Substituent Effects of Positive Poles in Aromatic Substitution. IV.[1a] The Effects of Sulfonium and Selenonium Poles on the Orientation and Rate of Nitration[1b]

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The nitration of $Ph(CH_2)_nZ(CH_3)_2^+$ (where $n = 0$, 1, or 2 and Z = S or Se) was investigated. The rate of nitration increased, the rate of para substitution increased, and the percentage of meta substitution decreased as the positive pole was removed further from the ring and also when a sulfonium salt was compared with a corresponding selenonium salt. Relative rates were determined. Evidence of a π(d-p) interaction of the sulfonium and selenonium poles was obtained. No evidence of a π(p-p) interaction was observed.

The relative importance of resonance, inductive, and field effects of various positive poles in aromatic substitution has been reconsidered in the light of recent discoveries. The trimethylammonium group, which cannot have resonance interaction, was found to interact with the aromatic nucleus by way of the field effect rather than the inductive effect.[2] A π(p-p) resonance interaction was found to be the most influential effect of the oxonium pole which directs almost completely para in nitrations.[3] The positive poles of phosphorus, arsenic, and antimony exhibit a considerable π(d-p) overlap.[4] In the case of sulfonium and selenonium salts, a relatively strong $-I$ effect (field and/or inductive effect) should operate as it does in the previously mentioned groups. However, sulfonium and selenonium salts can have π(p-p) and π(d-p) overlap unlike the positive poles of phosphorus, arsenic, and antimony which can only have π(d-p) overlap and oxonium salts which can only have π(p-p) overlap. In an attempt to gain some insight into the relative importance of the effects in electrophilic aromatic substitution, the rates of nitration and orientation of $PhZ(CH_3)_2^+$, $PhCH_2Z(CH_3)_2^+$, and $PhCH_2CH_2Z(CH_3)_2^+$ (where Z = S or Se) were studied.

Orientation.—Nitration of dimethylsulfonium and dimethylselenonium salts was first investigated by Baker and Moffitt.[5] More recent investigation indicated that the nitration of dimethylphenylsulfonium methyl sulfate (**1**) and dimethylphenylselenonium methyl sulfate (**2**) in concentrated sulfuric acid resulted in small amounts of para and ortho substitution in addition to the major product resulting from meta substitution.[6] The nitration of dimethylbenzylsulfonium picrate (**3**) and dimethylbenzylselenonium picrate (**4**) was investigated to include isomer distribution of all monosubstituted products. In addition to this, 2-phenylethyldimethylsulfonium picrate (**5**) and 2-phenylethyldimethylselenonium picrate (**6**) were nitrated.

Analysis of the reaction mixtures resulting from the nitration of **3**, **4**, **5**, and **6** was accomplished by making the reaction mixture basic with sodium carbonate, adding an excess of potassium permanganate, heating for a limited period of time, acidifying, and extracting the nitrobenzoic acids with ether. The acids were converted to the methyl esters with diazomethane and then analyzed gas chromatographically. A known mixture of *o*-, *m*-, and *p*-nitrobenzyldimethylsulfonium salts was treated in a manner identical with the nitration procedure and analysis. Good agreement of actual and theoretical ratios of isomers was obtained provided that the time of permanganate reflux was not more than 15 min (see Experimental Section, Table V). No evidence of starting material, disubstitution, or rearrangement of isomers was obtained. In the nitration of **3** a yield of 94% of the nitrated products was calculated using gas chromatographic techniques indicating that the nitrations proceeded in good yield. Quantitative analysis of the nitration products of **5** and **6** could not be accomplished.

The distribution of isomers, given in Table I, follows the expected results. That is, the amount of meta substitution decreases and para substitution increases as the positive pole is removed further from the ring as is the case for **1** and **3** and also **2** and **4**.[2] Ortho substitution also increases as the positive pole is removed further.

TABLE I

ISOMER DISTRIBUTION OBTAINED IN NITRATION OF AROMATICS HAVING POSITIVE POLES

Compd no.	Aromatic	Ortho, %	Meta, %	Para, %
	$PhN(CH_3)_3NO_3$[a,b]		89	11
	$PhOPh_2BF_4$[a,c]			100
1	$PhS(CH_3)_2SO_4CH_3$[a,d]	3.6	90.4	6.0
2	$PhSe(CH_3)_2SO_4CH_3$[a]	2.6	91.3	6.1
	$PhCH_2N(CH_3)_3$ picrate[a,e]		88	10
3	$PhCH_2S(CH_3)_2$ picrate[a]	16.0	39.1	45.0
4	$PhCH_2Se(CH_3)_2$ picrate[a]	18.8	11.9	69.1
3	$PhCH_2S(CH_3)_2$ picrate[f]	13.4	38.0	48.6
4	$PhCH_2Se(CH_3)_2$ picrate[f]	12.5	18.0	69.5
7	$PhCH_2S(CH_3)_2ClO_4$[a]	16.6	38.8	44.6

[a] Nitrations were carried out in concentrated H_2SO_4 and concentrated HNO_3. [b] J. H. Ridd and J. H. Utley, *Proc. Chem. Soc.*, 24 (1964). [c] Reference 3. [d] Each value is an average of three nitrations. The value for each nitration is an average of five gas chromatographs. All values range from ±0.1 to ±0.6. [e] R. F. Goss, W. Hanhart, and C. K. Ingold, *J. Chem. Soc.*, 250 (1927). [f] Nitrations were carried out in fuming HNO_3.

It was found that there was essentially no difference in isomer distribution whether a picrate or a perchlorate salt was used as is indicated by the nitration of **3** and **7**. Also, very little difference in isomer distribution was

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[1] (a) For part III, see H. M. Gilow, R. B. Camp, Jr., and E. C. Clifton, *J. Org. Chem.*, **33**, 230 (1968). (b) A preliminary report on part of this work has been given at the 25th Southwest Regional Meeting of the American Chemical Society, Tulsa, Okla., 1969, p 93. (c) H. M. G. and W. C. V. wish to thank the National Science Foundation College Science Improvement Program for support. (d) National Science Foundation Undergraduate Research Participant.

[2] T. A. Modro and J. H. Ridd, *J. Chem. Soc. B*, 528 (1968).

[3] N. N. Nesmayanov, T. P. Tolstaya, L. S. Isaeva, and A. V. Grid, *Dokl. Akad. Nauk SSSR*, **133**, 602 (1960).

[4] A. Gastaminza, T. A. Modro, J. H. Ridd, and J. H. P. Utley, *J. Chem. Soc. B*, 534 (1968).

[5] J. W. Baker and W. G. Moffitt, *J. Chem. Soc.*, 1722 (1930).

[6] H. M. Gilow and G. L. Walker, *J. Org. Chem.*, **32**, 2580 (1967).

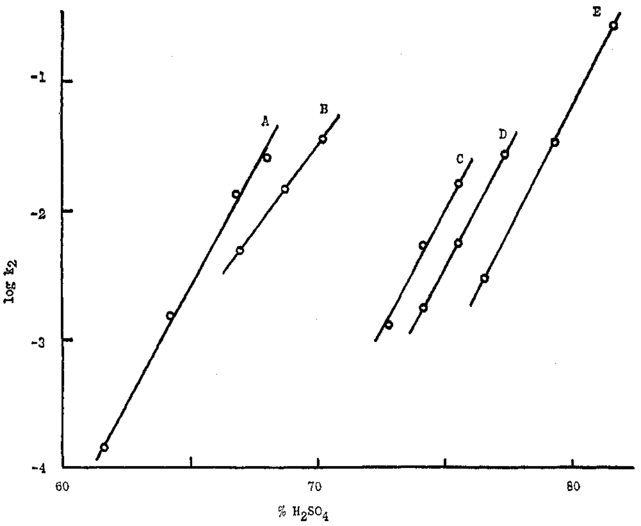

Figure 1.—Values of log k_2 *vs.* concentration of sulfuric acid: A, PhH [N. C. Deno and R. Stein, *J. Amer. Chem. Soc.*, **78**, 578 (1956)]; B, $PhCH_2CH_2S(CH_3)_2^+$ (**9**); C, $PhCH_2Se(CH_3)_2^+$ (**8**); D, $PhCH_2S(CH_3)_2^+$ (**7**); E, $PhCH_2N(CH_3)_3^+$ (ref 2).

found when concentrated sulfuric and concentrated nitric acid or fuming nitric acid was used.

Kinetics.—Equal molar concentrations of the sulfonium or selenonium salts and potassium nitrate were dissolved in a known concentration of sulfuric acid and the rate was determined. The nitration rate, which followed second-order kinetics, could be determined by following the change in concentration of nitric acid electrometrically and the organic substrate spectrophotometrically.[2] The methyl sulfate salts of the dimethylphenylsulfonium and dimethylphenylselenonium cations, **1** and **2**, and the perchlorate salts of **7**, **8**, **9**, and **10** were used in the kinetic studies so that the organic substrate would not interfere with the analysis. Second-order kinetics were followed at various concentrations of sulfuric acid for all of the substrates as is indicated in Table II.

The concentration of sulfuric acid and log k are plotted in Figure 1. The straight lines obtained for **7** and **8** have similar slopes as was obtained for benzene and some substrates with positive nitrogen poles. This permits the calculation of relative reactivities at a definite acidity as given in the last column of Table II. The relative reactivities of **1** and **2** are calculated from the fact that the nitration rates of phenyltrimethylammonium nitrate, **1** and **2**, are known at the same concentration of sulfuric acid. The plot obtained for **9** and **10** did not have a similar slope and hence the relative reactivity was not determined.

Since the rate of nitration of the phenyltrimethylammonium ion relative to that of benzene is known,[7] the data on orientation of nitration (Table I) and the relative rates of nitration (Table II) permit the calculation of partial rate factors given in Table III.

Table II

Rate Coefficients for Nitration in Aqueous Sulfuric Acid at 25°

Compd no.	Aromatic	H_2SO_4, %	10^2k_2 (l. mol^{-1} sec^{-1})	Relative reactivity
1	$PhS(CH_3)_2SO_4CH_3$	98.1	0.113[a]	1
2	$PhSe(CH_3)_2SO_4CH_3$	98.1	2.56	22.7
	$PhN(CH_3)_3NO_3$	98.1	0.94[b]	8.32
7	$PhCH_2S(CH_3)_2ClO_4$	77.3	2.69	1.69 × 10^5
7	$PhCH_2S(CH_3)_2ClO_4$	75.5	0.558	
7	$PhCH_2S(CH_3)_2ClO_4$	74.1	0.176	
8	$PhCH_2Se(CH_3)_2ClO_4$	75.5	1.62	2.46 × 10^5
8	$PhCH_2Se(CH_3)_2ClO_4$	74.1	0.515	
8	$PhCH_2Se(CH_3)_2ClO_4$	72.7	0.132	
	$PhCH_2N(CH_3)_3NO_3$	74.5	0.0560[c]	1.95 × 10^4
9	$PhCH_2CH_2S(CH_3)_2ClO_4$	70.1	3.44	
9	$PhCH_2CH_2S(CH_3)ClO_4$	68.7	1.44	
9	$PhCH_2CH_2S(CH_3)_2ClO_4$	67.0	0.488	
10	$PhCH_2CH_2Se(CH_3)_2ClO_4$	70.1	3.52	
10	$PhCH_2CH_2Se(CH_3)_2ClO_4$	68.7	1.45	
10	$PhCH_2CH_2Se(CH_3)_2ClO_4$	67.0	0.503	
	$PhCH_2CH_2N(CH_3)_3NO_3$	68.3	0.823[c]	5.50 × 10^7

[a] The rate coefficient was determined by following the change in concentration of nitric acid. A value of 0.120 was obtained for $PhS(CH_3)_2^+$ when the rate was followed spectrophotometrically. [b] Estimated from the rate determined in 98.7% sulfuric acid[4] assuming that the rate would change with the concentration of sulfuric acid as determined by R. J. Gillespie and D. G. Norton [*J. Chem. Soc.*, 971 (1953)]. [c] Reference 4.

Discussion

From the relative reactivities it is clear that the dimethylsulfonium pole is a more strongly deactivating group than is the dimethylselenonium pole and that the further removed the pole is from the ring the less deactivating it becomes.[2] These results are to be expected but were not completely clarified from orientation data alone. For example, **1** and **2** have significantly different rates of nitration but form similar ratios of ortho, meta, and para nitro derivatives.

The ammonium pole is known to have such a strong $-I$ effect that meta and para substitution result.[7,8] The trimethylphenylammonium ion is 8.32 times as reactive as the dimethylphenylsulfonium ion but results in more para and less ortho substitution. If the deactivating effect of the dimethylphenylsulfonium ion were only due to a stronger $-I$ effect, considerable para and little or no ortho substitution would be expected. Since little para and some ortho substitution was observed, a $-M$ effect [π(d–p) overlap] must be important in electrophilic aromatic nitration involving the sulfonium ion. The nitro group as well as the positive poles involving phosphorus, arsenic, and antimony have been classified as $-I$ $-M$ substituents.[4] π(d–p) overlap of the sulfonium group has been established[9–13] but little has been done concerning the importance of π(d–p) overlap in aromatic substitution. It is not surprising that π(d–p) overlap, as well as the $-I$ effect, of the sulfonium group is important in electrophilic aromatic substitution.

π(p–p) overlap would result in a more reactive system and increased amounts of ortho and para substitution. The fact that the dimethylsulfonium pole deactivates the aromatic nucleus considerably and directs primarily meta suggests that π(p–p) overlap does not occur or is unimportant as compared with π(d–p) overlap.

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(8) M. Brickman and J. H. Ridd, *ibid.*, 6845 (1965).

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(10) R. W. Taft and J. W. Rakshys, Jr., *ibid.*, **87**, 4387 (1965).

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TABLE III

PARTIAL RATE FACTORS FOR NITRATION AT 25°

Compd no.	Compd	10^8 relative rate, PhH = 1	$10^8 f_o$	$10^8 f_m$	$10^8 f_p$
1	$PhS(CH_3)_2^+$	0.407	0.0440	1.10	0.147
2	$PhSe(CH_3)_2^+$	9.22	0.719	25.3	3.37
	$PhN(CH_3)_3^+$	3.39[a]		9.05[b]	2.24
7	$PhCH_2S(CH_3)_2^+$	80,000	38,400	93,800	210,000
8	$PhCH_2Se(CH_3)_2^+$	100,000	56,400	35,000	415,000
	$PhCH_2N(CH_3)_3^+$	7950[a]		20,300[b]	3980

[a] Reference 2. [b] Reference 7.

The dimethylselenonium pole is not as deactivating since the larger and less electronegative selenium would not be expected to be as good an electron withdrawer.[12] Since **2** is 22.7 times as reactive as is **1** but yields essentially the same ratio of isomers, it appears that the selenonium groups also has a π(d–p) overlap. The fact that f_m for **2** is almost three times as large as for the trimethylammonium ion but f_p is only 1.5 times as large also indicates that π(d–p) overlap is deactivating the para position more than the meta position.

Gastamiza, Modro, Ridd, and Utley[4] have pointed out that, in the cases where the $-M$ effect is important, ortho substitution may also be important suggesting that the $-M$ effect operates much more strongly on the para than on the ortho position. This is somewhat surprising since the strong $-I$ effect of positive poles strongly hinders ortho substitution. The f_o of **1** and **2** are appreciable, giving support to this approach.

When comparing the relative reactivities of the benzyl series, it is interesting to note that **7** is more reactive than is the trimethylbenzylammonium ion. It is known that the dimethylsulfonium group has a stronger $-I$ effect than the trimethylammonium group (σ_m of 1.00[8] and 0.88,[14] respectively). This suggests that **7** should be less reactive than the trimethylbenzylammonium ion; however, the opposite is true. The reactivity of **7** must be affected more by the hyperconjugative effect than is the trimethylbenzylammonium ion. The hyperconjugative effect apparently becomes more important for the sulfonium ion because the benzyl hydrogens of **7** are more acidic than the benzyl hydrogens of the ammonium ion.[15] The stronger acidity is related to the stronger electron-withdrawing effect of the sulfonium group and also the fact that the resulting ylide is stabilized by overlap with the d orbitals of sulfur.[16,17] The fact that f_o and f_p for **7** are relatively large and f_p of the trimethylbenzylammonium ion is relatively small (f_o = 0) also indicates that the ortho/para-directing hyperconjugative effect of **7** is important.

The overall effect of substituent groups is related to the phenyl proton nmr chemical shift. Spiesecke and Schneider[18] have found a relation between Hammett σ values and the chemical shift of para hydrogens. Figure 2 indicates the relationship of the log relative rate of nitration to the proton chemical shift. Since Hammett's values and relative rates are related, it is not surprising that the chemical shifts of sulfonium and selenonium salts are also related to the log relative rate of nitration.

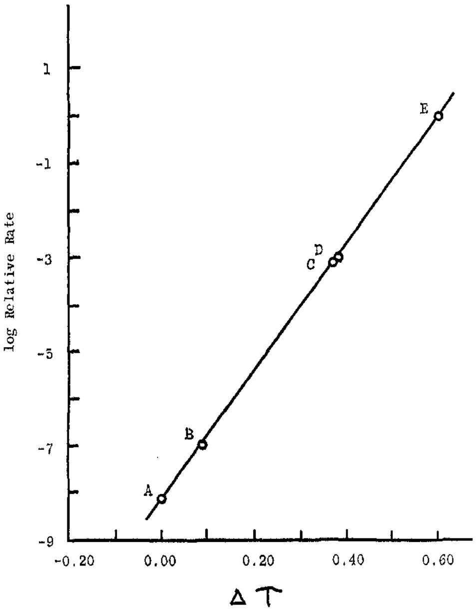

Figure 2.—The relation of the log relative rate of nitration (PhH = 1) and chemical shift difference ($\Delta\tau$) of phenyl hydrogens measured in relation to chemical shift of phenyl hydrogens of **1**: A, $PhS(CH_3)_2^+$ (**1**); B, $PhSe(CH_3)_2^+$ (**2**); C, $PhCH_2S(CH_3)_2^+$ (**7**); D, $PhCH_2Se(CH_3)_2^+$ (**8**); E, PhH.

Experimental Section

Proton nmr spectra were obtained on a Varian HA-60 spectrometer; chemical shifts are reported relative to TMS as an internal standard in CF_3CO_2H. Gas chromatographic analyses were performed on an F & M Model 700 chromatograph using a 3 ft × 1/8 in. column with 2.5% Bentone 34 and 2.5% silicone 200 on 60–80 mesh Chromosorb W DMCA/W. Ultraviolet spectra were obtained on a Beckman Model DB spectrometer. Microanalyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn. All melting points were determined using a Thomas-Hoover capillary melting-point apparatus. Melting points are uncorrected.

Materials.—Dimethylphenylsulfonium methyl sulfate (**1**) and dimethylphenylselenonium methyl sulfate (**2**) were prepared as described previously.[6] Dimethylbenzylsulfonium picrate (**3**) and dimethylbenzylselenonium picrate (**4**) were prepared using the method of Baker and Moffitt.[5] Picrate **3** had mp 133–134° (reported mp 134°). Picrate **4** had mp 117–118° (reported mp 118°). Perchlorates **7** and **8** were also prepared using the procedure of Baker and Moffitt except that a saturated solution of aqueous sodium perchlorate was added to the bromide salts rather than sodium picrate. After three crystallizations from 95% ethanol, a 51% yield of sulfonium salt **7** was obtained, mp 105–105.5°. *Anal.* Calcd for $C_9H_{13}ClO_4S$: C, 42.77; H, 5.18. Found: C, 42.93; H, 5.26.

After two crystallizations from 95% ethanol, a 51% yield of selenonium salt **8** was obtained, mp 91–92°. *Anal.* Calcd for $C_9H_{13}ClO_4Se$: C, 36.08; H, 4.37. Found: C, 36.27; H, 4.35.

The concentrated sulfuric acid used to carry out nitrations was reagent grade and meets ACS specifications (sp gr 1.84, 95.5–96.5%), and the concentrated nitric acid used was also reagent grade and meets ACS specifications (sp gr 1.42, 70–71%). The

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(15) W. v. E. Doering and A. K. Hoffman, *ibid.*, **77**, 521 (1955).

(16) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 71.

(17) See ref 11, p 158.

(18) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).

TABLE IV

PROTON NMR SPECTRA OF SULFONIUM AND SELENONIUM SALTS[a]

Compd no.	Compd	Phenyl protons	Methyl protons	Benzyl protons	β-Phenylethyl protons
1	$PhS(CH_3)_2^+$	2.13 (m, 5 H)	6.68 (s, 6 H)		
2	$PhSe(CH_3)_2^+$	2.22 (s, 5 H)	6.82 (s, 6 H)		
7	$PhCH_2S(CH_3)_2^+$	2.50 (s, 5 H)	7.17 (3, 6 H)	5.39 (s, 2 H)	
8	$PhCH_2Se(CH_3)_2^+$	2.51 (s, 5 H)	7.34 (s, 6 H)	5.37 (s, 2 H)	
9	$PhCH_2CH_2S(CH_3)_2^+$	2.59 (s, 5 H)	7.16 (s, 6 H)	6.67 (m,[b] 2 H)	6.28 (m,[b] 2 H)
10	$PhCH_2CH_2Se(CH_3)_2^+$	2.60 (s, 5 H)	7.40 (s, 6 H)	6.88 (m,[b] 2 H)	6.27 (m,[b] 2 H)

[a] Chemical shifts are given in τ units. The letters m and s denote multiplet and singlet, respectively. [b] An A_2B_2 pattern with a chemical shift difference of about 24 Hz.

fuming nitric acid used was 90% fuming, analytical reagent (Mallinckrodt). Solutions of sulfuric acid required as reaction media for kinetic runs were obtained by diluting concentrated sulfuric acid or adding 20% fuming sulfuric acid, analytical reagent (Mallinckrodt), and were standardized by titration of a known weight with aqueous sodium hydroxide.

2-Phenylethyldimethylsulfonium Perchlorate (9) and 2-Phenylethyldimethylsulfonium Picrate (5).—2-Phenylethyl bromide (Aldrich Chemical Co.) was added dropwise to a refluxing solution of sodium methyl thiolate similar to the procedure of Fehnel and Carmack.[19] The methyl 2-phenylethyl sulfide obtained {14.2 g, 0.039 mol, bp 78–79° (1.3 mm), $n^{25}\text{D}$ 1.5530 [reported bp 111° (12 mm), $n^{24-25}\text{D}$ 1.5494[20] and bp 111° (12 mm)[21]]} was added to 13.2 g (0.093 mol) of iodomethane and stirred overnight at room temperature. The crude solid was broken up under acetone, washed twice with acetone, and dissolved in 25 ml of water. A saturated solution of sodium perchlorate or sodium picrate was added until no more precipitate formed. After two crystallizations from 95% ethanol, the pure perchlorate **9** was obtained (15.4 g, 62% yield), mp 86–87°. *Anal.* Calcd for $C_{10}H_{15}ClO_4S$: C, 45.02; H, 5.67. Found: C, 45.01; H, 5.85.

After two crystallizations from 95% ethanol, the pure picrate **5** was obtained (20.1 g, 55% yield), mp 102–103°. *Anal.* Calcd for $C_{16}H_{17}N_3O_7S$: C, 48.60; H, 4.34. Found: C, 48.67; H, 4.55.

2-Phenylethyldimethylselenonium Perchlorate (10) and 2-Phenylethyldimethylselenonium Picrate (6).—2-Phenylethyl bromide (37.0 g, 0.20 mol) was slowly added to dimethyl selenide[22] (15.4 g, 0.14 mol) and stirred on a magnetic stirrer for about 1 month in a tightly stoppered flask. The mixture was filtered and the precipitate was thoroughly and rapidly washed with acetone and dissolved in 20 ml of water, and a saturated aqueous solution of sodium perchlorate or sodium picrate was added until no more precipitate formed. The precipitate was isolated by filtration and then crystallized twice from 95% ethanol. The perchlorate **10** was obtained in a 12% yield (5.4 g), mp 72–73° (Table IV). *Anal.* Calcd for $C_{10}H_{15}ClO_4Se$: C, 38.29; H, 4.82. Found: C, 38.13; H, 4.82.

The picrate **6** was obtained in an 11% yield (6.3 g), mp 112–113°. *Anal.* Calcd for $C_{16}H_{17}N_3O_7S$: C, 48.60; H, 4.34. Found: C, 48.76; H, 4.55.

***o*-, *m*-, and *p*-Nitrobenzylimethylsulfonium Perchlorate (11, 12, and 13).**—Perchlorates **11**, **12**, and **13** were prepared according to the procedure of Moffitt and Baker[5] except that a saturated solution of sodium perchlorate was added to an aqueous solution of the corresponding sulfonium bromides. The *o*-nitro perchlorate **11** was isolated in an 80% yield, mp 104–105°. *Anal.* Calcd for $C_9H_{12}O_6NS$: C, 36.05; H, 4.04. Found: C, 36.05; H, 4.09.

The *m*-nitro perchlorate **12** was isolated in a 71% yield, mp 122–124°. Found: C, 35.84; H, 4.14.

The *p*-nitro perchlorate **13** was isolated in an 85% yield, mp 155–156°. Found: C, 36.55; H, 3.95.

Nitration and Analysis of Reaction Mixture.—Nitration of **1** and **2** has been previously described.[6] Picrates **3**, **4**, **5**, **6**, and perchlorate **7** were nitrated by adding 1 g of the salt to a mixture of 3 ml of concentrated sulfuric acid and 2 ml of concentrated nitric acid cooled to ice bath temperature and stirred for 15 min. The mixture was then poured on 25 g of crushed ice and made basic with solid Na_2CO_3. A saturated solution of $KMnO_4$ (200 ml) was added to the mixture, heated to reflux with stirring, and then methanol was added dropwise to destroy excess $KMnO_4$. (If reflux is continued for 15 min or longer, correct results will not be obtained.) Manganese dioxide was removed by suction filtration; the filtrate was acidified with dilute sulfuric acid and extracted with three 100-ml portions of ether. An excess of an ether solution of diazomethane (prepared from Diazald, Aldrich Chemical Co.) was added to the ether extracts and dried over anhydrous Na_2SO_4 and the ether was evaporated on a rotary evaporator. The residue was dissolved in 3 ml of chloroform and the mixture of methyl nitrobenzoates was analyzed gas chromatographically. The results are given in Table I.

A known mixture of *o*-, *m*-, and *p*-nitrobenzyldimethylsulfonium perchlorate (**11**, **12**, and **13**) was treated in a manner identical with the nitration procedure described. The results in Table V help to verify that the results obtained from gas chromatographic analysis is an accurate analysis of the reaction products. It was assumed that this analysis was also accurate for the other systems studied.

TABLE V

GAS CHROMATOGRAPHIC ANALYSIS OF A KNOWN MIXTURE OF *o*-, *m*-, AND *p*-NITROBENZYLDIMETHYLSULFONIUM PERCHLORATE

	Ortho, %	Meta, %	Para, %
Calcd	34.22	34.67	31.10
Anal.[a]	34.3	34.1	31.7

[a] Each value is an average of five gas chromatographic analyses.

Each individual nitro perchlorate **11**, **12**, and **13** was treated in a manner identical with the nitration procedure described. Only the corresponding methyl *o*-, *m*-, and *p*-nitrobenzoate was observed gas chromatographically. This indicated that there were no rearrangements occurring during the reaction or work-up.

From gas chromatographic techniques it was determined that for the nitration of picrate **3** 94% of the theoretically possible products could be accounted for. It was assumed that the other nitrations studied also gave good yields of monosubstituted products and that gas chromatographic analysis can account for more than 90% of the theoretically possible monosubstituted products. No disubstitution was observed.

Picrates **3** and **4** were also nitrated with fuming nitric acid at −8° for 1 hr. The reaction mixture was analyzed in a manner identical with the above description. Results are given in Table I.

Kinetics.—The nitrations of **1**, **7**, **8**, **9**, and **10** were started by mixing equal volumes of a sulfuric acid solution of the aromatic and KNO_3, of the same concentration, at 25.0°. Aliquot portions were withdrawn at suitable times and quenched in water, and the uv spectrum was examined. When the nitration of benzyl-

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[20] W. H. Saunders, Jr., and R. A. Williams, *ibid.*, **79**, 3712 (1957).

[21] J. von Braun, W. Teuffert, and K. Weissbach, *Justus Liebigs Ann. Chem.*, **472**, 121 (1929).

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TABLE VI

NITRATION OF $PhCH_2CH_2Se(CH_3)_2ClO_4$ IN 68.7% SULFURIC ACID AT 25.0° [a]

Time, sec	0	900	1800	2700	3600	4800	6120	7200
OD (270 mμ)	0.042	0.073	0.100	0.123	0.147	0.170	0.197	0.208
$10^{-2} \times$ eq 1	0.053	0.094	0.132	0.164	0.196	0.228	0.264	0.279
k_2 l. mol^{-1} sec^{-1}		0.0138	0.0142	0.0142	0.0147	0.0145	0.0150	0.0142

[a] Initial concentration of selenonium salt and potassium nitrate = 5.96×10^{-3} *M*. Rate of nitration of **1** and **2** was also determined by analyzing the reaction mixture, at known time intervals, for nitric acid [W. D. Treadwell and H. Vontabel, *Helv. Chim. Acta*, **20**, 573 (1937)]. Reaction rates determined are given in Table II.

dimethylsulfonium perchlorate (**7**) was complete, the extinction coefficient was 8657 at 260 mμ. At 260 mμ *o*-, *m*-, and *p*-benzyldimethylsulfonium perchlorate (**11**, **12**, and **13**) had extinction coefficients of 5510, 7685, and 10,699, respectively. Assuming the ratio of isomers is the same as given in Table I, the calculated extinction coefficient for the reaction mixture is 8693 which is in good agreement with the actual value. Extinction coefficients for the other nitro isomers formed from the other aromatics were not determined, but it was assumed that the other isomers behaved similarly. There is no reason to believe that the side reactions are important since all of the extinction coefficients of the completely nitrated products were similar. The concentration of nitro compounds in the reaction mixture was determined by the method of Modro and Ridd[2] using the equation

$$x = Y\text{D} - \epsilon_1 a/\epsilon_2 - \epsilon_1$$

where x is the combined concentration of nitrated compounds, Y is the dilution factor during quenching, D is the experimental optical density, ϵ_1 and a are the extinction coefficient of the starting material and concentration of starting material, and ϵ_2 is the extinction coefficient corresponding to a complete reaction. The value of ϵ_1, ϵ_2, and the wavelengths used for following the nitration of the sulfonium and selenonium salts were as follows: **1**, $\epsilon_1 = 783$, $\epsilon_2 = 5696$ at 256 mμ; **7**, $\epsilon_1 = 272$, $\epsilon_2 = 8657$ at 260 mμ; **8**, $\epsilon_1 = 329$, $\epsilon_2 = 9880$ at 268 mμ; **9**, $\epsilon_1 = 63$, $\epsilon_2 = 7028$ at 266 mμ; **10**, $\epsilon_1 = 47$, $\epsilon_2 = 7383$ at 270 mμ. All of the aromatics gave good agreement with the second-order kinetic equation. A typical run is shown in Table VI.

Registry No.—**1**, 6203-16-3; **2**, 13118-29-1; **3**, 29005-91-2; **4**, 29032-26-6; **5**, 29005-92-3; **6**, 29032-27-7; **7**, 18624-67-4; **8**, 29032-28-8; **9**, 29005-94-5; **10**, 29032-29-9; **11**, 29005-95-6; **12**, 29005-96-7; **13**, 29005-97-8.

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Intermediates in Nucleophilic Aromatic Substitution. X.[1,2] Kinetic and Proton Magnetic Resonance Investigations of the Interaction of Nucleophiles with 1,3,6,8-Tetranitronaphthalene

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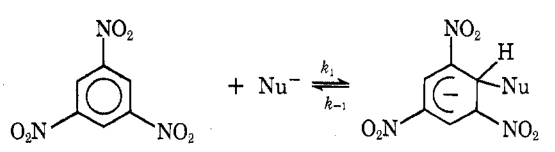
Equilibrium constants for the formation of complexes between 1,3,6,8-tetranitronaphthalene (**4**) and hydroxide and sulfite ions in water and between **4** and methoxide ions in methanol have been determined to be (1.1 ± 0.05)10^4, (1.8 ± 0.1)10^4, and *ca.* 10^4 l. mol^{-1}, respectively. The attainment of the equilibrium for the formation of the hydroxyl adduct of **4** (**5a**) has been followed kinetically in aqueous $Na_2B_4O_7$ buffers. The obtained data afforded rate constants for the formation (k_1) and for the decomposition (k_{-1}) of **5a**. Both k_1 and k_{-1} increase linearly with increasing buffer concentration. Solvent isotope effects of $k_1^{OH^-}/k_1^{OD^-} = 0.505$ and $k_{-1}^{OH^-}/k_{-1}^{OH^-} = 1.7$ have been determined for **5a**. Pmr investigations of the methoxyl and hydroxyl adducts of **4** have established that nucleophilic attack and rehybridization occur at C-4.

The interaction of 1,3,5-trinitrobenzene (**1**) with hydroxide,[4-6] sulfite,[6-8] and sulfide[7,8] ions in aqueous solutions as well as with alkoxide ions in alcohols[9-11] have been shown to involve the formation of Meisenheimer, or σ, complexes. Quantitative data for the equilibria



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and rate constants for these processes have become available recently.[4-11] The equilibrium constants for the formation of the corresponding complexes formed by the interaction of hydroxide ions with 1,2,3,5- (**2**) and 1,2,4,5-tetranitrobenzene (**3**)[12] afforded a comparison of the stabilities of the tri- and tetranitro-substituted cyclohexadienylide ions. Although kinetic

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