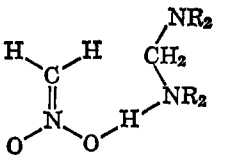
as an explanation of the enhanced rates. It is further noted that several mechanisms may operate and that their relative importance varies with conditions.

The unusually large negative entropies of activation are probably due in part to the unfavorable stereochemistry of the transition state; *i.e.*, for reaction to occur, the methylene carbon atom of the methylenebisamine must be situated at a point perpendicular to the plane of the $H_2C{=}N<$ group. The usually relaxed six-membered ring does not readily allow this configuration. The necessary configuration is rendered even less likely by the nearly linear O—H- - -N hydrogen bond. Therefore, the transition state probably requires a large strain from the normal hydrogen-bonded adduct VIII.



VIII

Ion-pair character in the hydrogen-bonded cyclic transition state may also contribute to the large entropies of activation. The importance of this effect, however, is difficult to assess.

The *meso* Reactivity of Porphyrins and Related Compounds. I. Nitration

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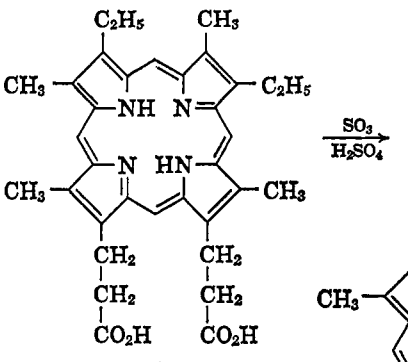
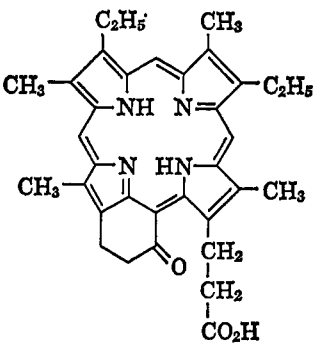
The nitration of octaalkylporphyrins under a variety of conditions has been studied. Octaethylporphyrin gave a mononitro derivative under mild conditions, and this is shown to be the *meso*-substituted compound. Longer reaction times led to the α,β- and α,γ-dinitrooctaethylporphyrins and to a tri-*meso*-substituted derivative. Mononitro compounds have also been obtained from octamethylporphyrin and mesoporphyrin. Nitration of octaethylchlorin with nitronium tetrafluoroborate gave the γ-nitro and γ,δ-dinitro derivatives: dehydrogenation of the former yielded the same nitrooctaethylporphyrin as had been obtained by direct substitution of the porphyrin.

The direct *meso* substitution of porphyrins has been a particularly obscure problem, although several examples of such reactions, *e.g.*, mesorhodin formation,[1] halogenation,[2] and nitration, have been advanced. The obscurity has lain essentially in proving the presence of a *meso* substituent in the product. Because we consider it likely that *meso* reactivity is important in the biological degradation, and possibly also in the biological action, of the natural porphyrins, chlorins, and corrins, an investigation of such reactivity is being carried out using n.m.r. spectroscopy to detect *meso* substitution. Nitration was chosen for the initial work firstly because there is much information available about this reaction in simpler systems,[3] and secondly because in the porphyrin case there appeared to be considerable doubt as to whether *meso* substitution was indeed involved.

Fischer and his colleagues carried out occasional investigations on the nitration of porphyrins over a period of about 16 years. Coproporphyrin,[4] isouroporphyrin II,[5] etioporphyrins I and II,[6] phylloporphyrin,[7] pyrroporphyrin,[8] deuteroporphyrin,[8] mesoporphyrin,[8] and rhodoporphyrin[8] were nitrated, generally with concentrated or fuming nitric acid as the reagent. The reactions were disconcertingly complex; for example, (i) mono-, di-, and trinitro compounds were obtained from etioporphyrin I under conditions[6]



I



II

which differed in slight, but evidently highly important, detail; (ii) good analyses, especially of carbon, were often not observed, owing in part, apparently, to contamination by halogen[6,8]; (iii) oxidative cleavage was observed[4]; (iv) even if the reactions observed were solely monosubstitutions at a *meso* position, all the above examples, the type I porphyrins excepted, would be expected to give mixtures of positional isomers.

Although certain reservations were apparent,[9] Fischer seems to have favored the *meso* formulation[6,8] for the nitro compounds, even for certain compounds containing a free β-position.[8] The important arguments for *meso* substitution were as follows. (i) Analogous halogenated derivatives were known. Thus etioporphyrin

(1) H. Fischer and H. Orth, "Die Chemie des Pyrrols," Vol. II-1, Akademische Verlagsgesellschaft, Leipzig, 1937, p. 544.

(2) See ref. 1, p. 235.

(3) P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Butterworth and Co. (Publishers) Ltd., London, 1959.

(4) H. Fischer and J. Hilger, *Z. physiol. Chem.*, **149**, 65 (1925); H. Fischer and W. Fröwis, *ibid.*, **195**, 49 (1931).

(5) H. Fischer and E. Thurnher, *ibid.*, **204**, 68 (1932).

(6) H. Fischer and A. Treibs, *Ann.*, **466**, 188 (1928); H. Fischer and W. Neumann, *ibid.*, **494**, 225 (1932).

(7) H. Fischer, M. Speitmann, and H. Meth, *ibid.*, **508**, 154 (1934).

(8) H. Fischer and W. Klendauer, *ibid.*, **547**, 123 (1941).

(9) See ref. 1, p. 263.

gave a tetrachloro derivative which was formulated with *meso* substitution since on oxidation it gave etioxanthoporphyrinogen. The halogenated derivatives will be considered later, but it can be seen at once that this argument was weakened not only by the slight ambiguity regarding the structure of xanthoporphyrinogens, but also by the observation[6] that the halogen in the tetrachloroporphyrin is, in any case, rather labile. (ii) Nitromesoporphyrin did not give a rhodin on treatment with oleum–sulfuric acid, whereas mesoporphyrin did[1,8] (*e.g.*, I → II). While this would accord with γ substitution in the nitro compound, it might also be ascribed to the deactivating effect of a nitro group established elsewhere in the conjugated system. (iii) The bromination of mononitrophylloporphyrin under the same conditions as those used for the parent compound was taken, with certain spectroscopic observations, to indicate[8] that the 6-position was still free in the nitro compound, and that *meso* substitution had therefore occurred.

The *meso*-substituted structure was, however, rejected by Stern and Molvig[10] on the basis of the visible spectra of mono- and dinitroetioporphyrins, which were of the etio, not the phyllo, type. Substitution in a side chain was suggested. At the outset of the present work, substitution on nitrogen appeared to be a third reasonable possibility, while the possibility of dealkylation followed by nitration was also considered.

To simplify the problem, a symmetrically substituted porphyrin, octaethylporphyrin (III), was selected and conditions were established (fuming nitric acid–acetic acid, 0°, 1.5 min.) which gave a monosubstitution product in high yield. This compound was dimorphic but usually gave red-brown rhomboids, m.p. 239–240°; thin layer chromatography suggested that the compound was homogeneous and demonstrated that it was free from starting material. Total analysis was consistent with the mononitro formulation. The infrared spectrum confirmed the presence of the nitro group (1532 and 1378 cm.$^{-1}$); these peaks are outside the normal ranges of 1630–1550 and 1300–1250 cm.$^{-1}$ attributed respectively to the asymmetric and symmetric stretching modes of the NNO_2 group,[11] and the N-nitroamine structure is therefore unlikely. The bands did, however, correspond to the vibrations of the CNO_2 group, and the occurrence of the symmetric mode at the high-frequency end of the range is in accord with a structure containing a noncoplanar aromatic nitro group[11] (Table I: compare the values for 2-nitropropane, *p*-nitrotoluene, and 2-nitro-*m*-xylene with that for mononitrooctaethylporphyrin).

The electronic absorption spectrum was of the etio type (Table II), and it showed a small bathochromic shift compared to the parent compound for each of the four peaks (4–5 mμ). The Soret band underwent a slight hypsochromic shift, possibly associated with increased relative absorption in the 380-mμ region. Solutions of this and other nitroporphyrins in neutral solvents were red-brown rather than red, and did not show the strong orange-red fluorescence shown by the parent porphyrins in ultraviolet light. The etio spectral type substantiates Stern and Molvig's measurement

TABLE I

INFRARED SPECTRA OF NITRO COMPOUNDS[a]

Compd.	CH_2Cl_2 ν_{as}-NO_2, cm.$^{-1}$	CCl_4 ν_{s}-NO_2, cm.$^{-1}$
Nitrobenzene	1528	1348
o-Nitrotoluene	1528	1349
m-Nitrotoluene	1529	1350
p-Nitrotoluene	1525	1346
2-Nitro-*m*-xylene	1528	1370
2-Nitropropane	1552	1358
α-Mononitrooctaethylporphyrin (IV)	1532	1378
α,β-Dinitrooctaethylporphyrin (V)	1534	1375
α,γ-Dinitrooctaethylporphyrin (VI)	1534	1371
α,β,γ-Trinitrooctaethylporphyrin (VII)	1536	1365[b]
meso-Mononitromesoporphyrin dimethyl ester(s)	1537	1375
γ-Mononitrooctaethylchlorin (X)	1525	1359[b]
γ,δ-Dinitrooctaethylchlorin (IX)	1530	1359[b]

[a] Given as ν, cm.$^{-1}$. [b] Measured in chloroform.

on the analogous nitroetioporphyrin, but it is not proposed to draw firm conclusions from this observation, since, as we shall show elsewhere,[12] the correlation of *meso* substitution with phyllo-type spectrum is by no means securely based. The n.m.r. spectrum (Table III) provided strong support for the *meso*-nitro structure (IV), however. Whereas the n.m.r. spectrum of octaethylporphyrin in deuteriotrifluoroacetic acid had a singlet at τ −0.98 corresponding to four *meso* protons,[13,14] the spectrum of the mononitro compound had two singlets in this region at τ −0.85 (2 protons) and −0.76 (1 proton). This observation accords with that made on *meso*-methyletioporphyrin[13] and, as in that case, the most shielded methine proton appears to be that furthest from the site of substitution. The results rule out the other possible formulations. Thus the N-nitroamine structure would be expected to give two equal singlets in the *meso* region (*cf.*[15] N-methyletioporphyrin). The nitroalkyl structure would require four *meso* protons, and a multiplet corresponding to a deshielded alkyl group (*cf.*[16] Me_2CHNO_2 in CCl_4, τ 5.42) which is not observed (Table III). Dealkylation followed by β nitration would also give a product containing four *meso* protons; the product from a less likely process—alkyl migration to methine bridge followed by β nitration—while it would require only three *meso* protons, would be expected to show a quartet in the n.m.r. at τ ~5 (*meso* CH_2CH_3, *cf.*[13] *meso* Me of *meso*-methyletioporphyrin at τ 5.15). Instead the alkyl group signals showed a general shift to high field compared to the parent porphyrin, which can be interpreted in detail in terms of the *meso*-nitro structure (*vide infra*).

Chemical structural evidence was not definitive, but accorded with the *meso* formulation. Thus chromic acid oxidation of the nitrooctaethylporphyrin and of octaethylporphyrin gave diethylmaleimide (isolated) in each case. The nitroporphyrin formed a nickel complex, analysis of which indicated the absence of an associated anion. This is a decisive piece of chemical evidence against the N-nitroamine structure: although the N-monosubstituted porphyrins may yield complexes

(10) A. Stern and H. Molvig, *Z. physik. Chem.*, **A177**, 365 (1936).

(11) K. Nakanishi, "Infrared Absorption Spectroscopy," Nankodo, Tokyo, 1962, p. 50; T. Kinugasa and S. Watarai, *J. Chem. Soc. Japan*, **83**, 476 (1962).

(12) R. Bonnett and G. F. Stephenson, unpublished work.

(13) R. J. Abraham, A. H. Jackson, G. W. Kenner, and D. Warburton, *J. Chem. Soc.*, 853 (1963), and references therein.

(14) R. B. Woodward and V. Skaric, *J. Am. Chem. Soc.*, **83**, 4676 (1961).

(15) W. S. Caughey and P. K. Iber, *J. Org. Chem.*, **28**, 269 (1963).

(16) W. Hofman, L. Stefaniak, T. Urbanski, and M. Witanowski, *J. Am. Chem. Soc.*, **86**, 554 (1964).

TABLE II

VISIBLE ABSORPTION SPECTRA OF PORPHYRINS AND THEIR NITRO DERIVATIVES IN CHLOROFORM

Porphyrins

Compd.	λ, mμ (ε) Soret		IV	III	II	Ia	I
Octaethylporphyrin (III)	401 (167,000)		499 (13,300)	534 (10,300)	566 (6,600)	594 (1,200)	618 (4,900)
α-Mononitrooctaethylporphyrin (IV)	400 (128,000)		504 (12,500)	538 (8,400)	571 (6,300)	...	623 (5,300)
α,β-Dinitrooctaethylporphyrin (V)	382 (82,600)	(396) (80,800)	508 (10,100)	538 (5,600)	578 (4,700)	...	628 (3,000)
α,γ-Dinitrooctaethylporphyrin (VI)	381 (122,000)	(394) (118,000)	505 (12,700)	538 (9,100)	576 (5,900)	...	628 (6,600)
α,β,γ-Trinitrooctaethylporphyrin (VII)	387 (76,400)	(405) (71,600)	514 (10,300)	(537) (5,400)	590 (4,000)	...	638 (1,900)
α-Aminooctaethylporphyrin	415 (176,000)	(420) (165,000)	519 (11,300)	555 (5,200)	588 (3,600)	...	644 (5,800)
Octamethylporphyrin	400		498	532	566	594	620
			Etio type				
α-Nitrooctamethylporphyrin	397		502	535	570	...	624
			Etio type				
Mesoporphyrin dimethyl ester	401 (154,000)		498 (12,500)	533 (8,900)	566 (6,000)	594 (1,200)	619 (4,500)
Nitromesoporphyrin dimethyl ester	399 (104,000)		503 (10,300)	536 (6,800)	571 (5,200)	...	625 (4,200)

Chlorins[a]

Octaethylchlorin (VIII)	γ-Nitrooctaethylchlorin (X)	γ,δ-Dinitrooctaethylchlorin (IX)
392 (155,000)	392 (90,000)	394 (86,000)
491 (11,000)		
498 (11,500)	497 (10,800)	499 (12,200)
525 (3,600)		(530) (2,800)
544 (2,800)	536 (2,000)	560 (1,300)
592 (3,600)	(605) (3,400)	(617) (3,900)
617 (3,500)	(621) (3,700)	626 (4,100)
644 (48,500)	650 (32,800)	662 (43,000)

[a] Values are given as λ, mμ (ε).

TABLE III

N.M.R. SPECTRA OF PORPHYRINS AND THEIR NITRO DERIVATIVES IN TRIFLUOROACETIC ACID[a]

Compd.	*meso* (s)	CH_2 (q)	CH_3 (t)	NH (br)
Octaethylporphyrin (III)	−0.98	5.72	8.13	14.65
α-Nitrooctaethylporphyrin (IV)	−0.85 (β,δ)	5.85 (5,6,7,8)	8.25 (5,6,7,8)	13.17
	−0.76 (γ)	5.96 (1,4)	8.35 (1,4)	13.66
		6.31 (2,3)	8.57 (2,3)	
α-Aminooctaethylporphyrin	0.60 (β,δ)	6.30	8.36	8.99
	1.05 (γ)	6.40	8.60	10.35
α,β-Dinitrooctaethylporphyrin (V)	−0.49	5.91 (7,8)	8.29 (7,8)	12.07
		6.04 (1,6)	8.42 (1,6)	
		6.37 (2,5)	8.64 (2,5)	
		6.50 (3,4)	8.75 (3,4)	
α,γ-Dinitrooctaethylporphyrin (VI)	−0.75	6.01 (1,4,5,8)	8.43 (1,4,5,8)	12.31
		6.33 (2,3,6,7)	8.59 (2,3,6,7)	
α,β,γ-Trinitrooctaethylporphyrin (VII)	−0.51	6.25 (1,8)	8.50 (1,8)	11.37
		6.43 (2,7)	8.66 (2,7)	
		6.56 (3,4,5,6)	8.81 (3,4,5,6)	
Octamethylporphyrin	−0.96	...	6.27 (singlet)	14.86
α-Nitrooctamethylporphyrin	−0.86 (β,δ)	...	6.35 (singlet, 5,6,7,8)	13.94
	−0.81 (γ)		6.43 (singlet, 1,4)	
			6.71 (singlet, 2,3)	

[a] Unless otherwise indicated, signal multiplicities are those given at the top of the columns.

with divalent metals,[17] these must contain an extra anion. Two types of reduction were observed. Hydrogenolysis occurred with hydrazine in the presence of Raney nickel. Stannous chloride in hydrochloric acid gave a new porphyrin as greenish rods, m.p. 258–259°, which is formulated, following Johnson,[18] as the *meso*-amino derivative on the basis of analysis, the n.m.r. spectrum (Table III), and the infrared absorption [3540 ($\nu_{as\text{-}NH_2}$), 3450 ($\nu_{s\text{-}NH_2}$), and 3300 (ν_{NH}, porphyrin) cm.$^{-1}$]. In the n.m.r. spectrum of the compound in deuteriotrifluoroacetic acid at room temperature the

(17) W. K. McEwen, *J. Am. Chem. Soc.*, **68**, 711 (1946); R. C. Ellingson and A. H. Corwin, *ibid.*, **68**, 1112 (1946).

(18) A. W. Johnson and D. Oldfield, *Tetrahedron Letters*, 1549 (1964).

signal corresponding to the γ-proton disappeared quickly, while that corresponding to the β- and δ-protons disappeared slowly; on replacing the acid by trifluoroacetic acid and heating for a short time, both signals reappeared.

The mononitration of octamethylporphyrin and mesoporphyrin were also examined. The purification of octamethylporphyrin gave considerable difficulty, and analyses in this series were unsatisfactory.[19] The best samples were prepared by sublimation in high vacuum of the recrystallized porphyrin, and these gave the expected n.m.r. spectrum. Nitration gave a mononitro derivative, the n.m.r. spectrum of which was particularly simple (Table III) and which indicated *meso* substitution. Mesoporphyrin dimethyl ester gave a mononitro derivative, m.p. 152–160°, the n.m.r. spectrum of which was complex. In the "*meso*" region four unequal signals appeared corresponding to *ca.* three protons. This indicates the presence of isomeric *meso*-substituted mesoporphyrins; recrystallization raised the melting point to 162–166°, but the product was still an isomeric mixture.

Further Nitration.—Studies on nitration under different conditions to give polynitro compounds were continued with octaethylporphyrin. It was shown (Table IV, Experimental) that under suitable conditions dinitro compounds and a trinitro compound could be prepared. Thus nitric acid–sulfuric acid at 0° for 0.5 min. gave about 40% of dinitroporphyrin and 4% of trinitroporphyrin, while fuming nitric acid previously treated with urea gave, after 12 min. at room temperature, about 45% of dinitroporphyrin together with a trace of mononitroporphyrin. The trinitro compound was best prepared using nitrating mixture at 0° for 1–1.5 min. Other nitrating media were examined using thin layer chromatography to follow the reaction (Table IV). Nitronium tetrafluoroborate in sulfolane (100°/1 hr.) led to no more than a possible trace of the mononitro compound.

TABLE IV

NITRATION OF OCTAETHYLPORPHYRIN UNDER VARIED REACTION CONDITIONS

Conditions	Time, min.	Method of product detn.	Products, %[a] Mononitro	Dinitro	Trinitro
HOAc–fuming HNO_3, 0° → room temp.	1.5	Isolation	92	...	...
	12	T.l.c.	xxx	x	...
	30	T.l.c.	...	xxx	...
	160	T.l.c.	...	xxx	x
Concd. H_2SO_4–concd. HNO_3, 0° → room temp.	0.5	Isolation	Trace	38	4
	1	Isolation	Trace	12	22
	1.5	Isolation	...	Trace	20
Fuming HNO_3, 20°	0.03	Isolation	26	Trace	...
	0.5	Isolation	...	4	...
Urea-treated fuming HNO_3, 22°	2	Isolation	72	...	...
	12	Isolation	2	46	...
	30	Isolation	...	5	8
Concd. HNO_3, room temp.	10	T.l.c.[b]	xx	...	...
NO_2BF_4–sulfolane, 100°	60	T.l.c.[b]	Trace?	...	...
NO_2BF_4–H_2SO_4, 18°	60	T.l.c.[b]	xx	...	...

[a] % yields refer to once-crystallized compounds; proportions estimated visually: xxx = major, xx = moderate, x = minor component. [b] Unchanged octaethylporphyrin was also detected.

The dinitrooctaethylporphyrin fraction proved to be a mixture of two compounds which were distinguishable on thin layer chromatography, a technique which we have found of great value in the porphyrin series. The isomers were generally found in roughly equal proportions and could be separated by fractional crystallization from chloroform–methanol. The less soluble isomer, brown rods, m.p. 280–282°, gave a satisfactory analysis for a dinitro derivative. The visible spectrum was not one of the recognized types, band I being slightly more intense than band II, but showed a further bathochromic shift compared with the mononitro compound (Table II). The n.m.r. spectrum indicated (Table III) that the two nitro groups are substituted at *meso* positions, and, since only two types of alkyl group are apparent, further suggests that the arrangement is α,γ (VI). It is of interest that this, the less soluble isomer, traveled faster on the absorbent layer, presumably because, with α,γ substitution, it is less polar. The more soluble, more polar isomer formed brown cubes, m.p. 224–226°; again it gave a satisfactory analysis for a dinitro derivative and the spectrum (etio type) showed a slight bathochromic shift compared to the mononitro compound. The n.m.r. spectrum again indicated *meso* substitution, but was more complex than that of the α,γ compound: four types of ethyl groups were apparent and this strongly suggests that the more soluble isomer is the α,β-dinitro compound (V, *vide infra*). Thus both α,β- and α,γ-dinitrooctaethylporphyrins are identified in the mixture of polynitro compounds.

A further nitration product was obtained as brown rhomboids, m.p. 227–228°. The analysis was not entirely satisfactory, but agreed fairly well with the trinitro formulation, and the visible spectrum (Table II) showed a further bathochromic shift with respect to the dinitro compounds. The n.m.r. spectrum shows a singlet (1H) in the "*meso*" region and three differently shielded types of ethyl group in agreement with the α,β,γ-trinitrooctaethylporphyrin structure (VII).

Nitration of Octaethylchlorin.—Only one chlorin, mesopurpurin-7 trimethyl ester, appears to have been successfully nitrated in the past,[20] and under conditions which mononitrate octaethylporphyrin (fuming nitric acid–acetic acid) the octaethylchlorin (VIII) appeared to suffer degradation. Nitration was therefore attempted with nitronium tetrafluoroborate in sulfolane; both mononitrochlorin (X) and dinitrochlorin (IX) were isolated, but further nitration was not observed. This accords with Woodward's observation[14] on the reactivity of chlorins with electrophilic reagents, and with the observation (*vide supra*) that the nitronium salt did not effectively nitrate the porphyrin under these conditions.

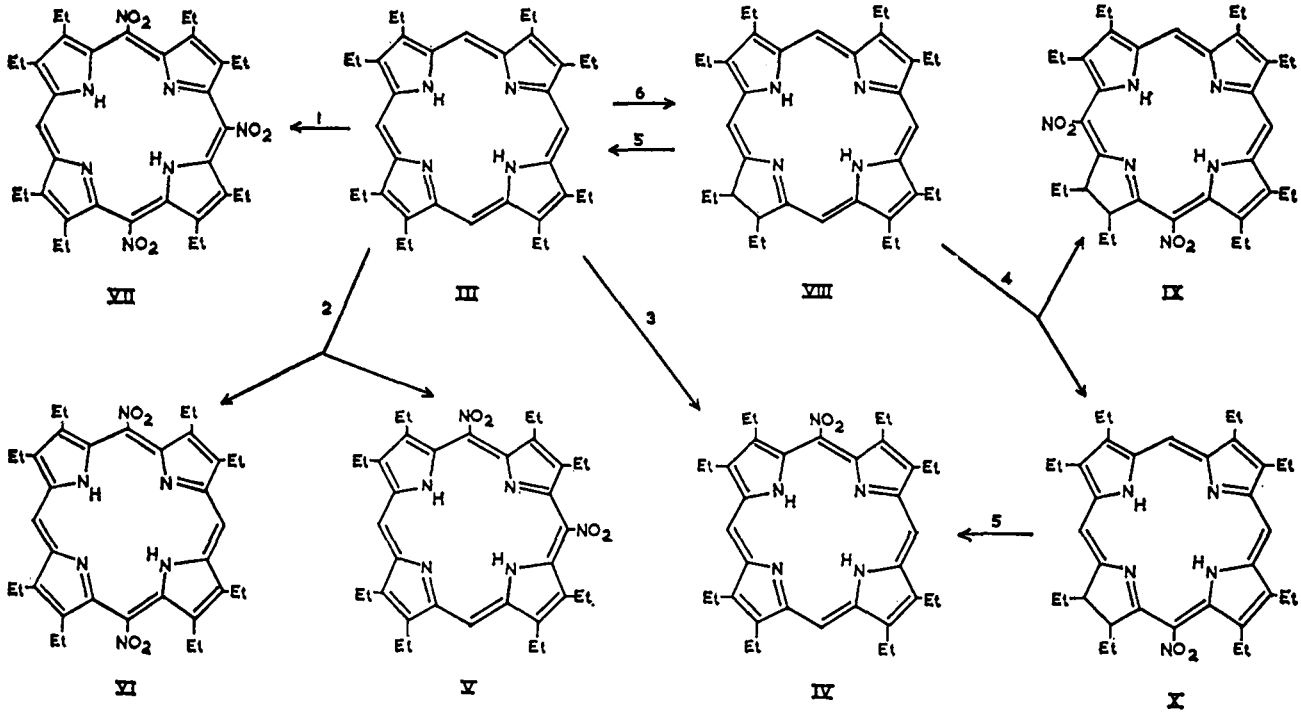
The visible spectra (Table II) of the nitrochlorins were of the chlorin type: the strong high wave-length bands of the chlorin, nitrochlorin, and dinitrochlorin appear at 644, 650, and 662 mμ, respectively. The infrared spectra are recorded in Table I, and it is interesting that the asymmetric stretching mode now occurs at a lower frequency than in the nitroporphyrins; presumably this reflects the somewhat less crowded situation about the *meso* substituent in the chlorins. The n.m.r. spectra of the nitrochlorins were much more

(19) G. M. Badger, R. L. N. Harris, R. A. Jones, and J. M. Sasse, *J. Chem. Soc.*, 4329 (1962).

(20) H. Fischer and E. Dietl, *Ann.*, **547**, 234 (1941).

CHART I

NITRATION OF OCTAETHYLPORPHYRIN AND OCTAETHYLCHLORIN



1. HNO_3–H_2SO_4, 0°, 1.0 min.
2. Fuming HNO_3–urea, room temp., 12 min.
3. Fuming HNO_3–HOAc, 0°, 1.5 min.
4. NO_2BF_4–sulfolane, 24°, 2 hr.
5. 2,3-Dichloro-4,5-dicyanobenzoquinone
6. Na–$C_5H_{11}OH$ (on haemin)

complex than those of the nitroporphyrins, but clearly indicated that, as expected,[14,21] nitration had occurred at the γ- and δ-positions. Thus the spectrum of the γ-nitrochlorin had signals at τ 0.23, 0.57 (α,β), and 1.64 (δ), while that of the γ,δ-dinitrochlorin had a singlet at τ 0.64 (α,β).

The dehydrogenation of the nitrochlorins was attempted with 2,3-dichloro-4,5-dicyanobenzoquinone. γ-Nitrooctaethylchlorin (X) gave a 32% yield of α-nitrooctaethylporphyrin (IV, identified by thin layer chromatography, and visible and n.m.r. spectra), much degradation apparently accompanying the dehydrogenation. The γ,δ-dinitrochlorin could not be converted to the corresponding porphyrin; this is presumably due to the steric compression which arises on incipient formation of a planar carbonium ion at C-7 or C-8.[22] In the mononitro example a carbonium ion can be accommodated at C-8 (*i.e.*, away from the γ-*meso* substituent), but even so the dehydrogenation is considerably slower than that of octaethylchlorin itself.

The observed reactions are summarized in Chart I. It is intended to defer a mechanistic commentary on them so that nitration, halogenation,[12] and deuteration can be discussed together.

N.m.r. Spectra.—Some of the n.m.r. observations are collected in Table III.

For structural work trifluoroacetic acid (or deuteriotrifluoroacetic acid) was found to be a satisfactory solvent for the majority of compounds. Chloroform was less satisfactory not only because of the low solubility of certain compounds but also because chemical shifts were concentration dependent in this solvent.[23] Moreover, signals representing nonequivalent protons were in general more clearly resolved in the acid medium. The integration values were in satisfactory agreement with the structural features (Table III) except for the NH signals which were often very broad and difficult to integrate.

The parent porphyrins showed the expected spectra—three singlets for octamethylporphyrin and two singlets, a triplet, and a quartet for octaethylporphyrin. The effect of *meso* substitution appears most clearly in the octamethylporphyrin case. There is a general decrease in induced ring current; thus the signals due to *meso* protons move to higher field, while the NH signal moves downfield (Figure 1). The methyl groups are no longer equivalent but fall into three groups. Four methyl groups are shifted slightly upfield ($\Delta\tau$ = +0.08), two are further shielded ($\Delta\tau$ = +0.16), while the other two are considerably shielded ($\Delta\tau$ = +0.44). A rather different pattern has been observed[13] in α-methyloctamethylporphyrin, where only two peaks [assigned to the methyl groups at (1,2,3,4) and (5,6,7,8), respectively] are found corresponding to the β-methyl protons ($\Delta\tau$ = +0.27, +0.15). Evidently several factors are operating here, but it is thought likely that the most important effects are as follows. (i) *A decrease in ring current associated with the buckling of the porphyrin ring.* *meso* substitution in an octasubstituted porphyrin leads to overcrowding[24] which could be partly relieved by the buckling of the porphyrin ring;

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(22) L. M. Jackman, *Adv. Org. Chem.*, **2**, 341 (1960).
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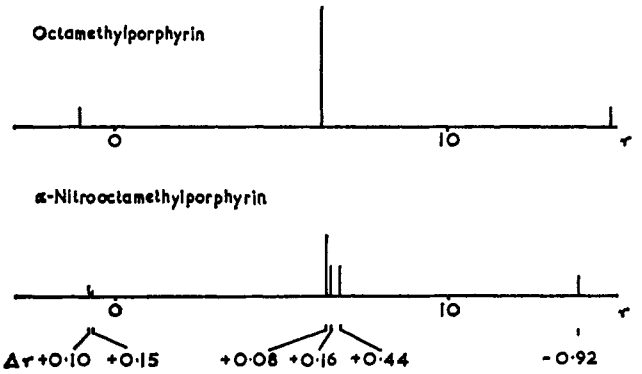

Figure 1.—Diagrammatic representation of the n.m.r. spectra of octamethylporphyrin and α-nitrooctamethylporphyrin: $\Delta\tau$ = τ (*meso*-substituted porphyrin) − τ (porphyrin).

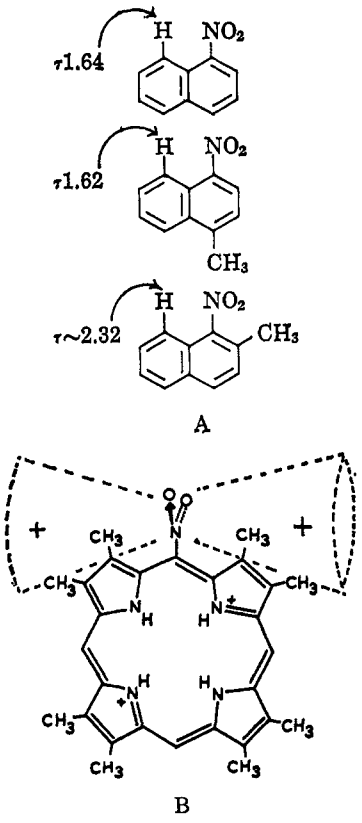

Figure 2.—Long-range shielding effect of the nitro group: A, data from literature[26]; B, effect of *meso*-nitro group in porphyrin system (the porphyrin system is expected to be nonplanar; see text).

such buckling might be especially noticeable in acid solution where additional stress arises from electrostatic repulsion in the dication. The deformability of the porphyrin ring[25] has been clearly demonstrated by the X-ray structure analysis of α,β,γ,δ-tetraphenylporphyrin and related compounds. In so far as such buckling leads to a restriction on the induced ring-current flow it causes a general diminution of deshielding outside the ring. (ii) *An enhanced decrease in deshielding of alkyl protons adjacent to the meso substituent.* β groups near the *meso* substituent are forced out of the average plane and thus suffer an especial loss of deshielding influence. Explanations in similar terms have already been advanced[13] to account for the effect of *meso* methylation. (iii) *A long-range shielding by the nitro group.* For steric reasons it is unlikely that the *meso*-nitro group will be able to conjugate effectively with the macrocycle. Indeed, in the *meso*-phenyl case[25] the phenyl and porphyrin rings are almost perpendicular, and the nitro group would be expected to prefer a similar conformation; *i.e.*, electron withdrawal will be much reduced. The expected long-range shielding effect of the *meso*-nitro group and a pertinent example[26] from the literature[27,28] upon which it is based are shown in Figure 2. The effect accords with two strongly shielded alkyl groups (2,3), two subject to much less shielding (1,4), and four groups (5,6,-7,8) essentially unaffected or even slightly deshielded.

This interpretation appears to apply also to α-nitrooctaethylporphyrin, although this case is somewhat more complex since multiplets rather than singlets have to be analyzed. Thus in the methylene signal two alkyl residues have $\Delta\tau$ +0.59 and the corresponding methyl has $\Delta\tau$ +0.44 (Table III), whereas the (5,6,7,8) ethyl groups have $\Delta\tau_{CH_2}$ +0.13 and $\Delta\tau_{CH_3}$ +0.12. The spectra of the dinitro compounds are particularly revealing: the α,γ compound (VI) has $\Delta\tau_{CH_2}^{max}$ +0.61, while the α,β derivative (V), in which two nitro groups are interacting on ring B, has $\Delta\tau_{CH_2}^{max}$ +0.78. The trinitro compound (VII) showed the greatest shift of all ($\Delta\tau_{CH_2}^{max}$) +0.84), and, as expected, this was associated with four alkyl groups, *i.e.*, those on the two rings (B and C) between two substituted *meso* positions.

Experimental

General.—Ultraviolet spectra were taken on a Unicam SP-800B; calibration with a holmium glass filter. Infrared spectra were taken on a Unicam SP-200; calibration with a polystyrene film. N.m.r. spectra were taken on a Varian A-60, using ~10% solutions in trifluoroacetic acid with tetramethylsilane as internal reference. Where spectral data are not given below they are collected in Tables I, II, and III. Melting points were determined on a Kofler block; fluorescence was detected using a Gallenkamp 125W mercury discharge lamp. Thin layer chromatography was used throughout for investigating reaction progress and sample purity: unless otherwise stated the system used was 1.5% acetone in petroleum ether (60–80°) on silica gel (Shandon). Column chromatography was carried out on magnesium oxide (Hopkins and Williams M.F.C.) or alumina (Spence "H") with purified solvents. Solvent composition ratios refer to volumes. In naming the porphyrins and chlorins the numbering (1–8) of the β-positions is omitted.

Porphyrins.—Octaethylporphyrin (III) was prepared by the method of Eisner, Lichtarowicz, and Linstead.[29] The porphyrin formed red needles (from benzene) which did not melt below 340°, although a phase change with loss of crystallinity occurred at *ca.* 300° (lit.[29-31] 318°, 292–293°, 322°).

Anal. Calcd. for $C_{36}H_{46}N_4$: C, 80.85; H, 8.67; N, 10.48. Found: C, 80.93; H, 8.33; N, 10.50.

Octamethylporphyrin was prepared by Johnson's method.[32] The crude porphyrin was extracted twice from a thimble with purified *o*-dichlorobenzene and then sublimed at 400° (mercury diffusion pump). The compound did not melt below 325°.

Anal. Calcd. for $C_{28}H_{30}N_4$: C, 79.58; H, 7.16; N, 13.26. Found: C, 78.23; H, 7.05; N, 13.35.

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Mesoporphyrin dimethyl ester was prepared from the free acid with diazomethane, followed by chromatography on Florisil with ethyl acetate. It formed red needles, m.p. 209–210° (lit.[33] 212°) from chloroform–methanol.

Mononitration. α-Nitrooctaethylporphyrin (IV).—To octaethylporphyrin (200 mg.) was added an ice-cold mixture of fuming nitric acid (*d* 1.5) and glacial acetic acid (32 ml., 1:1), and the mixture was shaken vigorously without further cooling for 1.5 min. A color change (red → violet) occurred. The solution was poured into iced water (800 ml.), the suspension was extracted with ether, and the ethereal layer was washed with aqueous sodium bicarbonate and then with water. Chromatography on magnesium oxide and elution with benzene gave **α-nitrooctaethylporphyrin** (200 mg., 92%). The compound was dimorphic and from chloroform–methanol mixtures gave either red-brown rhomboids, m.p. 239–240°, or red-brown rods, m.p. 251–252°, or mixtures of the two forms. The solution properties of the two forms were indistinguishable and on one occasion a sample of higher melting point was observed to have changed into the lower melting form on standing for several months at room temperature.

Anal. Calcd. for $C_{36}H_{45}N_5O_2$: C, 74.58; H, 7.82; N, 12.08; O, 5.52. Found: C, 74.79; H, 7.79; N, 12.37; O, 5.15.

The **nickel complex**, prepared in acetic acid, chromatographed on alumina (petroleum ether (60–80°)–benzene 1:1), and crystallized from chloroform–methanol, gave red needles: m.p. 292–293°; $\lambda_{max}^{CHCl_3}$ 397 mμ (ε 145,000), 525 (9800), and 560 (21,600).

Anal. Calcd. for $C_{36}H_{43}N_5NiO_2$: C, 67.94; H, 6.81; N, 11.00. Found: C, 68.23; H, 7.06; N, 11.25.

α-Nitrooctamethylporphyrin.—Octamethylporphyrin (100 mg.) was shaken at room temperature for 45 sec. with concentrated nitric acid (17 ml., *d* 1.4) and was then poured into iced water (800 ml.). The precipitated solid was filtered off, washed with aqueous sodium bicarbonate and water, and then dried (96 mg.). The solid was taken up in boiling nitrobenzene (7 ml.), the solution was filtered, and the hot filtrate was diluted with methanol (14 ml.) to give **α-nitrooctamethylporphyrin** (38 mg., 34%) which did not melt below 360°.

Anal. Calcd. for $C_{28}H_{29}N_5O_2$: C, 71.92; H, 6.25; N, 14.98. Found: C, 69.93; H, 5.97; N, 14.53.

Isomeric Nitromesoporphyrin Dimethyl Esters.—Mesoporphyrin dimethyl ester was nitrated at 25° using the method given for octaethylporphyrin (above), except that chromatography was carried out on alumina (ether and dichloromethane 2:1). One crystallization from chloroform–methanol gave the mononitro compounds, red-brown needles, m.p. 152–160° (62 mg., 58%). Three recrystallizations from the same solvent raised the melting point to 162–166° (lit.[8] 165°).

Anal. Calcd. for $C_{36}H_{41}N_5O_6$: C, 67.58; H, 6.46; N, 10.95. Found: C, 67.58; H, 6.35; N, 10.91.

Polynitration. α,β- and α,γ-Dinitrooctaethylporphyrins.—Octaethylporphyrin (50 mg.) was shaken with fuming nitric acid (urea treated,[6] 20 ml.) at 22° for 12 min. and then poured into iced water (200 ml.). The suspension was extracted as before, and the product was chromatographed on alumina. Benzene eluted two fractions: (i) dinitrooctaethylporphyrin, red-brown crystals, m.p. 235–260° (27 mg., 46%) from chloroform–methanol (thin layer chromatography indicated the presence of two components); (ii) a trace of α-nitrooctaethylporphyrin.

The mixed dinitroporphyrins (125 mg.) from several experiments were fractionally crystallized six times from chloroform–methanol (1:3) to give **α,γ-dinitrooctaethylporphyrin (VI)** (62 mg., 23% over-all) as brown rods, m.p. 280–282°.

Anal. Calcd. for $C_{36}H_{44}N_6O_4$: C, 69.20; H, 7.10; N, 13.45. Found: C, 69.31; H, 7.13; N, 13.54.

The material in the mother liquors from the first three crystallizations just referred to was crystallized twice from chloroform–methanol (1:20) to give **α,β-dinitrooctaethylporphyrin (V)** (34 mg., 13% over-all) as brown prisms, m.p. 224–226°.

Anal. Found: N, 12.98.

α,β,γ-Trinitrooctaethylporphyrin (VII).—Octaethylporphyrin (100 mg.) was shaken with an ice-cold mixture (20 ml., 1:1) of concentrated nitric acid (*d* 1.4) and concentrated sulfuric acid for 1 min. without further cooling. The greenish brown solution was extracted as before. Chromatography on magnesium oxide gave three fractions, eluted in the following order: (i) 20% benzene in petroleum ether gave 27 mg. (22%) of **α,β,γ-trinitrooctaethylporphyrin (VII)** as brown rhombs, m.p. 227–229°, from benzene–methanol (*Anal.* Calcd. for $C_{36}H_{43}N_7O_6$: C, 64.56; H, 6.47; N, 14.64; O, 14.33. Found: C, 64.10; H, 6.85; N, 13.80; O, 13.31.); (ii) 70% benzene in petroleum ether gave the mixed dinitroporphyrins (14 mg., 12%), m.p. 244–254°, from chloroform–methanol; (iii) benzene eluted a trace of mononitroporphyrin.

Reactions of α-Nitrooctaethylporphyrin. A. Oxidation. 1.—Octaethylporphyrin (50 mg.) in ice-cold aqueous sulfuric acid (50%, 3 ml.) was treated dropwise with a cold aqueous solution of chromium trioxide (128 mg. in 3 ml.) and then shaken at room temperature for 9 hr. The mixture was extracted with three 25-ml. portions of ethyl acetate and then extracted continuously with ether (21 hr.). The combined extracts were washed with saturated salt solution, dried, and concentrated. A sample was removed for vapor phase chromatography. The remainder was taken to dryness and sublimed (100°at 1 mm.) to give crude diethylmaleimide (21 mg.) which, recrystallized from aqueous ethanol, had m.p. 67–68° (lit.[30] 68°).

2.—α-Nitrooctaethylporphyrin (50 mg.) treated in the same way gave 7.2 mg. of crude diethylmaleimide.

Samples of solutions and of crystalline maleimide from 1 and 2 were examined by vapor phase chromatography (5-ft. column, silicone SE30 on firebrick, 205°, helium carrier). The only maleimide detectable from the nitroporphyrin was that formed on oxidizing octaethylporphyrin (diethyl maleimide, retention volume 254 ml.). Small samples of this imide were isolated after vapor phase chromatography of the two oxidation runs; the infrared spectra of these were identical.

B. Hydrogenolysis.—α-Nitrooctaethylporphyrin (10 mg.), hydrazine hydrate (1 ml.), and Raney nickel (~0.1 g.) were refluxed in dry, sulfur-free benzene (10 ml.) for 10 min. Excess Raney nickel was then added, and refluxing was continued to destroy the hydrazine. Thin layer chromatography of the filtered reaction mixture indicated that the main product behaved identically with octaethylporphyrin.

C. Reduction.[18]—A mixture of α-nitrooctaethylporphyrin (150 mg.) in ether (150 ml.) and stannous chloride dihydrate (46.5 g.) in concentrated hydrochloric acid (150 ml.) was refluxed for 5 min., cooled, and diluted with iced water (300 ml.). The mixture was extracted with ether, and the ethereal extract was washed with water, then with aqueous sodium bicarbonate, and finally with water. The dried concentrate was chromatographed on alumina (chloroform–ether 2:1) and crystallized from chloroform–methanol (66 mg., 46%). Three recrystallizations gave **α-aminooctaethylporphyrin** as green rods, m.p. 258–259°.

Anal. Calcd. for $C_{36}H_{47}N_5$: C, 78.64; H, 8.62; N, 12.74. Found: C, 78.81; H, 8.63; N, 12.40.

Acetone (13%) in petroleum ether was necessary for the examination of this compound on thin layer chromatography.

Nitration of Octaethylchlorin. A.—Octaethylchlorin (1.5 mg., m.p. 230–231°, lit.[29] 232°) was treated with an ice-cold mixture of fuming nitric acid (*d* 1.5) and glacial acetic acid (2 ml., 1:1 v./v.) for 1 min. (color change green → red) and then poured into iced water. Extraction in the normal way followed by thin layer chromatography showed that the bulk of the product did not move from the base line; no nitro derivative was identified.

B.—A solution of octaethylchlorin (100 mg.) in hot sulfolane (75 ml.) was prepared under nitrogen. The cold solution was treated with nitronium tetrafluoroborate (1.15 g.) in sulfolane (20 ml.) and kept at 24° for 2 hr. The solution was poured into excess aqueous sodium bicarbonate, which was then extracted with ether. The ethereal layer was washed with water, dried, and evaporated. The residue was chromatographed on alumina to give three fractions, eluted in the following order: (a) 20% benzene in petroleum ether gave **γ,δ-dinitrooctaethylchlorin (IX)** (11 mg., 9%); (b) 30% benzene in petroleum ether gave **γ-nitrooctaethylchlorin (X)** (47 mg., 43%) as red-brown rhombs, m.p. 218–219°; (c) benzene eluted a trace of octaethylchlorin

C.—An experiment carried out as described under B except that the reaction temperature was higher (31°) gave essentially only the **γ,δ-dinitrooctaethylchlorin (IX)** (51 mg., 44%), m.p. 242.5–243°.

Anal. Calcd. for $C_{56}H_{46}N_6O_4$: C, 68.98; H, 7.40; N, 13.41. Found: C, 68.26; H, 7.43; N, 13.33.

The Dehydrogenation of γ-Nitrooctaethylchlorin.—γ-Nitrooctaethylchlorin (25 mg.) and 2,3-dichloro-4,5-dicyanobenzoquinone (25 mg.) dissolved in dry benzene (6 ml.) were kept in the dark at room temperature for 24 hr. The solution was then chromatographed on magnesium oxide. Elution with benzene

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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 τ 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 τ 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 τ 2.0 and 2.6. The n.m.r. spectrum of *p*-nitrobiphenyl also shows a doublet (τ 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 τ 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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