(44), 257 (22), 255 (19), 195 (100), 177 (96), 175 (65), 135 (33); mol wt calcd ($C_{21}H_{30}{}^{81}BrNO_3{}^{80}Se$) 505.0554, found 505.0483.

Preparation of *dl*-3β-Bromo-8-epicaparrapi Oxide (15) from 23. Selenide **23** (87 mg, 0.174 mmol) in 3 mL of THF was added to a solution of $NaIO_4$ (45 mg, 0.208 mmol) in 3 mL of 7:3 absolute MeOH/H_2O and stirred at room temperature for 20 h. Et_2O and saturated $NaHCO_3$ were added, the Et_2O layer was washed with brine, dried ($MgSO_4$), and concentrated to give **15** (47 mg, 0.156 mmol, 90%, >95% pure by NMR).

Preparation of *dl*-3β-Bromo-8-caparrapi Oxide (25) from 24. By a procedure analogous to that above, selenide **24** (250 mg, 0.497 mmol) was converted into **25** (139 mg, 0.462 mmol, 93%), which was purified by preparative TLC on silica gel (2 × 200 × 200 mm, 19:1 hexanes/EtOAc) to give pure **25** (116 mg, 0.388 mmol, 78%) as a colorless oil: IR (neat) 3060, 2950, 2860, 1640, 1460, 1390, 1375. 1145, 1110, 1075, 990, 915, 870, 840, 775, 690 cm^{-1}; NMR ($CDCl_3$) δ 0.89, 1.01, 1.26, 1.31 (4 s, 4 CH_3), 1.3–2.3 (m, 9 H), 3.91 (m, ABX, 1 H), 4.87 (dd, J = 11, 2 Hz, 1 H), 5.07 (dd, J = 18, 2 Hz, 1 H), 5.83 (dd, J = 11, 18 Hz, 1 H); MS (EI) m/e (%) 287 (4), 285 (4), 275 (17), 273 (17), 257 (8), 255 (9), 175 (38), 135 (42), 43 (100); exact mass ($M^+ - CH_3$) calcd ($C_{14}H_{22}{}^{79}BrO$) 285.0853, found 285.0871; MS (CI, CH_4) 303, 301 ($M + H^+$).

Acknowledgment. This research was supported by funds provided by the Research Corporation, a DuPont Young Faculty Award, an Institutional Research Grant from the American Cancer Society, and the Graduate School, University of Minnesota. The NMR instrument was purchased through NSF departmental instrumentation grant number CHE 76-05167.

Registry No. 1, 71041-54-8; 2, 71041-55-9; 3, 71041-56-0; 4, 71041-57-1; 6, 71075-17-7; 7, 71041-58-2; 8, 64532-88-3; 9, 19432-10-1; (*E*)-10a, 67858-88-2; (*Z*)-10a, 71041-59-3; 10b, 29665-88-1; 10c, 71041-60-6; 10d, 71041-61-7; 10e, 71041-62-8; 10f, 2211-29-2; *cis*-11a, 71041-63-9; *trans*-11a, 71041-64-0; 11b, 71041-65-1; 11b′, 71041-66-2; 11c, 71041-67-3; 11d, 71041-68-4; 11d′, 71041-69-5; 11e, 71041-70-8; 11e′, 71041-71-9; *cis*-12a, 71041-72-0; *trans*-12a, 71041-73-1; 12b, 71041-74-2; 12b′, 71041-75-3; 12d, 71041-76-4; 12d′, 71041-77-5; 12e, 71041-78-6; 12e′, 71041-79-7; *cis*-13a, 71041-80-0; *trans*-13a, 71041-81-1; 13b, 71041-82-2; 13b′, 71041-83-3; 13c, 71041-84-4; 13d, 71041-85-5; 13d′, 71041-86-6; 13e, 71041-87-7; 13e′, 71041-88-8; 14b, 71041-89-9; 14b′, 71041-90-2; 14c, 71041-91-3; 15, 71075-18-8; 17, 71041-92-4; 18, 71041-93-5; 19, 71041-94-6; 20, 71050-11-8; 21, 71041-95-7; 22, 71041-96-8; 23, 71041-97-9; 24, 71075-19-9; 25, 71075-20-2; homogeranic acid, 459-85-8; mercuric trifluoroacetate, 13257-51-7; geranyl acetic acid, 5579-63-5; (*E*)-geranylacetone, 3796-70-1; trimethylsilyl cyanide, 7677-24-9; TsCl, 98-59-9; *o*-$NO_2PhSeCN$, 51694-22-5.

Mercury Salt Catalyzed Nitration of Benzene Derivatives

Leon M. Stock* and Terry L. Wright

Department of Chemistry, University of Chicago, Chicago, Illinois 60637

Received May 8, 1979

The isomer distributions and product yields have been determined for the mercuric acetate catalyzed nitration of 1,2- and 1,3-dimethylbenzenes, 1,1′-biphenyl, (1,1-dimethylethyl)benzene, the halobenzenes, and methoxybenzene. In most instances, the mercury salt catalyzed reaction exerts a strong influence on the reaction rate and on the product distribution. The isomer distributions are effectively controlled in the reactions of the hydrocarbons. Moreover, the side-chain substitution and ipso reaction products are suppressed in the catalyzed nitration of 1,2-dimethylbenzene. The halobenzenes undergo mercury(II)-catalyzed nitration, but the reactions are slow. The nitration of the mercurated methoxybenzenes produces 15% 2- and 85% 4-nitromethoxybenzene in 90% yield. However, the catalytic reaction has not been successfully accomplished. All the experimental results are in accord with the view that the mercuration reaction is the rate- and product-determining process in this nitration reaction.

Mercuration is the rate-determining and product-determining step in the mercuric acetate catalyzed nitration of methylbenzene[1-3] (eq 1). The subsequent nitroso-

$$C_6H_5CH_3 + Hg(OAc)_2 \rightarrow CH_3C_6H_4Hg(OAc) + HOAc \quad (1)$$

demercuration and oxidation reactions occur rapidly[3] (eq 2 and 3). Thus, the isomer distribution obtained in the

$$CH_3C_6H_4HgOAc + NO^+ \rightarrow CH_3C_6H_4NO + HgOAc^+ \quad (2)$$

$$CH_3C_6H_4NO + HNO_3 \rightarrow CH_3C_6H_4NO_2 + HNO_2 \quad (3)$$

catalyzed nitration of methylbenzene reflects the isomer distribution obtained in the initial mercuration reaction. Inasmuch as mercuration and uncatalyzed nitration yield different product distributions, the mercury acetate catalyzed nitration provides a method for the control of the isomer distribution. We have examined the merit of this approach by the study of the isomer distributions for the catalyzed nitration of eight other benzene derivatives.

Results and Discussion

The xylenes, (1,1-dimethylethyl)benzene, 1,1′-biphenyl, the halobenzenes, and methoxybenzene were examined in the course of this work. The results for mercuration, uncatalyzed nitration, and catalyzed nitration are summarized in Table I.

The mercuric acetate catalyzed nitration of 1,2-dimethylbenzene proceeds smoothly to give the isomeric products in 75% yield in 2 h. The isomer distribution obtained in the catalyzed reaction is very similar to the isomer distribution obtained in the mercuration reaction and significantly different from the isomer distribution obtained in the nitration reaction under comparable conditions. More importantly, the array of byproducts, including aldehydes, esters, and benzylic nitration products

(1) T. Osawa, T. Yoshida, and K. Namba, *Kogyo Kayaku*, **27**, 162 (1966).
(2) H. Komoto, F. Hayano, T. Takami, and S. Yamato, *J. Polym. Sci., Polym. Chem. Ed.*, **9**, 2983 (1971).
(3) L. M. Stock and T. L. Wright, *J. Org. Chem.*, **42**, 2875 (1977).
(4) H. C. Brown and C. W. McGary, Jr., *J. Am. Chem. Soc.*, **77**, 2306 (1955).
(5) H. C. Brown and M. Dubeck, *J. Am. Chem. Soc.*, **81**, 5608 (1959).
(6) H. C. Brown and G. Goldman, *J. Am. Chem. Soc.*, **84**, 1650 (1962).
(7) L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, **1**, 35 (1963).

0022-3263/79/1944-3467$01.00/0

Table I. Isomer Distributions for the Mercuration and Nitration of Benzene Derivatives[a]

process and reaction conditions	isomer distribution, % 2	3	4	5	yield, %
Methylbenzene					
mercuration, $Hg(OAc)_2$, HOAc, 70 °C	32	15	53		
nitration, 90% HNO_3, HOAc, 80 °C[b]	58	3	39		7
nitration, 90% HNO_3, $Hg(OAc)_2$, HOAc, 80 °C[b,c]	31	15	55		65
1,2-Dimethylbenzene					
mercuration, $Hg(OAc)_2$, HOAc, 50 °C		25	75		
nitration, 90% HNO_3, HOAc, 80 °C[b]		38	62		7
nitration, 90% HNO_3, $Hg(OAc)_2$, HOAc, 80 °C[b,c]		23	77		75
1,3-Dimethylbenzene					
mercuration, $Hg(OAc)_2$, HOAc, 50 °C	11		87	2	
nitration, 90% HNO_3, HOAc, 80 °C[b]	9		91	0	18
nitration, 90% HNO_3, $Hg(OAc)_2$, HOAc, 80 °C[b,c]	17		82	1	93
1,1′-Biphenyl					
mercuration, $Hg(OAc)_2$, HOAc, 70 °C	5	23	72		
nitration, $AcONO_2$, Ac_2O, 0 °C[d]	69		31		
nitration, 90% HNO_3, $Hg(OAc)_2$, HOAc, 80 °C[b,c]	23	10	66		81
(1,1-Dimethylethyl)benzene					
mercuration, $Hg(OAc)_2$, HOAc, 70 °C	0	33	67		
nitration, 90% HNO_3, HOAc, 80 °C[b]	13	8	79		6
nitration, 90% HNO_3, $Hg(OAc)_2$, HOAc, 80 °C[b,c]	5	18	77		10
nitration, NO_2, 90% HNO_3, $Hg(OAc)_2$, HOAc, 80 °C[b,c]	1	29	70		79
Bromobenzene					
mercuration, $Hg(OAc)_2$, HOAc, 90 °C	28	26	46		
nitration, HNO_3, CH_3NO_2, 25 °C[d]	37	1	62		
nitration, NO_2, 90% HNO_3, $Hg(OAc)_2$, HOAc, 80 °C[b,c,e]	30	9	61		12
Chlorobenzene					
mercuration, $Hg(OAc)_2$, HOAc, 90 °C	30	22	48		
nitration, HNO_3, CH_3NO_2, 25 °C[d]	30	1	69		
nitration, NO_2, 90% HNO_3, $Hg(OAc)_2$, 80 °C[b,c,f]	29	9	62		20
Fluorobenzene					
mercuration, $Hg(OAc)_2$, HOAc, 90 °C	34	7	59		
nitration, HNO_3, CH_3NO_2, 25 °C[d]	15		85		
nitration, NO_2, 90% HNO_3, $Hg(OAc)_2$, 80 °C[b,c,g]	36	2	61		35
Methoxybenzene					
mercuration, $Hg(OAc)_2$, HOAc, 25 °C	14		86		
nitration, HNO_3, HOAc-Ac_2O, 25 °C[b]	71		29		15
nitration, HNO_3, $Hg(OAc)_2$, HOAc-Ac_2O, 25 °C[b,h]	56		44		76
nitration, $Hg(OAc)_2$, HNO_3, HOAc-Ac_2O, 25 °C[i]	15		85		75

[a] The mercuration data are assembled from the work of H. C. Brown and his students.[4-6] [b] This study. [c] The mole ratio in the catalyzed reactions is 1.0:1.0:0.016:5.0 for the aromatic compound-90% nitric acid-mercuric acetate-acetic acid. The reaction time is 2 h. [d] These representative data have been abstracted from ref 7. [e] Reaction time 22 h. [f] Reaction time 12 h. [g] Reaction time 8 h. [h] The reaction conditions are described in the Results and Discussion section. [i] A two-step process, the reaction conditions are described in the Results and Discussion section.

which result from ipso substitution and side-chain reactions and which are formed in significant quantity in the direct nitration, are completely suppressed in the catalytic process. The catalyzed reaction should, therefore, be valuable for the nitration of aromatic compounds such as indan and tetralin which are especially susceptible to ipso substitution under the conditions of the conventional nitration reaction.

1,3-Dimethylbenzene and 1,1′-biphenyl were examined as representative reactive hydrocarbons. The results presented in Table I indicate that the xylene and 1,1′-biphenyl undergo the catalyzed reaction readily and that the isomer distributions observed in these reactions are in accord with the results for the mercuration of the hydrocarbons. Although the metal-initiated reaction has only a minor influence on the product distribution for the xylene, a twofold increase in the quantity of the para isomer is realized for 1,1′-biphenyl.

(1,1-Dimethylethyl)benzene is less reactive than methylbenzene. The catalyzed nitration proceeds to only 10% completion under the conditions suitable for the more reactive molecules. However, the addition of nitrogen dioxide to the reaction mixture has an important influence. In the presence of this substance, the catalyzed reaction proceeds to almost 80% completion in 2 h. Presumably, the nitrogen oxides formed in the course of the reaction are in equilibrium with the nitrosodemercuration reagent. For the less reactive molecules, it is appparently necessary to increase the initial concentration of this demercuration reagent to accelerate the propagation reactions. In any event, quite effective control of the isomer distribution is achieved.

Extension of this reaction to the much less reactive halobenzenes provided mixed results. The catalyzed reactions of bromobenzene and chlorobenzene are slow even in the presence of nitrogen dioxide. Only 10–20% of the desired products are obtained in 12–24-h reaction intervals. Moreover, the finding that only about 9% rather than about 20% of the 3 isomer was produced suggests that the product distribution was not completely dictated by the mercuration. On the other hand, the reaction of fluorobenzene proceeds much more readily. The isomer dis-

Table II. Product Distributions for the Nitration of Methoxybenzene in Acetic Acid-Acetic Anhydride at 25 °C[a]

Hg-$(OAc)_2$	reagents, mmol HNO_3	other	isomer distribution, % 2	4	yield, %
0.3	2.4		61	39	27[b]
0.3	4.0		56	44	58[b]
0.3		N_2O_4, 4.1	66	34	54[b]
0.3	2.4	N_2O_4, 1.6	56	44	64
1.0	4.4		47	53	68[b]
2.0	4.7		44	56	81[b]
1.0	2.9	$HClO_4$, 2.7	59	41	30[b,c]

[a] The reactions were carried out by the addition of methoxybenzene (2 mmol) in acetic acid-acetic anhydride (15 g) to the other reagents in acetic acid-acetic anhydride (15 g). The addition required 3-5 h, and 17 h was allowed for the completion of the reaction. [b] Purple condensation products were observed. [c] Heterogeneous reaction.

tribution is substantially enriched in the 2 isomer, as expected for the catalyzed reaction. The observations for the halobenzenes suggest that more vigorous conditions are necessary for the effective mercury salt catalyzed nitration of deactivated benzenes.

The difficulties in the nitration of methoxybenzene and its derivatives are well-known. Higher molecular weight, often brightly colored compounds are formed in the reaction in mixed acid, aqueous nitric acid, or acetic acid.[8-10] It was not surprising, therefore, that the mercuric acetate catalyzed nitration reaction could not be effectively accomplished in acetic acid at 25 or 80 °C. Indeed, one of the prominent byproducts, the purple dianisyloxidoammonium salt,[10] is formed at an accelerated rate in the presence of the mercury catalyst. Many of the problems associated with the nitration of methoxybenzene can be avoided by the use of acetic anhydride as the solvent. In this medium the side reactions are suppressed, and the nitration products are obtained exclusively.[8,11,12] Accordingly, we studied the mercuric acetate catalyzed nitration of methoxybenzene in acetic acid containing 5 wt % acetic anhydride at 25 °C. Under these conditions, the uncatalyzed nitration yields 71% 2- and 29% 4-nitromethoxybenzene. Under the same conditions, the uncatalyzed or the perchloric acid catalyzed mercuration of methoxybenzene yields 14% (2-methoxyphenol)- and 86% (4-methoxyphenyl)(acetato-*O*)mercury.

The catalyzed reaction was conducted by the slow addition of a solution of the aromatic compound to a vigorously stirred solution of the other reagents. A procedure of this kind is essential to avoid the condensation reactions of the organomercury intermediates and nitrosomethoxybenzene. The results are summarized in Table II.

The reaction solutions became purple during these experiments. The results obtained in the first four experiments reveal that mercuric acetate exerts only a minor influence on the isomer distribution and that nitric acid and dinitrogen tetraoxide are equally effective. These results suggest that the isomer distribution results from concurrent nitration and mercuric acetate catalyzed nitration. To test this point, we increased the concentration of mercuric acetate to accelerate the catalytic process. The quantity of 2-nitromethoxybenzene decreased to 44% in the presence of a stoichiometric quantity of mercuric acetate. Thus, the catalytic reaction is not dominant. Experiments with perchloric acid, a known catalyst for mercuration,[4-6] were conducted. Unfortunately, the reaction mixtures rapidly darkened, and dimercurated products separated from solution during the addition of the aromatic compound. The isomer distribution presented for this reaction in Table II is not representative of the monomercuration reaction.

Our observations reveal that mercuration and nitration occur concurrently and that other factors, such as dimercuration in the presence of perchloric acid and condensation reactions in the presence of excess methoxybenzene, negate an effective mercury-catalyzed nitration. These difficulties were completely circumvented in a two-step process. In the first step, excess methoxybenzene was treated with mercuric acetate in acetic acid at ambient temperature to yield the monomercuration products. These solid products were obtained in 75–80% yield. In the second step, the mercury compounds were treated with an equivalent quantity of nitric acid in acetic acid–acetic anhydride to give 15% 2- and 85% 4-nitromethoxybenzene in 90% yield.

Conclusion

For methoxybenzene, the nitration and mercuration reactions occur competitively, and control of the product distribution has not been realized under catalytic conditions. However, a product mixture rich in the para isomer is readily obtained in a two-step sequence. Although the halobenzenes react slowly, the product distribution for fluorobenzene is quite effectively controlled. For the molecules of intermediate reactivity, 1,1′-biphenyl, the xylenes, and (1,1-dimethylethyl)benzene, the catalyzed nitration reaction proceeds quite smoothly in acetic acid at 80 °C to give an isomer distribution virtually identical with the distribution observed in mercuration. Side-chain derivatives and ipso substitution products are not obtained. For these compounds the catalyzed reaction can be applied advantageously for the attainment of novel isomer distributions and pure products.

Experimental Section

Materials. The starting materials and other reagents used in this work were analyzed reagents or were purified by well-known methods prior to use.

4-Nitrosomethoxybenzene. Known procedures for preparation of this compound involve oxidation reactions which invariably form unwanted 4-nitromethoxybenzene.[14] This problem was circumvented by the preparation of the compound from (acetato-*O*)(4-methoxyphenyl)mercury. A solution of nitrosonium tetrafluoroborate (0.80 g, 6.8 mmol) in sulfolane (20 mL) was added to a solution of (acetato-*O*)(4-methoxyphenyl)mercury (2.00 g, 5 mmol) in sulfolane (20 mL). The solution was stirred at room temperature for 20 min. The mixture was poured into water (50 mL) and extracted with ether (40 mL). The bright green ether layer was washed with water (3 × 50 mL) to remove the sulfolane. The ether solution was dried with sodium sulfate and concentrated

(8) P. H. Griffiths, W. A. Walkey, and H. B. Watson, *J. Chem. Soc.*, 631 (1934).
(9) (a) R. M. Schramm and F. H. Westheimer, *J. Am. Chem. Soc.*, 70, 1782 (1948); (b) C. A. Bunton, G. J. Minkoff, and R. I. Reed, *J. Chem. Soc.*, 1416 (1947).
(10) C. A. Bunton, E. D. Hughes, C. K. Ingold, D. I. H. Jacobs, M. H. Jones, G. J. Minkoff, and R. I. Reed, *J. Chem. Soc.*, 2628 (1950).
(11) J. G. Hoggett, R. B. Moodie, J. R. Penton, and K. Schofield, "Nitration and Aromatic Reactivity", Cambridge University Press, Cambridge, England, 1971. p 95.
(12) A. R. Butler and J. B. Hendry, *J. Chem. Soc. B*, 102 (1971).
(13) P. Kovacic and J. J. Hiller, Jr., *J. Org. Chem.*, 30, 1581 (1965).
(14) (a) R. E. Lutz and M. R. Lytton, *J. Org. Chem.*, 2, 68 (1937); (b) R. J. Sundberg and C.-C. Lang, *ibid.*, 36, 300 (1971).

in vacuo. The green residue was sublimed at 60 °C (1 mm) to yield 4-nitrosomethoxybenzene (0.35 g, 48%) which was free of 4-nitromethoxybenzene.

Analytical Procedures. The product distributions were established by gas chromatography using either 5% QF-1 or 4% OV-101 on Chromosorb G. The relationship between peak areas and composition was established by analysis of known mixtures of the reaction products containing an internal standard. These experiments showed that the isomer distributions could be established within ±1%. The concentrations of the 3-halonitrobenzenes were established by NMR as described subsequently.

Nitration of (1,1-Dimethylethyl)benzene. The hydrocarbon (2.91 g, 21.7 mmol) was dissolved in acetic acid (6 mL) and heated to 80 °C. Nitric acid (d = 1.5 g cm^{-3}, 1.1 mL) was added dropwise, and the reaction was maintained at 80 °C for 2 h. The reaction solution was poured into water, and the products were extracted into ether. A concentrated aliquot of the dried solution was analyzed by gas chromatography.

The catalyzed reaction was carried out in the same way except that mercuric acetate (0.32 mmol) was added to the solution of the aromatic compound in acetic acid.

The catalyzed reaction was also carried out in the presence of nitrogen dioxide. A solution of mercuric acetate (0.50 g, 1.51 mmol), (1,1-dimethylethyl)benzene (14.6 g, 109 mmol), and acetic acid (30 mL) was heated to 80 °C. Prior to the addition of nitric acid (d = 1.5 g cm^{-3}, 5.5 mL) nitrogen dioxide was passed into the reaction mixture for several minutes. Nitric acid was then added in the usual manner, and the reaction was allowed to proceed for 2 h.

Nitration of 1,2-Dimethylbenzene. The uncatalyzed reaction was carried out under the conditions used for (1,1-dimethylethyl)benzene. Gas chromatography revealed a complex mixture of products. All the compounds were collected and identified by comparison of their spectroscopic properties with those of authentic samples. The following compounds were obtained in the quantity indicated in a 2-h reaction: 2-methylbenzaldehyde (3%), (2-methylphenyl)methyl acetate (0.5%), 3-nitro-1,2-dimethylbenzene (2.7%), 4-nitro-1,2-dimethylbenzene (4.8%), 3,4-dimethylphenyl acetate (1%), and 1-methyl-2-(nitromethyl)benzene (2%).

The reaction was carried out with mercuric acetate as described for (1,1-dimethylethyl)benzene. Under these conditions 3- and 4-nitro-1,2-dimethylbenzenes were formed in 75% yield.

Nitration of 1,1′-Biphenyl and 1,3-Dimethylbenzene. The reactions were carried out as described for the corresponding reactions of (1,1-dimethylethyl)benzene. No byproducts were obtained. The results are summarized in Table I.

Nitration of the Halobenzenes. The reactions were carried out as described for the corresponding reactions of (1,1-dimethylethyl)benzene except that the reaction times were extended to 8, 12, and 22 h, respectively, for fluoro-, chloro-, and bromobenzene. A Dewar condenser was used to retain the nitrogen oxides during these long reaction intervals.

The para and meta isomers were not readily resolved by gas chromatography. Consequently, the ortho/(para + meta) ratio was established by chromatography. The (para + meta) fraction was collected and analyzed by NMR methods at 270 MHz. Known mixtures were studied to establish the reliability of the procedure. The results are presented in Table I.

Nitration of Methoxybenzene. Various control experiments were performed. It was established that 4-nitrosomethoxybenzene was quantitatively converted to 4-nitromethoxybenzene under the reaction conditions and that (acetato-O)(4-methoxyphenyl)mercury was also converted dominantly to 4-nitromethoxybenzene under these conditions.

A solution of nitric acid (0.296 g, 4.23 mmol) and acetic anhydride (1.0 g) in acetic acid (15.3 g) was prepared. A solution of methoxybenzene (0.206 g, 1.91 mmol) and acetic anhydride (0.30 g) in acetic acid (15.2 g) was added through a calibrated dropping funnel at the rate of 1 drop/10 s to the rapidly stirred solution. The reaction solution was light yellow when the addition was complete (2.5 h). The solution was poured into water, and the reaction products were isolated in the customary way and analyzed by gas chromatography. The results are summarized in Table I.

The mercuric acetate catalyzed reactions were performed in the same way except that mercuric acetate was added to the reaction mixture. The addition of methoxybenzene was carried out over 5 h, and the mixture was stirred for 17 h before the product distribution was determined. The quantities of the reagents and the results are summarized in Table II.

A solution of mercuric acetate (2.0 g, 6.3 mmol) in acetic acid (25 mL) was added to a stirred solution of methoxybenzene (13.8 g, 128 mmol) in acetic acid (25 mL). After 22 h the solvent was removed in vacuo. The dry residue was divided into two portions.

One portion was suspended in chloroform and treated with a solution of bromine in chloroform until the red color persisted. The solution was allowed to stand for 0.5 h. The chloroform was washed with aqueous sodium bisulfite and dried over sodium sulfate. Analysis of the solution revealed that the monobromides and dibromides were formed in 88 and 5%, respectively. The isomer distribution was 14% 2- and 86% 4-bromomethoxybenzene.

The second portion of the mercurated products was dissolved in acetic acid (15 mL). This solution was added to a solution of nitric acid (0.38 g, 4.0 mmol) and acetic anhydride (1.0 g) in acetic acid (15 mL) over a 5-h period. The reaction turned purple. After 17 h the reaction mixture was poured into water and analyzed. The reaction gave 15% 2- and 85% 4-nitromethoxybenzene in 90% yield.

The results were confirmed in replicate experiments.

Acknowledgment is made to the U.S. Army Research Office, Grant ARO DAAG-29-76-6-025, for the support of this work.

Registry No. Methylbenzene, 108-88-3; (acetato-O)(2-methylphenyl)mercury, 2948-49-4; (acetato-O)(3-methylphenyl)mercury, 21450-78-2; (acetato-O)(4-methylphenyl)mercury, 2440-35-9; 1-methyl-2-nitrobenzene, 88-72-2; 1-methyl-3-nitrobenzene, 99-08-1; 1-methyl-4-nitrobenzene, 99-99-0; 1,2-dimethylbenzene, 95-47-6; (acetato-O)(2,3-dimethylphenyl)mercury, 71205-06-6; (acetato-O)(3,4-dimethylphenyl)mercury, 51730-01-9; 1,2-dimethyl-3-nitrobenzene, 83-41-0; 1,2-dimethyl-4-nitrobenzene, 99-51-4; 1,3-dimethylbenzene, 108-38-3; (acetato-O)(2,6-dimethylphenyl)mercury, 21450-80-6; (acetato-O)(2,4-dimethylphenyl)mercury, 51665-02-2; (acetato-O)(3,5-dimethylphenyl)mercury, 57678-20-3; 1,3-dimethyl-2-nitrobenzene, 81-20-9; 2,4-dimethyl-1-nitrobenzene, 89-87-2; 3,5-dimethyl-1-nitrobenzene, 99-12-7; 1,1′-biphenyl, 92-52-4; (acetato-O)(o-biphenylyl)mercury, 71205-07-7; (acetato-O)(m-biphenylyl)mercury, 71205-08-8; (acetato-O)(p-biphenyl)mercury, 71205-09-9; 2-nitro-1,1′-biphenyl, 86-00-0; 3-nitro-1,1′-biphenyl, 2113-58-8; 4-nitro-1,1′-biphenyl, 92-93-3; (1,1-dimethylethyl)benzene, 98-06-6; (acetato-O)(3-*tert*-butylphenyl)mercury, 71205-10-2; (acetato-O)(4-*tert*-butylphenyl)mercury, 71205-11-3; 1-*tert*-butyl-2-nitrobenzene, 1886-57-3; 1-*tert*-butyl-3-nitrobenzene, 23132-52-7; 1-*tert*-butyl-4-nitrobenzene, 3282-56-2; bromobenzene, 108-86-1; (acetato-O)(2-bromophenyl)mercury, 71205-12-4; (acetato-O)(3-bromophenyl)mercury, 71205-13-5; (acetato-O)(4-bromophenyl)-mercury, 57025-72-6; 1-bromo-2-nitrobenzene, 577-19-5; 1-bromo-3-nitrobenzene, 585-79-5; 1-bromo-4-nitrobenzene, 586-78-7; chlorobenzene, 108-90-7; (acetato-O)(2-chlorophenyl)mercury, 71205-14-6; (acetato-O)(3-chlorophenyl)mercury, 71205-15-7; (acetato-O)(4-chlorophenyl)mercury, 21843-82-3; 1-chloro-2-nitrobenzene, 88-73-3; 1-chloro-3-nitrobenzene, 121-73-3; 1-chloro-4-nitrobenzene, 100-00-5; fluorobenzene, 462-06-6; (acetato-O)(2-fluorophenyl)mercury, 71205-16-8; (acetato-O)(3-fluorophenyl)mercury, 24261-93-6; (acetato-O)(4-fluorophenyl)mercury, 351-94-0; 1-fluoro-2-nitrobenzene, 1493-27-2; 1-fluoro-3-nitrobenzene, 402-67-5; 1-fluoro-4-nitrobenzene, 350-46-9; methoxybenzene, 100-66-3; (acetato-O)(2-methoxyphenyl)mercury, 24801-84-1; (acetato-O)(4-methoxyphenyl)mercury, 5780-90-5; 1-methoxy-2-nitrophenylbenzene, 91-23-6; 1-methoxy-4-nitrophenylbenzene, 100-17-4; 4-nitrosomethoxybenzene, 1516-21-8; nitrosonium tetrafluoroborate, 14635-75-7; mercuric acetate, 1600-27-7.