4′,5-Bis(bromomethyl)-2-methoxydiphenyl Ether (X).—This procedure is analogous to one used to prepare the bis(chloromethyl) compound.[7] Hydrogen bromide gas was passed through a stirred solution of 10.58 g (0.529 mole) of 2-methoxydiphenyl ether,[25] 10 ml of 40% formalin, and 75 ml of acetic acid for 2 hr. The mixture was poured onto about 200 ml of ice and allowed to stand overnight. The chloroform extract was washed with water, sodium bicarbonate solution, water, sodium carbonate solution, and water. After drying over magnesium sulfate, evaporation yielded 19.3 g (95%) of yellow-brown oil. Crystallization from hexane–petroleum ether (bp 30–60°), followed by recrystallizations from hexane, gave colorless crystals, mp 103–104°, in about 50% yield.

Anal. Calcd for $C_{15}H_{14}Br_2O_2$: C, 46.66; H, 3.66; Br, 41.40. Found: C, 46.78; H, 3.74; Br, 41.49.

α,α′-Bis-1-(6,7-dimethoxyisoquinolyl)-4′,5-dimethyl-2-methoxydiphenyl Ether (IX, R = H). Method A.—Application of the hydrogen bromide–zinc dust reduction method to the diol mentioned above gave an 81% yield of a solid, mp 109–112°, after recrystallization from ethanol–water and then benzene–hexane.

Anal. Calcd for $C_{37}H_{34}N_2O_6 \cdot 2H_2O$: C, 69.58; H, 6.00; N, 4.39. Found: C, 69.45; H, 5.75; N, 4.16.

Method B.—IV (3.48 g, 0.0109 mole) and X (2.15 g, 0.00557 mole) were condensed in the presence of phenyllithium at −40° to yield 5.77 g of cream colored solid, mp 113–120°. The solid (XI) was subjected to hydrolysis by refluxing with 1.54 g of potassium hydroxide, 100 ml of ethanol, and 50 ml of water for 2.5 hr. After dilution with water, filtration yielded 0.77 g (22%) of a brown solid. A solid identical with that obtained in method A could be obtained by extraction with 15% hydrochloric acid, followed by basification with ammonium hydroxide and filtration. The methiodide, prepared from either solid, mp 196–198° (from methanol–ethyl acetate), was obtained in 95% yield.

Anal. Calcd for $C_{37}H_{34}N_2O_6 \cdot 2CH_3I$: C, 52.83; H, 4.55; I, 28.63; N, 3.16. Found: C, 52.60; H, 4.69; I, 28.48; N, 3.01.

Both solids gave the same picrate, mp 141–145° from ethanol.

Anal. Calcd for $C_{49}H_{40}N_8O_{20}$: N, 10.56. Found: N, 10.46.

O-Methyldauricine (I, R = CH$_3$).—A solution of 0.4 g (0.000452 mole) of the dimethiodide salt above in 50 ml of methanol and 10 ml of water was treated with 1.5 g of sodium borohydride and the resulting mixture refluxed for 2.5 hr. It was filtered hot and reduced in volume by evaporation. After pouring onto ice, filtering, and washing with water, 0.23 g (81%) of cream colored solid, mp 88–100°, was obtained. The bispicrate was prepared and after recrystallization from ethanol melted at 137–140°.

Anal. Calcd for $C_{51}H_{52}N_8O_{20}$: C, 55.84; H, 4.78; N, 10.22. Found: C, 55.58; H, 4.63; N, 10.02.

The material gave a dimethiodide in quantitative yield. Recrystallization from methanol–ethyl acetate–gave material of mp 186–190°.

Anal. Calcd for $C_{41}H_{52}N_2I_2O_6 \cdot 2.5H_2O$ (as reported by Tomita and co-workers[5]): C, 50.88; H, 5.94; N, 2.90. Calcd for $C_{41}H_{52}N_2I_2O_6 \cdot 2H_2O$: C, 51.36; H, 5.89; N, 2.92. Found: C, 51.22; H, 5.68; N, 2.77.

Authentic O-Methyldauricine (I, R = CH$_3$).—This material was prepared by reaction of dauricine·$CHCl_3$[20] with diazomethane. A cream colored solid, mp 54–64°, whose infrared spectra was identical with the above synthetic O-methyldauricine resulted. The dimethiodide had mp 184–188°, lit.[5] mp 181–182°. It did not depress the melting point of the above synthetic dimethiodide and had an infrared spectra identical with that of the synthetic material.

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[25] H. E. Ungnade and E. F. Orwoll, ref 24, Coll. Vol. III, 1955, p 566.

Solvent Effects in Aromatic Nitration. Nitration by Acyl Nitrates

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A study of aromatic nitration by nitric acid in acetic anhydride shows this reagent affords a lower *ortho/para* ratio with halobenzenes than is obtained from mixed nitric–sulfuric acids, while toluene yields essentially the same product distribution with either reagent. The use of a cosolvent with acetic anhydride can bring about substantial changes in the orientation from nitration of chlorobenzene, although toluene again is insensitive to changes in the reaction medium. These results are interpreted in terms of interaction between charge induced at the *ortho* position of the substrate by the substituent-ring dipole and the electrophilic species, with the strength of the interaction showing a dependency on solvent polarity.

Acetyl nitrate has been the subject of a number of recent investigations, and an excellent description of the nitric acid–acetic anhydride system has been given by Bordwell and Garbisch[1] in connection with a study of the nitration of olefins. The anomalously high *ortho/para* ratios obtained from nitration of anisole[2] and acetanilide[3] with acetyl nitrate are well documented, while more recently similar behavior has been observed with other substrates, including methyl phenethyl ether[4] and cyclopropylbenzene.[5]

The first systematic study[6] of acyl nitrates was a part of Ingold's pioneering work in the field of aromatic nitration. It was adduced from kinetic evidence that benzoyl nitrate was a precursor of dinitrogen pentoxide and that the latter species effected substitution; a similar mechanism was presumed to operate in the acetyl nitrate system. More recently, however, Paul[7] found the kinetics of nitration of benzene by nitric acid in acetic anhydride to be inconsistent with attack by dinitrogen pentoxide. The susceptibility of the reaction to acid catalysis and inhibition by nitrate and acetate ion suggested that nitronium ion was the electrophilic moiety. It was also reported[8] that the same system affords a significantly lower *ortho/para* ratio of nitrohalobenzenes than does mixed acid, although these data apparently contravene the results of earlier investigations,[9,10] which indicate that the orientation is the same in either system. To accommodate his data, Paul suggests that the dipole between the nucleus and halogen, with the negative end directed out, induces a slight positive charge at the *ortho* position (relative to *para*). The interaction of this charge with nitronium ion is enhanced by solvents of low dielectric constant (acetic anhydride *vis-a-vis* sulfuric acid), and *ortho* substitution is correspondingly

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[1] F. G. Bordwell and E. W. Garbisch, Jr., *J. Am. Chem. Soc.*, **82**, 3588 (1960).

[2] P. H. Griffiths, W. A. Walkey, and H. B. Watson, *J. Chem. Soc.*, 631 (1934).

[3] F. Arnal and T. Lewis, *J. Soc. Chem. Ind.*, **48**, T 159 (1929).

[4] R. O. C. Norman and G. K. Radda, *Proc. Chem. Soc.*, 423 (1960).

[5] R. Ketcham, R. Cavestri, and D. Jambotkar, *J. Org. Chem.*, **28**, 2139 (1963).

[6] V. Gold, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2467 (1950).

[7] M. A. Paul, *J. Am. Chem. Soc.*, **80**, 5329 (1958).

[8] M. A. Paul, *ibid.*, **80**, 5332 (1958).

[9] J. D. Roberts, J. K. Sanford, F. L. J. Sixma, H. Cerfontain, and R. Zagt, *ibid.*, **76**, 4525 (1954).

[10] M. L. Bird and C. K. Ingold, *J. Chem. Soc.*, 918 (1938).

TABLE I

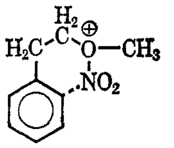
NITRATION OF HALOBENZENES

C_6H_5X	Reagent	Solvent	Mole,	Catalyst, 10^{-3} mole	Temp, °C	% nitrohalobenzene Yield	*ortho*	*para*
X = Cl	HNO_3	AcOH	1.25	...	25	1	33	67
X = Cl	HNO_3	H_2SO_4	0.50	...	25	90	34.6	65.4
X = Cl	$AcNO_3$	*a*	...	...	25	8	22	78
X = Cl	$AcNO_3$	*a*	...	H_2SO_4	25	66	19.5	80.5
X = Cl	$AcNO_3$	*a*	...	$HClO_4$	25	81	19.3	80.7
X = Cl	$AcNO_3$[b]	CCl_4	0.50	H_2SO_4	25	..	18	82
X = Cl[c]	N_2O_5	CCl_4	...	...	...	..	57	43
X = F	HNO_3	H_2SO_4	0.50	...	25	87	12.4	87.6
X = F	$AcNO_3$	*a*	...	H_2SO_4	25	87	6.2	93.8
X = F[d]	N_2O_5	CCl_4	...	...	Cold	94	28	72

[a] See Experimental Section. [b] Prepared from acetyl chloride and silver nitrate. [c] See ref 16. [d] See ref 15.

decreased. In the case of anisole, the dipole direction is reversed, and *ortho* substitution is increased.

In a recent series of papers, however, Norman[11,12] has rejected Paul's hypothesis and, on the basis of isomer distributions obtained with a number of monosubstituted benzenes, proposed that three factors govern orientation. (1) Direct nitration is effected by nitronium ion in both mixed acid and acetyl nitrate. Nitration by this species gives rise to the same isomer distribution in both systems. (2) The presence of a "basic site on the side chain" may allow protonation to occur in mixed acid. Nitration of the conjugate acid of the aromatic will alter the orientation to varying extents. (3) In acetyl nitrate solution, the presence of dinitrogen pentoxide should enable specific *ortho* nitration to occur if (a) a basic site in the side chain is present and (b) the charged intermediate is stereochemically suited to rearrange to the *ortho* position, *e.g.*[13]



The present investigation was undertaken to resolve the apparent discrepancies reported for the orientation from acetyl nitrate nitration of the halobenzenes, as well as to obtain additional information concerning the nature of the electrophilic species derived from this reagent.

Results and Discussion

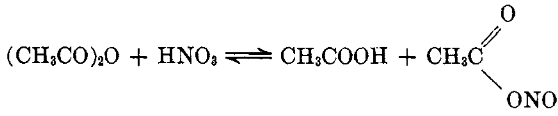
Nitration of the halobenzenes by fuming nitric acid in acetic anhydride was acid catalyzed and afforded *ortho/para* ratios significantly lower than those from mixed acid, qualitatively substantiating the results of Paul[14] (Table I). Catalytic quantities of sulfuric acid were found to lower these ratios slightly, both with acetyl and benzoyl nitrates. The foregoing observations detract from the argument that dinitrogen pentoxide plays a significant role under these conditions, since this reagent is known to give substantially greater quantities of the *ortho* isomeride with both chloro- and fluorobenzene[15-17] than does nitric acid in sulfuric acid. Further, it has been shown that an acid catalyst in dinitrogen pentoxide nitration causes a shift in orientation toward that obtained from mixed acid nitration, owing to an acid-catalyzed ionic dissociation.

$$N_2O_5 \overset{H^+}{\rightleftharpoons} NO_2^+ + NO_3^- \qquad (1)$$

Finally, Paul showed that nitrate ion retards acetyl nitrate nitration, while the opposite effect is observed with dinitrogen pentoxide.

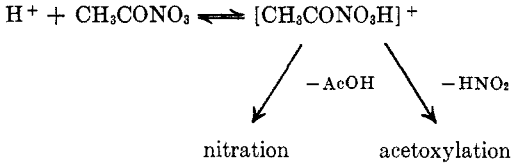
As an alternative to this species, protonated acetyl nitrate has been invoked to account for the stereoselective formation of *cis*-β-nitroacetates in the reaction with olefins,[1] since a stepwise process involving free ions is unlikely to lead to these products.[18] In a more recent report[19] involving acetoxylation of *o*-xylene, the same species has been suggested as the acetoxylating moiety. Both of these reactions, as well as aromatic nitration in acetic anhydride, can be explained in terms of the following equilibria.[20,21]

$$HNO_3 \rightleftharpoons H^+ + NO_3^- \qquad (2)$$



$$(CH_3CO)_2O + HNO_3 \rightleftharpoons CH_3COOH + CH_3C(=O)ONO_2 \qquad (3)$$

$$2CH_3CONO_3 \rightleftharpoons (CH_3CO)_2O + N_2O_5 \qquad (4)$$



$$H^+ + CH_3CONO_3 \rightleftharpoons [CH_3CONO_3H]^+ \qquad (5)$$

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[11] R. O. C. Norman and G. K. Radda, *J. Chem. Soc.*, 3030 (1961).

[12] J. R. Knowles and R. O. C. Norman, *ibid.*, 3888 (1961), and references cited therein.

[13] In a recent series, Kovacic has presented evidence to suggest linear coordination between reagent and substituent in stereochemically unfavorable situations as anisole: P. Kovacic and J. J. Hiller, *J. Org. Chem.*, **30**, 2872 (1965).

[14] See Experimental Section.

[15] V. Gold, E. D. Hughes, C. K. Ingold, and G. Williams, *J. Chem. Soc.*, 2452 (1950).

[16] G. Olah, A. Pavlath, I. Kuhn, and G. Varsanyi, *Acta Chim. Acad. Sci. Hung.*, **7**, 431 (1955).

[17] P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution—Nitration and Halogenation," Academic Press Inc., New York, N. Y., 1959, p 75.

[18] It is also significant that β-nitronitrates, formed from reaction of dinitrogen pentoxide with olefins, are minor products in this reaction, and their formation is almost completely suppressed by catalytic quantities of sulfuric acid. This is strong evidence against major participation of the nitrogen oxide.

[19] A. Fischer, J. Packer, J. Vaughan, and G. J. Wright, *Proc. Chem. Soc.*, 369 (1961).

[20] Ingold has suggested a number of additional reactions which can occur in the benzoyl nitrate system.[6] They undoubtedly occur in this system as well but have been omitted because they have no direct bearing on the present discussion.

[21] It has been shown that nitric acid is but very slightly ionized in acetic acid, unlike sulfuric and perchloric acids. See I. M. Kolthoff and A. Willman, *J. Am. Chem. Soc.*, **56**, 1007 (1934). Thus reaction 2 becomes significant only in the absence of a strong acid and accounts for the change in kinetics from second to first order when sulfuric acid is added.[7]

The above reactions, however, leave several questions unanswered. They do not explain the apparent discrepancy between results reported for isomer distribution of nitrochlorobenzenes, nor do they indicate any cause for the shift in orientations obtained with changing media. They also do not preclude formation of nitronium ion prior to attack on the substrate. Subsequent experiments were designed to gain more information about these aspects of the problem.

A survey of the effect of several solvents on the acetyl nitrate nitration of chlorobenzene (Table II) shows that profound changes in orientation can be brought about by variation of reaction medium. These data clearly indicate that no basic disagreement exists between the results of Paul and those of Ingold and Roberts, since these studies were carried out in different solvents. It is of further interest that, with some exceptions, the *ortho/para* ratio of nitrochlorobenzenes shows a general decrease with decreasing dielectric constant of the solvent, in accord with Paul's prediction. Accordingly, we feel these results are best interpreted in terms of an electrostatic interaction between electrophile and substrate, as originally suggested by Paul.[8]

TABLE II

NITRATION OF CHLOROBENZENE BY ACYL NITRATES

Effect of solvent			
$RCONO_3$	Cosolvent[a]	*ortho*	*para*
$R = CH_3$[b]	None	19.4	80.0
$R = CH_3$[b]	Acetonitrile	27.5	72.5
$R = CH_3$[b]	1,2,4-Trichlorobenzene	19.4	80.6
$R = CH_3$[b]	Chloroform	18.2	81.8
$R = CH_3$[b]	Carbon tetrachloride	14.9	85.1
$R = CH_3$[c]	Carbon tetrachloride	18	82
$R = C_6H_5$[c]	Carbon tetrachloride	19.8	80.2

[a] Unless otherwise specified, all mixtures contain acetic acid and acetic anhydride. See Experimental Section. [b] Prepared from acetic anhydride and nitric acid. [c] Prepared from the acyl chloride and silver nitrate in CCl_4; no acetic acid or anhydride present.

TABLE III

NITRATION OF CHLOROBENZENE AND TOLUENE AT 25 ± 1°

			Nitroaromatic orientation, %				
			Chlorobenzene		Toluene		
Nitrating agent	Solvent	Moles	*ortho*	*para*	*ortho*	*meta*	*para*
HNO_3[a]	H_2SO_4	0.50	34.6	65.3	56.4	4.8	38.4
HNO_3[a]	AcOH	1.25	33	67	56.9	2.8	40.3
$AcNO_3$[b]	CH_3CN	2.00	27.5	72.5	...	...	...
$AcNO_3$[b]	CH_3NO_2	2.00	27.7	72.3	60.0	4.0	36.0
$AcNO_3$[b]	Ac_2O	1.00	20.5	79.5	56.1	2.5	41.4
$AcNO_3$[b]	AcOH	0.35	19.4	80.6	53.7	2.8	43.5
$AcNO_3$[b,c]	CCl_4	0.50	18	82	55.0	2.5	42.6
$AcNO_3$[b]	CCl_4	0.50	14.9	85.1	54.8	2.5	42.8

[a] G. A. Olah, S. J. Kuhn, S. H. Flood, and J. C. Evans, *J. Am. Chem. Soc.*, **84**, 3687 (1962). [b] This work. [c] From acetyl chloride and silver nitrate.

An effect of solvent on substitution pattern has been encountered in other systems, including nitronium salt nitration of toluene,[22] and in that case was shown to be a function of the steric effects associated with solvation of the electrophile. That solvation might be related to the dielectric constant of the solvent is not a remote possibility and might be invoked to explain changes in orientation encountered in the present work. It seems reasonable to assume that the degree of solvation of the reagent in a solvent–substrate system would be affected very little by minor modifications in structure of the substrate; *i.e.*, that the steric requirements of a solvated electrophilic species in a given solvent should be essentially the same whether the substrate is chlorobenzene or toluene. Thus, while the magnitude of change of *ortho* substitution in a series of solvents will be different for toluene than for chlorobenzene, the direction of change should be the same for either aromatic. In fact, toluene is rather insensitive to changes in reaction medium (Table III), implying that steric factors associated with solvation are unimportant in this particular system.[23] As we indicated above, charge interaction between the substrate and reagent offers a better explanation for the effect of solvent on reaction, although a simple inductive effect cannot be the major cause of variation in *ortho/para* ratios. Toluene should exhibit an effect opposite to that of chlorobenzene if only an inductive effect is considered. Further, the methoxy group of anisole should exert an influence similar to halogen, since it, too, is electron withdrawing. Yet *ortho* substitution of anisole increases drastically in going from sulfuric acid to acetic anhydride.[24] In the case of the halobenzenes, these results are consistent with the concept of a charge induced at the *ortho* position by the ring-substituent dipole. Solvents of low dielectric allow more interaction between this charge and the electrophile, thereby decreasing *ortho* substitution. The direction and magnitude of change in orientation found with different substrates will be dependent on the direction and magnitude of the substituent dipole. One might also consider this to be a manifestation of a "space-field effect"[25] between the halogen atom and the *ortho* position, since it has been demonstrated[26] that indirect interactions between substituent and reaction site are important in other systems.

Still open to question is the nature of the electrophilic species, since the reactions presented do not imply the extent to which nitronium ion character is developed prior to attack on the substrate. As indicated earlier, evidence can be cited in favor of either nitronium ion or protonated acetyl nitrate.[27] While the present study does not allow an unequivocal choice to be made, certain observations are pertinent. The inexorable nature of the *ortho/para* ratio of nitrotoluenes with a variety of reagents and the inability of a change of acyl group to affect distribution of nitrochlorobenzenes[28] are consistent with a common species. Furthermore,

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[22] G. A. Olah and S. J. Kuhn, *J. Am. Chem. Soc.*, **84**, 3684 (1962).

[23] While selective solvation of the substituent might be considered as a cause of this behavior, results with other monosubstituted benzenes do not support this hypothesis.

[24] Although it has been suggested that anisole nitration involves a specific "*ortho* effect" in which preliminary coordination of the nitrating species with the ether oxygen occurs, an incipient four-membered ring must be involved. Yet the stereochemically more favorable five- and six-membered rings afford less *ortho* substitution.[11] See also K. Halvarson and L. Melander, *Arkiv Kemi*, **11**, 77 (1957).

[25] C. K. Ingold and C. C. N. Vass, *J. Chem. Soc.*, 417 (1928).

[26] (a) C. D. Ritchie and E. S. Lewis, *J. Am. Chem. Soc.*, **84**, 591 (1962); (b) H. D. Holtz and L. M. Stock, *ibid.*, **87**, 2404 (1965), and preceding papers. In a recent series, Dewar has presented compelling evidence to indicate that, in some aromatic systems, the π-inductive effect is in fact a direct field effect: M. J. S. Dewar and A. P. Marchand, *ibid.*, **88**, 354 (1966).

[27] It is implicit in the reaction scheme presented earlier that protonated acetyl nitrate is the precursor of nitronium ion, if the latter plays a role in this system.

[28] Similar observations have been made with other substrates. See ref 11.

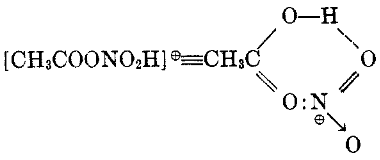
the relative rates of nitration of chlorobenzene and toluene are very close to those obtained from other nitrating systems involving nitronium ion, as shown in Table IV. Indeed, the only really compelling reason for assuming an electrophile other than nitronium ion is the stereoselective reaction with olefins.[1] These differences can be reconciled by considering protonated acetyl nitrate as a tightly solvated nitronium ion, *i.e.*

TABLE IV

COMPETITIVE NITRATION OF TOLUENE AND CHLOROBENZENE

C_6H_5X	Nitrating conditions	Temp, °C	$k_{ArH}/k_{benzene}$	Ref
X = CH_3	$AcNO_3$(H_2SO_4 cat.)	25	26.6 ± 1.6	*a*
X = CH_3	$AcNO_3$	25	25.2	*b*
X = CH_3	HNO_3–AcOH	45	24.5	*c*
X = Cl	$AcNO_3$(H_2SO_4 cat.)	25	0.034 ± 0.004	*a*
X = Cl	$AcNO_3$	25	0.035	*d*

[a] This work. [b] J. R. Knowles and R. O. C. Norman, *J. Chem. Soc.*, 2938 (1961). [c] H. Cohn, E. D. Hughes, M. H. Jones, and M. G. Peeling, *Nature*, 169, 291 (1952). [d] See ref 10.



A B

If this were a fairly accurate representation, it would be anticipated that generation of nitronium ion by mixed acid in acetic acid would afford isomer distributions approaching those of acetyl nitrate. This has been verified experimentally[29,30] (Table V), suggesting that nitronium ion (as a solvated species) does play a role in acetyl nitrate reactions.

TABLE V

NITRATION OF CHLOROBENZENE.
EFFECT OF NITRATING MEDIUM ON ISOMER DISTRIBUTION

PhCl, mole	HNO_3, mole	Cosolvent(s), moles	*ortho*	*para*
0.5	0.25	H_2SO_4,[a] 0.5	34.6	65.3
0.5	0.25	H_2SO_4,[a] 0.5 + AcOH, 1.25	25.6	74.4
0.5	0.25	Ac_2O, 1.0	20.5	79.5

[a] Heterogeneous medium.

It is unlikely that extreme variations in *ortho/para* ratios, such as those found in nitration of anisole and acetanilide with various reagents, are wholly a result of changes in solvent dielectric. Possibilities of reagent–substituent coordination,[13] or steric and electronic changes resulting from hydrogen bonding with or protonation of the substituent can effect substantial changes in orientation,[31] upon which solvent effects are superimposed.

However, it is clear that the orientation from nitration of certain monosubstituted benzenes is altered by changes in solvent, and these changes can be correlated in a general sense with solvent dielectric.

Experimental Section

Materials.—Chlorobenzene (Matheson Coleman and Bell) was distilled prior to use. A center, constant-boiling fraction, bp 131°, was used. Commercial toluene was distilled from sodium; a center cut, bp 109°, was collected. Reagent grade benzene was also distilled from sodium just prior to use. Other organic chemicals, reagent grade, were used as received. Reagent grade 90% nitric acid (Baker) was found to contain 89.1–90.2% acid by titration and was used as received.

Nitration of Chlorobenzene by Acetyl Nitrate. General Procedure.—Acetyl nitrate was prepared by the dropwise addition of 90% nitric acid (17.5 g, 0.25 mole) to acetic anhydride (39.5 g, 0.39 mole) with strong cooling to maintain the temperature below 40°. This mixture was then added during 1–1.5 hr to a rapidly stirred solution of chlorobenzene (56.3 g, 0.50 mole), acetic anhydride (13.1 g, 0.13 mole), and 96% sulfuric acid (0.1 g, 0.001 mole), which was immersed in a constant temperature bath at 25 ± 1.0°. After 3.0-hr total time, the reaction was quenched by addition of ice to the mixture. After hydrolysis was complete, the mixture was carefully treated with 10% potassium hydroxide at 0–5° until the solution was neutral to slightly acidic. The two layers were separated, and the aqueous layer was extracted four times with 75–100-ml portions of ether, which were combined with the organic layer. The ether solution was dried over anhydrous sodium sulfate and most of the ether was removed by distillation. Analysis of the residue (74.7 g) by gas–liquid partition chromatography (glpc) showed it to be a mixture of chlorobenzene (60.2%) and nitrochlorobenzenes (39.6%),[32] the latter having a composition of 19.4% *ortho*, 0.5% *meta*, and 80.0% *para* isomers. A careful search for dinitrated product showed it to be below the detectable limit (0.1%) of the analytical method.

Work-Up Procedure.—A mixture of composition similar to that obtained from the preceding example was synthesized, worked up according to the general procedure, and analyzed by glpc. The analyses showed an error in isomer distribution of <1.0% relative and an aromatic recovery of 96% minimum. Repetition of the procedure involving caustic neutralization employed by Paul[8] confirmed his analysis (90% *para*); however, the filtrate was found to contain a mixture of nitrochlorobenzenes which showed a higher *ortho/para* ratio than the filter cake. This procedure could not be used.

Competitive Nitrations. General Procedure.—A solution of toluene (46.1 g, 0.500 mole) and benzene (117.6 g, 1.50 moles) containing acetic anhydride (5.1 g, 0.05 mole) and 96% sulfuric acid (0.066 g, 0.65 mmole) was allowed to come to thermal equilibrium at 25.0 ± 0.5°. A solution of acetyl nitrate (0.05 mole) prepared from 90% nitric acid (3.5 g) and acetic anhydride (13.2 g, 0.13 mole) was added with rapid stirring during 2.5 min. After 1 hr, the mixture was poured on ice and worked up according to the general procedure. Analysis of the residue from distillation (92 g) gave the following analysis on a hydrocarbon-free basis: nitrobenzene, 5.4%; *o*-nitrotoluene, 52.0%; *m*-nitrotoluene, 2.0%; *p*-nitrotoluene, 40.6%. Runs were also carried out at benzene–toluene ratios of 2:1 and 1:1. The following results were obtained from the series: *ortho* = 54.7 ± 0.6%, f_o = 43.8; *meta* = 2.5 ± 0.3%, f_m = 2.0; *para* = 42.6 ± 0.6%, f_p = 68.0; $k_{toluene}/k_{benzene}$ = 26.6 ± 1.6.

Preparation of Acyl Nitrates from the Acyl Chloride. General Procedure.—To a rapidly stirred suspension of anhydrous silver nitrate (85.0 g, 0.50 mole) in carbon tetrachloride (154 g, 1.00 mole) was added benzoyl chloride (70.3 g, 0.50 mole) during 0.75 hr, at 0 to −5°. After stirring for 2 hr at that temperature, the mixture was filtered cold through a glass wool plug to yield 209 g of benzoyl nitrate solution. A total of 70.3 g of silver chloride (98%) was recovered. The benzoyl nitrate was divided into two equal portions and immediately added to a mixture of chlorobenzene (0.50 mole), nitromethane (2.3 g), and 96% sulfuric acid (0.1 g, 0.001 mole) during 0.75 hr at 25 ± 1°. The mixture was worked up according to the general procedure after 3.0-hr total reaction time.

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(29) A. K. Sparks, U. S. Patent 3,180,900. Kuhn and Olah reported that nitronium salts react with acetic acid to give acetyl nitrate: S. J. Kuhn and G. A. Olah, *J. Am. Chem. Soc.*, **83**, 4564 (1961).

(30) In the acetic acid–nitric acid system, water effectively competes with acetic acid for nitronium ion, and acetyl nitrate, or the conjugate acid probably does not form. Therefore, the high yield of *p*-nitrochlorobenzene is not obtained.

(31) A. Campbell and D. J. Shields, *Tetrahedron*, **21**, 211 (1965).

(32) Composition based on ether-free analysis. Concomitant infrared analysis showed 96% recovery of chlorobenzene as chlorobenzene and nitrochlorobenzenes; isomer analysis by this method agreed (±1%) with the glpc analysis.