzene.

Anal. Calcd for $C_{11}H_{15}Cl$: C, 72.31; H, 8.28; Cl, 19.41. Found: C, 72.30; H, 8.36; Cl, 19.20.

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The Preparation of α-Disulfones by Cobalt(III) Oxidation

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A new method for preparing disulfones in relatively high yield (35 to 56%) has been found (eq 1). A solution of $Co_2(SO_4)_3$ in 10 *N* H_2SO_4 will oxidize a sulfinic acid to a disulfone rapidly at 5°. Until now, the chief route to disulfones has been permanganate, H_2O_2, or peracetic acid oxidation of the sulfinic acid salts or of disulfides, etc. Yields were often low (4 to 16%) and product purification was sometimes difficult.[2] In

$$2RSO_2H + 2Co^{+3} \longrightarrow RSO_2SO_2R + 2Co^{+2} + 2H^+ \qquad (1)$$

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(1) Author to whom enquiries should be sent.

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