collection from an HPLC column, reinjection of the sample always showed contamination by triphenylphosphine oxide. Consequently, integrations of the $^{1}H$ NMR spectra of these materials were always high in the aromatic region. The same substances could be obtained by using the procedures delineated by Hendrickson and Schwartzman.[5,19]

**Physical Data for Alkoxytriphenylphosphonium Triflates. *cis*-Cyclobut-3-ene-1,2-diylbis[(methyleneoxy)triphenylphosphonium triflate]**: fluffy, glasslike solid (decomposes at 37 °C) when evacuated in partial vacuum; IR (neat) 3040, 3000 (m), 1590 (m), 1480 (m), 1430 (s), 1260 (vs), 1220, 1150 (s), 1030, (m), 990, 750 (s), 690 (s), 640 (s) $cm^{-1}$; $^{1}H$ NMR ($CDCl_3$) $\delta$ 7.4–8.1 (m, 32 H), 6.0 (s, 2 H), 4.2–4.8 (p, 4 H), 3.2–3.6 (m, 2 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 137.73 (s), 136.50 (d, $J$ = 0.11 Hz), 133.46 (d, $J$ = 0.58 Hz), 131.30 (d, $J$ = 0.68 Hz), 118.59 (d, $J$ = 5.33 Hz), 71.65 (d, $J$ = 0.43 Hz), 45.14 (d, $J$ = 0.33 Hz), for $^{31}P$ NMR data, see Table I.

***cis*-Cyclobutane-1,2-diylbis[(methyleneoxy)triphenylphosphonium triflate]**: thick liquid; IR (neat) 3050, 2960–2900, 1580, 1440 (vs.), 1250, 1230, 1160, 1120, 1040, 1000, 920, 740, 700, 640 $cm^{-1}$; $^{1}H$ NMR ($CDCl_3$) $\delta$ 7.5–8.2 (m, 33 H), 4.2–4.5 (p, 4 H), 2.6–3.2 (m, 2 H), 1.5–2.4 (m, 4 H); for $^{31}P$ NMR data, see Table I.

**Hexane-1,6-diylbis[oxytriphenylphosphonium triflate]**: $^{1}H$ NMR ($CDCl_3$) $\delta$ 7.4–8.2 (m, 35 H), 4.2–4.8 (q, 4 H), 1.2–1.8 (m, 8 H).

**1,2,2-Trimethylcyclopentane-1,3-diylbis[(methyleneoxy)triphenylphosphonium triflate].** This was prepared by the general procedure except that an excess of reagents was used, otherwise cyclic ether[12] was obtained: off-white, cottony solid when evacuated under partial vacuum; $^{1}H$ NMR ($CDCl_3$) $\delta$ 7.5–8.3 (m, 35 H), 4.0–2.7 (m, 4 H), 1.2–1.7 (m, 5 H), 1.15 (s, 3 H), 1.0 (s, 3 H), 0.65 (s, 3 H); for $^{31}P$ NMR data, see Table I.

**Neopentoxytriphenylphosphonium triflate:**[7] $^{1}H$ NMR ($CDCl_3$) $\delta$ 7.6–8.0 (m, 15 H), 3.9–4.0 (d, $J$ = 2 H), 1.1 (s, 9 H).

**Isobutoxytriphenylphosphonium triflate:**[7] $^{1}H$ NMR ($CDCl_3$) $\delta$ 7.5–8.0 (m, 15 H), 3.97–4.15 (t, $J$ = 6 Hz, 2 H, 1.6–2.5 (m, 1 H), 1.0 (d, $J$ = 8 Hz, 6 H).

***sec*-Butoxytriphenylphosphonium triflate**: $^{1}H$ NMR ($CDCl_3$) $\delta$ 7.8–8.0 (m, 17 H), 4.4–4.9 (m, 1 H), 1.4–1.8 (m, 2 H), 1.3 (d, $J$ = 6 Hz, 3 H), 0.5–0.8 (t, $J$ = 6 Hz, 3 H).

**General Procedures for Reacting Alkoxytriphenylphosphonium Triflates with Halides. Two-Phase Method.** The alkoxytriphenylphosphonium triflate was dissolved in chloroform and shaken with a saturated solution of alkali metal halide in a separatory funnel. After several minutes, the layers were separated, the $CHCl_3$ layer was dried over anhydrous $MgSO_4$ and filtered, and the solvent was removed by rotary evaporation. Column chromatography yielded the alkyl halide when reaction had occurred.

**One-Phase Method.** The alkoxytriphenylphosphonium triflate was dissolved in anhydrous acetone, and an excess of the appropriate lithium halide was added. The mixture was stirred until TLC indicated the reaction was complete. The mixture was filtered and the solvent removed by rotary evaporation. Column chromatography yielded the alkyl halide.

**Ion-Exchange Method.** An acetone solution of the alkoxytriphenylphosphonium triflate was eluted through a column packed with Dowex resin of the appropriate halide ion. The elution was allowed to occur over approximately a 3-h period. The collected fraction was then evaporated and the alkyl halide purified by column chromatography.

**Preparation of 1,2,2-Trimethyl-1,3-bis(bromomethyl)cyclopentane.** Elution of 0.2 g of the appropriate dialkoxytriphenylphosphonium ditriflate over a bromide ion-exchange resin produced reaction at the normal primary carbon: $^{1}H$ NMR ($CDCl_3$) $\delta$ 7.2–8.3 (m, 18 H), 4.24–4.45 (dd, $J$ = 6 Hz, 2 H), 3.0–3.7 (m, 2 H), 1.3–1.7 (m, 5 H), 1.15 (s, 3 H), 1.05 (s, 3 H), 0.7 (s, 3 H). Reaction of 0.1 g of this material with LiBr in anhydrous acetone for 3 days yielded 0.015 g of the desired dibromide: $^{1}H$ NMR ($CDCl_3$) $\delta$ 3.0–3.8 (m + s, 4 H), 1.4–2.0 (m, 5 H), 1.15 (s, 6 H), 0.95 (s, 3 H); see Table I for $^{31}P$ NMR data; $[\alpha]^{25}_{D}$ + 58° ($CDCl_3$). Anal. Calcd for $C_{10}H_{18}Br_2$: C, 40.30; H, 6.09. Found: C, 40.52; H, 5.99.

**Acknowledgment.** We thank the Research Corp. for their generous support of this research. We are deeply indebted to Dr. Dennis Owsley of Monsanto Corp. for a generous gift of *cis*-cyclobutene-3,4-dicarboxylic anhydride. S.R. thanks the American Hoechst Corp. for a fellowship.

**Registry No.** *cis*-1,2-Bis(hydroxymethyl)-3-cyclobutene, 77774-01-7; *cis*-1,2-bis[(tosyloxy)methyl]-3-cyclobutene, 1517-12-0; *cis*-1,2-bis(chloromethyl)-3-cyclobutene, 77774-02-8; *cis*-1,2-bis(bromomethyl)-3-cyclobutene, 77774-03-9; *cis*-1,2-bis(hydroxymethyl)cyclobutane, 54445-64-6; *cis*-1,2-bis[(tosyloxy)methyl]cyclobutane, 76497-45-5; *cis*-1,2-bis(chloromethyl)cyclobutane, 77774-04-0; *cis*-1,2-bis(bromomethyl)cyclobutane, 64811-90-1; *cis*-1,2-bis(iodomethyl)cyclobutane, 77774-05-1; (+)-(1*R*,3*S*)-1,2,2-trimethyl-1,3-bis(hydroxymethyl)cyclopentane, 68510-42-9; *cis*-cyclobut-3-ene-1,2-diylbis[(methyleneoxy)triphenylphosphonium triflate], 77774-07-3; *cis*-cyclobutane-1,2-diylbis[(methyleneoxy)triphenylphosphonium triflate], 77774-09-5; hexane-1,6-diylbis[oxytriphenylphosphonium triflate], 77774-11-9; (+)-(1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-diylbis[(methyleneoxy)triphenylphosphonium triflate], 77774-13-1; neopentoxytriphenylphosphonium triflate, 77774-14-2; isobutoxytriphenylphosphonium triflate, 77774-16-4; *sec*-butoxytriphenylphosphonium triflate, 77774-18-6; (+)-(1*R*,3*S*)-1,2,2-trimethyl-1,3-bis(bromomethyl)cyclopentane, 77774-19-7; *l*-(–)-(menthyloxy)triphenylphosphonium triflate, 77774-21-1.

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(19) Schwartzman, S. M. *Ph.D. Dissertation*, Brandeis University, 1975.

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# Aromatic Substitution. 48.[1] Boron Trifluoride Catalyzed Nitration of Aromatics with Silver Nitrate in Acetonitrile Solution

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Benzene, alkylbenzenes, halobenzenes, and anisole were nitrated with silver nitrate/boron trifluoride in acetonitrile solution. Correlation of competitive rates with $\pi$- and $\sigma$-complex stabilities indicated that the transition state of highest energy lies relatively early on the reaction coordinate. Data indicate that nitrations occur via a polarized complex of the nitrating agent, with the catalyst undergoing nucleophilic displacement by the aromatic substrate.

Electrophilic nitration of aromatic hydrocarbons has been studied extensively. The nitrating agents commonly used are nitric acid in the presence of other acids, mixed nitric acid–carboxylic acid anhydrides, nitronium salts, and

Table I. Competitive $BF_3$-Catalyzed Nitration of Benzene and Alkylbenzenes with Silver Nitrate in Acetonitrile Solution at 25 °C

| ArH | $k_{ArH}/k_B$ | isomer distribution, % | ortho/para ratio |
|---|---|---|---|
| benzene | 1.0 | | |
| toluene | 24.5 | 59, ortho; 4, meta; 37, para | 1.59 |
| ethylbenzene | 27.9 | 52, ortho; 4, meta; 44, para | 1.18 |
| isopropylbenzene | 21.6 | 26, ortho; 6, meta; 68, para | 0.38 |
| *n*-propylbenzene | 23.1 | 46, ortho; 4, meta; 50, para | 0.92 |
| *tert*-butylbenzene | 21.7 | 9, ortho; 10, meta; 81, para | 0.11 |
| *o*-xylene | 112 | 63, 3-nitro; 37, 4-nitro | |
| *m*-xylene | 139 | 13, 2-nitro; 87, 5-nitro | |
| *p*-xylene | 123 | | |
| 1,2,3-trimethylbenzene | 706 | 59, 4-nitro; 41, 5-nitro | |
| 1,2,4-trimethylbenzene | 805 | 7, 3-nitro; 66, 5-nitro; 27, 6-nitro | |
| 1,3,5-trimethylbenzene | 738 | | |
| 1,2,3,4-tetramethylbenzene | 2460 | | |
| 1,2,4,5-tetramethylbenzene | 2570 | | |

Table II. Nitration of Toluene with Various Reagents

| reagent[a] | solvent | $k_T/k_B$ | distribution, % | | | ortho/para ratio |
|---|---|---|---|---|---|---|
| | | | ortho | meta | para | |
| $NO_2^+BF_4^-$ | $CH_3CN$ | 4.3 | 65 | 4 | 31 | 2.10[b] |
| $AgNO_3/BF_3$ | $CH_3CN$ | 24.5 | 59 | 4 | 37 | 1.59 |
| $CH_3ONO_2/BF_3$ | $CH_3NO_2$ | 25.5 | 64 | 3 | 33 | 1.94 |
| $C_6H_5COONO_2$ | $CH_3CN$ | 30.7 | 64 | 5 | 31 | 2.06 |
| *N*-nitro-2-picolinium tetrafluoroborate | $CH_3CN$ | 36.5 | 64 | 3 | 33 | 1.94 |
| $CH_3COONO_2$ | $CH_3CN$ | 44.3 | 61 | 2 | 37 | 1.65 |

[a] The temperature was 25 °C in all cases. [b] Due to the limited solubility of the nitronium salt in acetonitrile the reaction is not completely homogeneous.

nitrate esters.[2-4] Topchiev et al.[5] nitrated aromatic hydrocarbons with metal nitrates in the presence of various Lewis acids under heterogeneous conditions. The order of reactivity under these conditions was found to be $AgNO_3 > KNO_3 > NaNO_3 > NH_4NO_3 > Pb(NO_3)_2 > Ba(NO_3)_2$. A maximum yield of 58% of nitrobenzene was obtained with silver nitrate. The order of activity for the catalysts was established as $AlCl_3 > BF_3 > FeCl_3 > SiCl_4$. Low yields and the heterogeneous nature of the reactions due to the limited solubility of metal nitrates in common organic solvents rendered the reaction of very limited use. No mechanistic studies were reported either for the same reasons.

Nitrations with nitronium salts show low substrate selectivity, although high positional selectivity is maintained.[6] Schoefield and Moodie[7] pointed out the reactions under these conditions for aromatics more reactive than toluene seem to reach an encounter-controlled limit. Thus the low substrate selectivity nitration of aromatics is so fast that it can frequently result in incomplete mixing of the reactants before the reaction. However, regioselectivities of the nitrations remain high, in accordance with an inevitable two-step mechanism involving separate intermediates for the substrate and regioselectivity-determining steps (encounter complex or oriented π complex and arenium ions or σ complexes, respectively.)

There is therefore a need to develop nitrating reagents which avoid difficulties associated with incomplete mixing of reagents before reaction. Alkyl and metal nitrates do not act as nitrating agents in the absence of catalysts. Thus one can mix together the two reactants and then add a soluble catalyst to start the reaction. We have previously studied the boron trifluoride catalyzed nitration of aromatics with alkyl nitrates. In the present study we report on the use of silver nitrate as a nitrating agent catalyzed by boron trifluoride in acetonitrile solution (eq 1) to meet

$$\mathrm{ArH} \xrightarrow{\mathrm{AqNO_3BF_3}} \mathrm{ArNO_2} \tag{1}$$

these conditions as well. Due to the good solubility of silver nitrate in acetonitrile the reactions are homogeneous and easy to handle, and, if necessary, silver is easily recovered from the tetrafluoroborate salt.

For mechanistic studies competitive nitrations were carried out as follows. A mixture of benzene and the appropriate substituted benzene in acetonitrile was mixed with a solution of silver nitrate in acetonitrile keeping the molar ratio of aromatics to silver nitrate at 20:1, in order to maintain a constantly large excess of the aromatics. The resulting solution is stirred at 25 °C, and a solution of boron trifluoride in acetonitrile was added with stirring. Under these conditions mononitration of aromatics takes place with excellent yields. No dinitro products or other byproducts are formed in the nitrations. Products were generally analyzed by GLC.

**Nitration of Alkylbenzenes.** Data of nitration of alkylbenzenes, including substrate and positional selectivities for mononitro alkylbenzenes, are given in Table I.

For the studied alkylbenzenes, the relative reaction rates are in the order $C_2H_5C_6H_5 > CH_3C_6H_5 > n\text{-}C_3H_7C_6H_5 > i\text{-}C_3H_7C_6H_5 \approx t\text{-}C_4H_9C_6H_5$. The ortho/para ratios follow the expected trend from 1.59 for toluene to 0.11 for *tert*-butylbenzene, in accord with increasing steric hindrance

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[1] For part 47, see: Olah, G. A.; Narang, S. C.; Fung, A. P. *J. Org. Chem.* **1981**, *46*, 2706.

[2] Olah, G. A.,; Narang, S. C.; *Pol. J. Appl. Chem.*, in press.

[3] Olah, G. A.; Kuhn, S. J. "Friedel-Crafts and Related Reactions"; Wiley-Interscience: New York, 1964; Vol. 3, pp 1393–1491.

[4] For a comprehensive listing of reagents, see: Olah, G. A.; Lin, H. C.; Olah, J. A.; Narang, S. C. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 1045–1049.

[5] Topchiev, A. V. "Nitration of Hydrocarbons and Other Organic Compounds"; Pergamon Press: New York, 1959.

[6] Olah, G. A. *Acc. Chem. Res.* **1971**, *4*, 240–248.

[7] Hoggett, H. G.; Moodie, R. B.; Penton, J. R.; Schoefield, K. "Nitration and Aromatic Reactivity"; Cambridge University Press: New York, 1971.

[8] Olah, G. A.; Lin, H. C. *J. Am. Chem. Soc.* **1974**, *96*, 2892–2898.

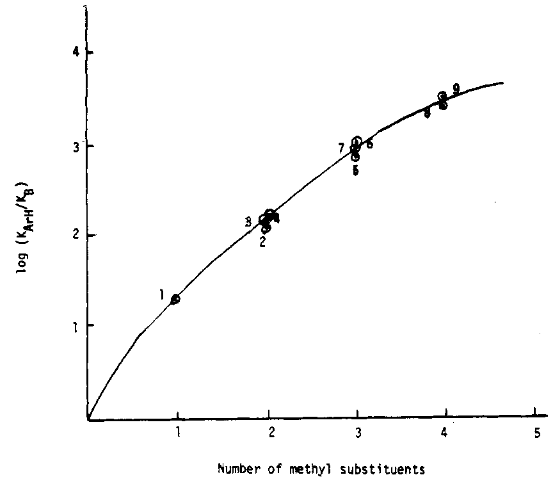

**Figure 1.** Numbers 1–9 refer to the following aromatic substrates: 1, toluene; 2, *o*-xylene; 3, *m*-xylene; 4, *p*-xylene; 5, 1,2,3-trimethylbenzene; 6, 1,2,4-trimethylbenzene; 7, 1,3,5-trimethylbenzene; 8, 1,2,3,4-tetramethylbenzene; 9, 1,2,4,5-tetramethylbenzene.

to ortho substitution due to the increasing bulk of the alkyl group. Similar trends were previously observed in electrophilic aromatic nitration with other reagents.

With respect to the nitration of toluene, Table II shows a comparison of its nitration with various reagents. The results of Table II clearly indicate that there is no correlation between substrate and positional selectivity in the nitration of toluene with various reagents. Thus, for example, in the nitration with $CH_3ONO_2/BF_3$ and $AgNO_3/BF_3$, the substrate selectivity shows hardly any change (25.5 and 24.5, respectively) although the positional selectivity, as expressed by the ortho/para ratio, changes considerably (from 1.94 to 1.59). Thus, we restate our previously held view that in these nitrations, substrate and positional selectivities are determined in separate independent steps. Whereas the first step., i.e., formation of the π complex (or encounter-controlled step), determines the substrate selectivity, the second step, i.e, formation of the individual σ complexes, determines the positional selectivity of nitration.

Figure 1 shows a plot of the relative rates of nitration of methylbenzenes relative to benzene against the number of methylsubstituents on the aromatic ring. The data of Table I have already shown that the relative rates increase with the increasing number of methyl substituents on the ring. However, there is no linear correlation between the two.

**Table III. Relative Nitration Rates and Their Comparison with π and σ Basicities**

| ArH | rel nitration rates | rel stability π complex[a] | rel stability σ complex[b] |
|---|---|---|---|
| benzene | 1.0 | 1.0 | 1 |
| toluene | 24.5 | 1.5 | 790 |
| 1,2-dimethylbenzene | 112 | 1.8 | 7 900 |
| 1,3-dimethylbenzene | 139 | 2.0 | 1 000 000 |
| 1,4-dimethylbenzene | 123 | 1.6 | 3 200 |
| 1,2,3-trimethylbenzene | 706 | 2.4 | 2 000 000 |
| 1,2,4-trimethylbenzene | 805 | 2.2 | 2 000 000 |
| 1,3,5-trimethylbenzene | 738 | 2.6 | 630 000 000 |
| 1,2,3,4-tetramethylbenzene | 2460 | 2.6 | 20 000 000 |
| 1,2,4,5-tetramethylbenzene | 2570 | 2.8 | 10 000 000 |

[a] Andrews, L. J.; Keefer, R. M. "Molecular Complexes in Organic Chemistry"; Holden-Day: San Francisco, 1964. [b] Mackor, E. L.; Hofstra, A.; van der Waals, J. H. *Trans. Faraday Soc.* **1958**, *54*, 66, 187.

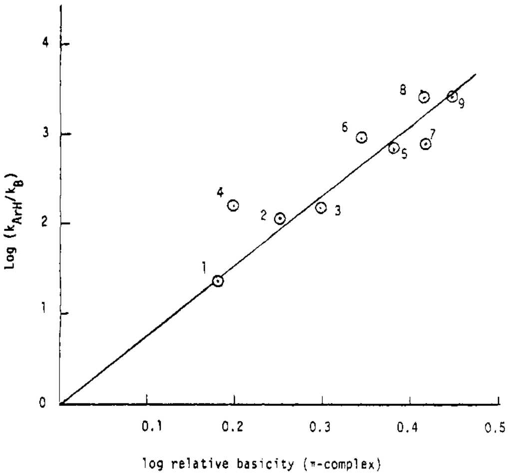

**Figure 2.** Plot of the relative basicity for the π complex against log ($k_{ArH}/k_B$).

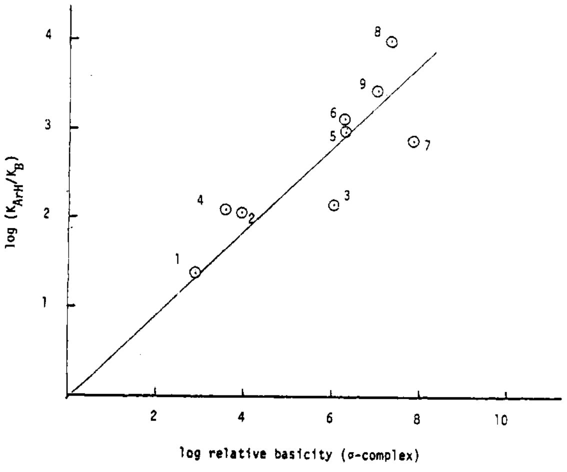

**Figure 3.** Plot of the relative basicity for the σ complex against log ($k_{ArH}/k_B$).

We have, furthermore, attempted a correlation between the relative reactivities and the corresponding π- and σ-complex stabilities of these alkylbenzenes. Condon[9] and subsequently Brown and Stock[10] and others[11] found that in a large number of substitution reactions, the relative reactivities show a better correlation with σ-complex stabilities rather than with π-complex stabilities. On the other hand, nitrations with nitronium salts showed trends comparable with π complexes. Table III shows the comparison between relative reactivities of nitration with silver nitrate/boron trifluoride and π- and σ-complex basicities. Figures 2 and 3 show plots of π- and σ-complex basicities against logarithms of relative reactivities. Comparison of the two figures shows that the present system is intermediate between π- and σ-complex stabilities. The transition state of highest energy in the nitration of aromatics with silver nitrate/boron trifluoride lies relatively early on

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(9) Condon, F. E. *J. Am. Chem. Soc.* **1952**, *74*, 2528–2529.

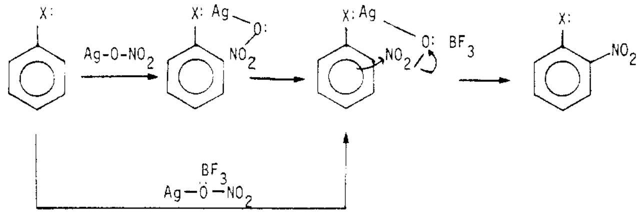
(10) Brown, H. C.; Stock, L. M. *J. Am. Chem. Soc.* **1957**, *79*, 1421–1425.

(11) Mackor, E. L.; Schmit, P. J.; Vander Waals, J. H. *Trans. Faraday Soc.* **1957**, *53*, 1309–1316.

Table IV. $BF_3$-Catalyzed Nitration of Monosubstituted Benzenes with Silver Nitrate in Acetonitrile Solution at 25 °C

| | | distribution, % | | |
|---|---|---|---|---|
| substrate | $k_{ArH}/k_B$ | ortho | meta | para |
| benzene | 1.0 | | | |
| toluene | 24.5 | 59 | 4 | 37 |
| anisole | 115.0 | 44 | 1 | 55 |
| fluorobenzene | 0.06 | 27 | 1 | 72 |
| chlorobenzene | 0.03 | 44 | 1 | 55 |
| bromobenzene | 0.07 | 25 | 1 | 74 |
| iodobenzene | 0.05 | 17 | 3 | 80 |

Scheme I



the reaction coordinate, and there is no direct relationship between substrate and positional selectivity

**Nitration of Anisole and Halobenzenes.** Data on the nitration of substituted benzenes having substituents containing nonbonded pairs of electrons are listed in Table IV. The data show that the $k_{ArH}/k_B$ ratios are similar to those obtained with methyl nitrate/boron trifluoride and other common nitrating systems. However, a comparison of ortho–para ratios for nitration of anisole, fluorobenzene and chlorobenzene with silver nitrate/boron trifluoride compared to nitration of these substrates with other reagents shows that a higher amount of the ortho nitro product is formed than with other reagents. One likely reason for this unusual isomer distribution is the well-known complexing ability of $Ag^+$ with oxygen, nitrogen, and halogens. Thus, it is possible that the nitrating agent (silver nitrate or silver nitrate/boron trifluoride complex) complexes with the nonbonded pairs of electrons on the substituent, thereby enabling preferential nitration at the proximal ortho position. Previously suggested[12] "coordinative ortho nitration", with the $NO_2^+$ ion attacking first at the heteroatom and then moving into the ortho position, was shown to be unlikely as these[13] processes would involve a symmetry-forbidden four-center transition state in contrast to the favorable six-membered ring transition states in the presently suggested mechanism (see Scheme I).

Nitration of bromobenzene and iodobenzene with silver nitrate–boron trifluoride did not show any unusually high ortho substitution. The larger size of bromine and iodine atoms and the longer carbon–halogen bond length in the cases of bromo- and iodobenzene make increasing ortho substitution less likely. In addition, the silver–bromine and silver–iodine bonds are weaker than silver–chlorine or silver–fluorine bond, thereby making the complexation of silver ion less likely in the cases of bromo- and iodobenzene.

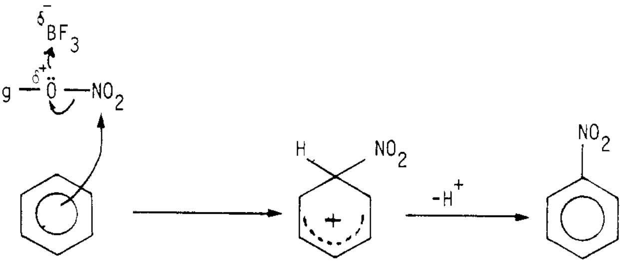
**Nature of the Nitrating Agent.** It was previously shown that it is possible to prepare nitronium salts from metal nitrates and boron trifluoride.[14] One could therefore come to the conclusion that nitration of aromatics with the present nitrating system proceeds through the formation of the nitronium ion in the first step which then nitrates the aromatic ring as is the case in nitration with a nitric acid–sulfuric acid system. An alternative possibility is the formation of a polarized coordination complex ($AgONO_2 \cdot BF_3$), which then undergoes a displacement reaction with the aromatic.

Table V. Boron Trifluoride Catalyzed Mononitration of Polymethylbenzenes with Silver Nitrate in Acetonitrile Solution

| polymethylbenzene | % yield of isolated product | polymethylbenzene | % yield of isolated product |
|---|---|---|---|
| 1,2,3,4,5-$Me_5$ | 92 | 1,2,4,5-$Me_4$ | 87 |
| 1,2,3,4-$Me_4$ | 86 | 1,2,3,5-$Me_4$ | 83 |

A solution of silver nitrate–boron trifluoride in acetonitrile at room temperature under the used reaction conditions,[15] however, did not show the presence of nitronium ion by IR and Raman spectroscopy. A low concentration of nitronium ion (1–2%) which is not detectable by these methods may still be present in these solutions, which would be sufficient to nitrate the aromatics at an appreciable rate. However, the data in TablesI and IV indicate that the present nitrating system gives different substrate and positional selectivities than observed in nitrations with nitronium tetrafluoroborate in acetonitrile solution.

Substrate selectivity data indicate that silver nitrate/boron trifluoride is a more selective nitrating system than $NO_2^+BF_4^-$. A comparison of ortho/para ratios for monosubstituted benzenes (Table IV) shows that there is less ortho and more para substitution in nitrations with silver nitrate/boron trifluoride compared to nitrations with $NO_2^+BF_4^-$. These observations tend to indicate the intervention of a relatively more selective nitrating agent with larger steric bulk than the nitronium ion. We therefore conclude that silver nitrate/boron trifluoride system in acetonitrile nitrates via a polarized complex which undergoes displacement by the aromatic substrate.



As part of our spectroscopic investigation of reaction intermediates, we have followed these nitrations also by $^{11}B$ NMR. Data support the view presented above that there is indeed a complex formation between silver nitrate and boron trifluoride. A detailed investigation of these nitrations by $^{11}B$ and $^{15}N$ NMR will be reported elsewhere.

**Preparative Nitrations.** Silver nitrate is a highly efficient nitrating agent under these reaction conditions. Thus, we have been able to carry out selective mononitrations of polymethylbenzenes (Table V) to obtain the corresponding nitroalkylbenzenes in excellent yields.

## Experimental Section

**Procedure for Competitive Nitration.** In a typical experiment, 50 mmol (3.9 g) of benzene, 50 mmol (4.6 g) of toluene,

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(12) Kovacic, P.; Hiller, J. J. *J. Org. Chem.* **1965**, *30*, 2871–2873.

(13) Olah, G. A.; Melby, E. G. *J. Am. Chem. Soc.* **1973**, *95*, 4971–4975.

(14) Sprague, R. W.; Garrett, A. B.; Sisler, H. H. *J. Am. Chem. Soc.* **1960**, *82*, 1059–1064.

(15) Silver nitrate, however, in nitromethane solution reacts with $HF-BF_3$ or $BF_3$ to give nitronium tetrafluoroborate and silver tetrafluoroborate.

and 5 mmol (0.85 g) of silver nitrate were mixed with 35 mL of dry acetonitrile. Into this solution was added 4.5 mL of saturated boron trifluoride/acetonitrile solution under a dry nitrogen atmosphere. The reaction mixture was vigorously stirred, and the temperature was kept constant at 25 °C during the reaction. The reaction time was generally 5 h (10 h, for halobenzenes). The reaction solution was then quenched with ice–water, extracted with ether, washed with 5% sodium bicarbonate solution, dried over magnesium sulfate, concentrated, and analyzed by gas–liquid chromatography.

**Analytical Procedure.** The analyses of all products were carried out by gas–liquid chromatography with a Varian Associates Model 3700 gas chromatograph equipped with a hydrogen flame ionization detector and with a 25 m × 0.25 mm i.d. OV-101 glass capillary column with helium as a carrier gas. Peak areas were measured with a Varian CDS III electronic integrator. The results of competitive nitrations are the average of three independent reactions. The average deviation of the substrate selectivities was less than 1.0, and that of isomer distribution was ±1.096.

**Procedure for Nitration of *p*-Xylene.** *p*-Xylene (10.6 g, 0.1 mol) and silver nitrate (1.7 g, 0.01 mol) were mixed with 50 mL of dry acetonitrile. Into this solution was added 5 mL of boron trifluoride/acetonitrile solution. The reaction mixture was vigorously stirred, and the temperature was kept constant at 25 °C during the reaction. After an 18-h reaction time, the reaction solution was quenched with ice–water, extracted with ether, washed with 5% of sodium bicarbonate solution, dried over magnesium sulfate, concentrated, and distilled under reduced pressure; yield 1.39 g (91.4%).

**Mononitration of Polymethylbenzenes.** Equimolar amounts of polymethylbenzenes and silver nitrate were mixed with a sufficient amount of acetonitrile to give a clear solution. Into this solution was added 4 mL of boron trifluoride/acetonitrile solution at 0 °C. The resulting mixture was then kept at 25 °C for 8 h. After the usual workup, mononitrated products were obtained which were further purified by recrystallization (ethanol or ethanol/petroleum ether) and identified by physical and spectral as well as gas chromatographic characteristics.

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**Registry No.** Benzene, 71-43-2; toluene, 108-88-3; ethylbenzene, 100-41-4; isopropylbenzene, 98-82-8; *n*-propylbenzene, 103-65-1; *tert*-butylbenzene, 98-06-6; *o*-xylene, 95-47-6; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; 1,2,3-trimethylbenzene, 526-73-8; 1,2,4-trimethylbenzene, 95-63-6; 1,3,5-trimethylbenzene, 108-67-8; 1,2,3,4-tetramethylbenzene, 488-23-3; 1,2,4,5-tetramethylbenzene, 95-93-2; anisole, 100-66-3; fluorobenzene, 462-06-6; chlorobenzene, 108-90-7; bromobenzene, 108-86-1; iodobenzene, 591-50-4; 1,2,3,4,5-pentamethylbenzene, 700-12-9; 1,2,3,5-tetramethylbenzene, 527-53-7; silver nitrate, 7761-88-8; acetonitrile, 75-05-8; $BF_3$, 7637-07-2.

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# Reactivity of Carbon Acids toward 4,6-Dinitrobenzofuroxan. Studies of Keto–Enol Equilibria and Diastereoisomerism in Carbon-Bonded Anionic σ Complexes

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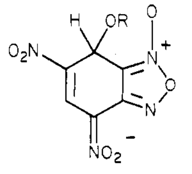
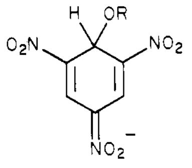
4,6-Dinitrobenzofuroxan (DNBF) reacts with monoketones and β-diketones in dimethyl sulfoxide solution to give carbon-bonded σ adducts. As shown by NMR, the reactions occur in the absence of any added base, emphasizing the highly electrophilic character of this heterocycle. With monoketones only ketonic adducts are formed, while with β-diketones both enolic and/or ketonic σ complexes are observed. The presence of two chiral centers in the DNBF–cyclopentanone adduct enabled the first characterization of two diastereomeric σ complexes. The structure of both kinetically and thermodynamically favored diastereomers are tentatively assigned on the basis of the geometry of the transition states leading to them. It is also shown that enolic σ adducts are formed from the reaction of 1,3,5-trinitrobenzene with β-diketones in the presence of base.

4,6-Dinitrobenzofuroxan is a much stronger electrophile than polynitro aromatic compounds like trinitrobenzene (TNB), 1,3,6,8-tetranitronaphthalene (TNN), and 1,2,3,5-tetranitrobenzene (TTNB). Thus, it reacts very easily with water or methanol in aqueous or methanolic solution, in the absence of any added hydroxide or methoxide ion, to give the σ adducts 1.[1] Such a reaction does not occur, even to a small extent, in the formation of hydroxyl or methoxyl adducts 2–4 from TNB, TNN, and TTNB. These are the most electrophilic benzenes known to date.[2-6] This remarkable behavior of 4,6-dinitro-



1a, R = H
b, R = $CH_3$



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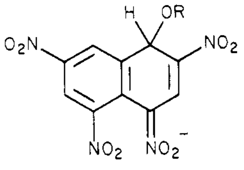

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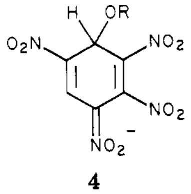

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[1] Terrier, F.; Millot, F.; Norris, W. P. *J. Am. Chem. Soc.* 1976, *98*, 5883.