brought off a trace of unreacted chlorin, followed by the main product which was crystallized from chloroform–methanol to give **α-nitrooctaethylporphyrin** (8 mg., 32%), m.p. 247.5–249.5°. The visible and n.m.r. spectra of this compound were essentially identical with those of the compound prepared by nitration of octaethylporphyrin. The two samples behaved identically on thin layer chromatography.

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# The Orientation of Electrophilic Substitution in 1,3,5-Triphenylbenzene

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Nitration of 1,3,5-triphenylbenzene gives 62% of the central-ring isomer, 23% of the peripheral-ring *ortho* isomer, and 15% of the peripheral-ring *para* isomer. Aluminum chloride catalyzed acetylation of 1,3,5-triphenylbenzene gives only the peripheral-ring *para* isomer. The products have been characterized by their infrared and n.m.r. spectra. The steric requirements of electrophilic substitution on 1,3,5-triphenylbenzene are discussed.

There are a total of 12 activated positions for electrophilic substitution in 1,3,5-triphenylbenzene. These positions form three nonequivalent sets which are subject to rather different steric and electronic influences. Although there exist in the literature a few scattered reports of products and yields,[1–10] no quantitative study of the orientation pattern has yet appeared.

We have found that nitration of 1,3,5-triphenylbenzene in acetic anhydride at 25° gives three mononitration products: A, m.p. 145°; B, m.p. 131°; and C, m.p. 155°. Only one mononitration product has been previously reported, the central-ring isomer, 2-nitro-1,3,5-triphenylbenzene, m.p. 142–143°.[2] The identity of this compound has been conclusively established[7a] by independent synthesis from 2,4,6-triphenylpyrylium fluoroborate and sodium nitromethide. We have prepared 2-nitro-1,3,5-triphenylbenzene by the original literature method[2] and found it to be identical with product A of this study.

Product B was identified as 1-(*o*-nitrophenyl)-3,5-diphenylbenzene and product C as 1-(*p*-nitrophenyl)-3,5-diphenylbenzene on the basis of their infrared and n.m.r. spectra. The intense carbon–nitrogen symmetrical stretching frequency occurs at 1369, 1358, and 1348 cm.$^{-1}$ for A, B, and C, respectively. In view of the known relationship between frequency and molecular crowding[11] these values should represent the central-ring, peripheral-ring *ortho*, and peripheral-ring *para* derivatives, respectively. For reference, the frequencies of *o*-nitrobiphenyl (1355 cm.$^{-1}$) and *p*-nitrobiphenyl (1348 cm.$^{-1}$) were determined.

The n.m.r. spectra of B and C show a complex pattern of signals between $\tau$ 2.0 and 2.6 as opposed to a relatively simple pattern for A in the same region. The spectrum of C has, in addition, a two-proton doublet at $\tau$ 1.52 and 1.66 interpretable as half of an AB pattern for the four protons of the substituted peripheral ring. The other half of this AB pattern would be buried in the complex signals between $\tau$ 2.0 and 2.6. The n.m.r. spectrum of *p*-nitrobiphenyl also shows a doublet ($\tau$ 1.73 and 1.87) with the same coupling constant and relative peak heights as for C. No downfield doublet was found in the spectra of the other two nitration isomers, 1,3,5-triphenylbenzene, *o*-nitrobiphenyl, or *m*-nitrobiphenyl.

Although the upfield half of the possible AB pattern cannot be located with any certainty, the existent range of signals between $\tau$ 2.0 and 2.6 sets the limits for the chemical shift between the *ortho* amd *meta* protons as 30 and 50 c.p.s. at 60 Mc.p.s. in deuteriochloroform. Recently Kurland and Wise[12] have reported the chemical shift between the *ortho* and *meta* protons in 4,4′-dinitrobiphenyl as 32.4 c.p.s. at 60 Mc.p.s. in tetrachloroethane. Fitting the relative intensities (1:1.9) and the coupling constant ($J$ = 9 c.p.s.) of the doublet in the spectrum of product C to the synthetic AB spectra of Wiberg and Nist[13] gives a predicted chemical shift between the protons of about 30 c.p.s.

The product composition of the nitration reaction was found by infrared analysis to be 62% central-ring isomer, 23% peripheral-ring *ortho* isomer, and 15% peripheral-ring *para* isomer. Although there is an uncertainty about the analysis of the peripheral-ring *ortho* isomer, owing to poor resolution of its C–N stretching frequency, the infrared percentages are close to those of actually isolated materials (see Experimental) and are undoubtedly within 5% of the true values.

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(11) L. L. Ingraham, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 505. Among the data presented therein are the frequencies for nitrobenzene (1341 cm.$^{-1}$), *o*-nitrotoluene (1345 cm.$^{-1}$), and nitromesitylene (1363 cm.$^{-1}$).

(12) R. J. Kurland and W. B. Wise, *J. Am. Chem. Soc.*, **86**, 1876 (1964).

(13) K. B. Wiberg and B. J. Nist, "Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1922, p. 5.

The acetylation of 1,3,5-triphenylbenzene with acetic anhydride in nitrobenzene gives only one product (D), an acetyl compound, m.p. 147–148°. The proton magnetic resonance and infrared spectra of the product remaining after steam distillation of the nitrobenzene showed the product to be completely free of isomers. Examination of the elution chromatographic fractions failed to reveal the presence of any material other than D and recovered triphenylbenzene.

The only known acetyl-1,3,5-triphenylbenzene, m.p. 125°,[3] has been shown[14] to be the central-ring isomer, 1-acetyl-2,4,6-triphenylbenzene, by synthesis from 2,4,6-triphenylpyrylium fluoroborate and the potassium salt of 2,4-pentanedione. The central-ring acetyl compound, m.p. 127–128°, prepared from the central-ring bromo compound by the literature method,[3] showed a carbonyl stretching frequency at 1705 cm.$^{-1}$ compared with 1690 cm.$^{-1}$ for D. The carbonyl-stretching frequency for *p*-acetylbiphenyl (1692 cm.$^{-1}$) indicates that D is the peripheral-ring *para* isomer, 1-(*p*-acetylphenyl)-3,5-triphenylbenzene.

The examination of proton magnetic resonance spectra confirms the identification of D as the peripheral-ring *para* isomer. The central-ring isomer shows several signals between $\tau$ 2.2 and 2.7 and a three-proton singlet at $\tau$ 8.11; D shows, in addition to the signals between $\tau$ 2.2 and 2.7, a two-proton doublet (relative intensities 1:2.0) at $\tau$ 1.84 and 1.98 and a three-proton singlet at $\tau$ 7.45; *p*-acetylbiphenyl has a spectrum similar to that of D with a two-proton doublet (relative intensities 1:2.2) at $\tau$ 1.93 and 2.08 and a three-proton singlet at $\tau$ 7.43. The upfield singlets can readily be ascribed to the acetyl methyl groups and the downfield doublets can be identified as partial AB patterns by the same arguments as used before. Fitting the doublet of either D or *p*-acetylbiphenyl to the synthetic AB spectra of Wiberg and Nist[13] gives a predicted chemical shift between the *ortho* and *meta* protons of about 25 c.p.s. The range for this value computed from the collection of signals for D between $\tau$ 2.2 and 2.7 is 19 and 36. Owing to the simpler pattern in this region for *p*-acetylbiphenyl, it is possible to pick out the probable other half of the AB pattern and thereby determine a value of 22 c.p.s. for the chemical shift between the protons.

The similarity of the methyl resonances for 1-(*p*-acetylphenyl)-3,5-diphenylbenzene and *p*-acetylbiphenyl indicates that these are normal values and therefore the methyl group in 1-acetyl-2,4,6-triphenylbenzene is abnormally shielded. This large shielding (0.66–0.68 p.p.m.) is undoubtedly due to the anisotropy of the two tilted benzene rings which flank the acetyl group. Shielding in this manner amounts to a "built-in" benzene solvent shift and as such the magnitude would be expected to be considerably greater than the usual[15] 0.2–0.4-p.p.m. solvent shift observed for the solvent benzene relative to the solvent deuteriochloroform.

The literature reports for electrophilic substitution reactions of 1,3,5-triphenylbenzene which have included yields and detailed structure proofs are summarized in Table I. It is evident that the normal position of substitution is the central ring and that the acetylation gives an abnormal orientation. Abnormal orientations in Friedel–Crafts acylation reactions have been frequently reported, particularly in nitrobenzene, with explanations of both a steric effect due to solvent and equilibrium control being advanced.[16] In addition there is a preliminary report in the literature given without yields or reaction solvents that the acetylation of 1,3,5-triphenylbenzene yields central-ring substitution.[9] The solvent effects and reversibilities of both the benzoylation and acetylation reactions are currently under investigation. These results will be reported in a later communication.

TABLE I

ELECTROPHILIC SUBSTITUTION REACTIONS OF 1,3,5-TRIPHENYLBENZENE

| Reaction | % yield of substitution at | | | Reference |
|---|---|---|---|---|
| | Central ring | Peripheral ring | | |
| | | *ortho* | *para* | |
| $Br_2$, $CS_2$ | 91, 96 | | | *a, b, c, d* |
| $C_6H_5COCl$, $AlCl_3$, $CS_2$ | 90, 98 | | | *a, e* |
| $Cl_2$, $I_2$, $CCl_4$ | 76 | | | *f* |
| $HNO_3$, HOAc or $C_2H_5OH$ | 70 | | | *g, h* |
| $HNO_3$, $Ac_2O$ | 62[i] | 23[i] | 15[i] | This work |
| $Ac_2O$, $AlCl_3$, $C_6H_5NO_2$ | 0 | 0 | 100[i] | This work |

[a] Ref. 3. [b] Ref. 6. [c] Ref. 8. [d] Ref. 10. [e] Ref. 5. [f] Ref. 7b. [g] Ref. 2. [h] Ref. 7a. [i] Corrected for recovered triphenylbenzene.

For the remaining reactions, the preference for central-ring attack is quite pronounced, particularly when the statistical factor of the total number of activated positions is considered. It is known that 1,3,5-triphenylbenzene is not flat; the peripheral rings are actually twisted about 38° out of the plane of the central ring in solution[17] and would be expected to offer appreciable steric hindrance to the approach of an electrophile. Quite evidently this steric repulsion is not sufficient to offset the considerable resonance effects which favor attack at the central ring, even though the internuclear ring interactions have been greatly diminished by loss of coplanarity.

Although it is usually dangerous to attach quantitative significance to incidental yields, the difference in the yields of central-ring product for bromination and nitration must be accepted as real. The reported[3] yield of 91% for central ring bromination is for pure material after recrystallization; this yield or better has been repeated several times in the author's laboratory and by others.[10] Therefore, the difference in the amount of central-ring attack for these two reactions can be used to test further the significance of steric effects in the reactions of 1,3,5-triphenylbenzene. The steric requirement of molecular bromination is appreciably greater than that of nitration by nitronium ion as shown by relative *ortho* percentages in reactions with various substituted benzenes.[18,19] The observed smaller amount of central-ring attack for nitration

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(14) K. Dimroth and G. Neubauer, *Chem. Ber.*, **92**, 2042 (1959).

(15) We have found that $\delta_{CDCl_3} - \delta_{C_6H_6}$ for the methyl frequency of 1-(*p*-acetylphenyl)-3,5-diphenylbenzene is 0.35 p.p.m.; for other recent examples, see N. S. Bhacca and D. H. Williams, *Tetrahedron Letters*, 3127 (1964).

(16) For a recent summary, see P. H. Gore, "Friedel–Crafts and Related Reactions," Vol. III, G. A. Olah, Ed., John Wiley and Sons, Inc., New York, N. Y., 1964, pp. 5–8.

(17) R. J. W. LeFevre, A. Sundaram, and K. M. S. Sundaram, *J. Chem. Soc.*, 3180 (1963).

(18) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963).

(19) A. F. Holleman, *Chem. Rev.*, **2**, 218 (1925).

indicates that steric factors are relatively unimportant for electrophilic attack on 1,3,5-triphenylbenzene.

The difference in amount of central-ring attack for nitration and bromination can be explained on the basis of the selectivity of the two processes. Highly discriminating electrophiles would be expected to give central-ring attack almost exclusively, whereas less discriminating electrophiles should show a more random pattern of substitution. Molecular bromine has been found to be about 20 times as discriminating as the nitronium ion.[18]

## Experimental

The infrared values were determined in $CCl_4$ solution on a Beckman IR-7 prism-grating spectrophotometer calibrated against polystyrene. The n.m.r. values were determined in $CDCl_3$ solution (unless otherwise specified) on a Varian A-60 spectrometer, using tetramethylsilane as an internal standard.

**Nitration of 1,3,5-Triphenylbenzene.**—To a stirred solution of 9.20 g. (0.030 mole) of 1,3,5-triphenylbenzene in 200 ml. of acetic anhydride at 26° was slowly added a solution of 1.4 ml. (0.030 mole) of fuming nitric acid dissolved in 20 ml. of acetic anhydride. The slightly yellow solution was allowed to stir at room temperature for 24 hr., then poured onto ice and dilute sulfuric acid. Dichloromethane was added and the organic layer was separated, washed thoroughly with sodium carbonate solution, dried over calcium sulfate, and concentrated. The residual sirup was dissolved in benzene and chromatographed, using a column of Woelm activity grade I neutral alumina. Recovered triphenylbenzene (5.55g., 60% recovery) was readily separated by eluting with 1:4 benzene–petroleum ether (b.p. 30–60°). Several chromatograms were required to resolve the nitration mixture. Elution with benzene-petroleum ether mixtures, benzene, and then benzene–ether mixtures produced the following fractions in order of elution: A, 1.90 g. (18%), m.p. 144–145°; B, 0.34 g. (3%), m.p. 114–115° (dimorphic, stable form melts at 130–131°); and C, 0.21 g. (2%), m.p. 154–155°. Inspection of the infrared spectra of the unresolved fractions (0.66 g.) indicated the presence of an additional 1% yield of A, 3% of B, and 3% of C.

A, when mixed with 2-nitro-1,3,5-triphenylbenzene prepared by the method of Vorlander, Fischer, and Wille,[2] melted at 144–145°. The infrared spectra of the two materials were identical. B was identified (see text) as **1-(*o*-nitrophenyl)-3,5-diphenylbenzene.**

*Anal.* Calcd. for $C_{24}H_{17}NO_2$: C, 82.1; H, 4.88. Found: C, 82.1; H, 4.74.

C was identified (see text) as **1-(*p*-nitrophenyl)-3,5-diphenylbenzene.**

*Anal.* Calcd. for $C_{24}H_{17}NO_2$: C, 82.1; H, 4.88. Found: C, 81.8; H, 4.63.

**Analysis of the Nitration Product.**—The apparent extinction coefficients of the symmetrical C-N stretching frequencies were determined separately for solutions of A, B, and C at known concentration. Comparison of these values with those of the initial reaction mixture and assumption of Beer's law indicated 62% of A, 23% of B, and 15% of C. The C–N peak of B was obscured by the larger peaks of A (present in greater amount) on one side and C (greater extinction coefficient) on the other. The optical density of the B peak was determined by subtracting out the background due to A and C. Absorption of 1,3,5-triphenylbenzene was negligible in this region.

**Acetylation of 1,3,5-Triphenylbenzene.**—To a stirred solution of 4.60 g. (0.015 mole) of 1,3,5-triphenylbenzene and 1.51 g. (0.015 mole) of freshly distilled acetic anhydride in 50 ml. of nitrobenzene was added 7.00 g. (0.052 mole) of anhydrous aluminum chloride. As the aluminum chloride dissolved, the solution darkened and the temperature rose to 43° within 8 min. After this time, the temperature gradually fell. Thirty minutes after the addition of aluminum chloride, the mixture was poured onto ice and hydrochloric acid. Dichloromethane was added and the layers were separated. The organic layer was thoroughly washed with water and steam distilled. The residue was dissolved in a small amount of benzene and chromatographed using a Florisil column. Recovered triphenylbenzene (1.42 g., 31% recovery) was eluted with 2:1 hexane–benzene. When no more triphenylbenzene appeared in the eluate, the column was washed with ether. Evaporation of the combined ether fractions gave 2.45 g. (46%) of **1-(*p*-acetylphenyl)-3,5-diphenylbenzene,** m.p. 145–147°. Recrystallization from ethanol raised the melting point to 147–148°. This material was dimorphic; a freshly concentrated chromatography fraction occasionally melted around 122° before resolidifying and melting higher.

*Anal.* Calcd. for $C_{26}H_{20}O$: C, 89.7; H, 5.8. Found: C, 89.8; H, 5.7.

Infrared spectra of the initial reaction mixture and every chromatographic fraction showed no carbonyl stretching frequency other than 1690 cm.$^{-1}$. The n.m.r. spectrum of the steam-distillation residue showed an absorption at $\tau$ 8.11 which was not distinguishable from background under conditions where the noise was less than 3% of the amplitude of the $\tau$ 7.45 peak.

**Reference Compounds.**—*p*-Nitrobiphenyl, m.p. 114–115°, and *o*-nitrobiphenyl, m.p. 36–37°, were prepared by the method of Bell, Kenyon, and Robinson.[20] *m*-Nitrobiphenyl, m.p. 58–59°, was prepared by the method of Kaslow and Summers.[21] *p*-Acetylbiphenyl, m.p. 122–123°, was prepared by the method of Vogel.[22] 1-Acetyl-2,4,6-triphenylbenzene, m.p. 127–128°, was prepared by the method of Kohler and Blanchard.[3]

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