

was refluxed for 20 min, cooled, and decanted from the nickel which was washed with three 10-ml portions of ether. The combined ethereal extracts were dried over magnesium sulfate and concentrated. The oil was then taken up in 2 ml of hexane and chromatographed on alumina (5–10 g, Alcoa F-20) with hexane to remove alcohol and ketone (produced in the metal-ammonia reduction). The eluent was concentrated and analyzed by glpc on a 9-ft 20% Carbowax 20M on firebrick column at 150°.

cis-3,3,5-Trimethylcyclohexyl Ethyl Ether.—*cis*-3,3,5-Trimethylcyclohexanol³¹ (20 g) was converted to its acetate by treatment with acetic anhydride (50 ml) and pyridine (10 g) (4 hr heating on steam bath). The acetate (23 g, 89%) boiled at 72° (3.5 mm), n_D^{20} 1.4392.

Anal. Calcd for C₁₁H₂₀O₂: C, 71.69; H, 10.94. Found: C, 72.07; H, 11.19.

Reduction was carried out by the method of Pettit and co-workers³² starting with 4.92 g of the acetate in 120 ml of boron trifluoride etherate which was added to 2.28 g of LiAlH₄ in 60 ml of ether. Reaction was effected with cooling for 90 min followed by 1-hr reflux. After decomposition with 10% sodium hydroxide the ether layer was concentrated, chromatographed over Alcoa F-20 alumina with hexane and concentrated again to give upon distillation 2.5 g (55%) of *cis*-3,3,5-trimethylcyclohexyl ethyl ether, bp 77–80° (20 mm). Repetition of the chromatography yielded pure material, bp 48–49° (3.5 mm), n_D^{20} 1.4350.

Anal. Calcd for C₁₁H₂₂O: C, 77.58; H, 13.02. Found: C, 77.64; H, 13.05.

trans-3,3,5-Trimethylcyclohexyl ethyl ether was synthesized analogously from the *trans* alcohol.³¹ The acetate, bp 60–60.5° (2 mm), n_D^{20} 1.4399, was obtained in 82% yield.

Anal. Calcd for C₁₁H₂₀O₂: C, 71.69; H, 10.94. Found: C, 72.04; H, 11.15.

The ether was obtained in 68% yield, bp 74–75° (20 mm), n_D^{20} 1.4338.

(31) E. L. Eliel and H. Haubenstock, *J. Org. Chem.*, **26**, 3504 (1961).

(32) G. R. Pettit, U. R. Ghatak, B. Green, T. R. Kasturi, and D. M. Piatak, *ibid.*, **26**, 1685 (1961).

Anal. Calcd for C₁₁H₂₂O: C, 77.58; H, 13.02. Found: C, 77.86; H, 13.40.

trans-4-*t*-Butylcyclohexyl propyl ether was obtained analogously from *trans*-4-*t*-butylcyclohexanol and propionic anhydride, followed by reduction. The ether boiled at 112–114° (10 mm), n_D^{20} 1.4476.

Anal. Calcd for C₁₃H₂₆O: C, 78.72; H, 13.21. Found: C, 79.13; H, 13.20.

trans,trans-4-*t*-Butylcyclohexyloxyethyl Disulfide.—*trans*-4-*t*-Butylcyclohexyloxyethyl mercaptan of 98% stereoisomeric purity (Table IV) (0.95 g, 4.5 mmol) in 8 ml of 5% NaOH solution was treated with 0.5 ml of 30% hydrogen peroxide. Excess peroxide was destroyed with solid sodium metabisulfite and the product was extracted three times with a 20-ml portion of ether. Drying and concentration yielded 0.92 g (97%) white solid, recrystallized from ethanol to give white plates, mp 51.5–52°.

Anal. Calcd for C₂₄H₄₆O₂S₂: C, 66.92; H, 10.77; S, 14.89. Found: C, 67.16; H, 10.76; S, 14.77.

β -Chloroethyl benzyl sulfide was prepared from 40 g (0.25 mol) of β -hydroxyethyl benzyl sulfide³³ and 120 ml of concentrated hydrochloric acid by refluxing (with a gas trap) for 4 hr. The mixture was poured into 200 ml of water, the organic layer separated, and the aqueous layer was twice extracted with 100-ml portions of ether. The combined organic product was washed once with water and once with concentrated aqueous NaCl, dried, and concentrated to give after distillation 33 g (75%) of β -chloroethyl benzyl sulfide, bp 91.5° (0.6 mm), n_D^{20} 1.5682.

Anal. Calcd for C₉H₁₁ClS: C, 57.89; H, 5.93; Cl, 18.99. Found: C, 58.44; H, 6.00; Cl, 18.86.

Registry No.—*cis*-3,3,5-Trimethylcyclohexyl ethyl ether, 24691-15-4; *cis*-3,3,5-trimethylcyclohexanol (acetate), 24691-16-5; *trans*-3,3,5-trimethylcyclohexyl ethyl ether, 24691-17-6; *trans*-3,3,5-trimethylcyclohexanol (acetate), 24691-18-7; *trans*-4-*t*-butylcyclohexyl propyl ether, 24691-19-8; *trans,trans*-4-*t*-butylcyclohexyloxyethyl disulfide, 24691-20-1; β -chloroethyl benzyl sulfide, 4332-51-8.

Aromatic Nitration by Silver Nitrate Impregnated Silicic Acid in the Presence of Carbon Tetrachloride

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Carbon tetrachloride reacts rapidly with excess silver nitrate impregnated silicic acid at room temperature to produce carbon dioxide and a nitrating agent. With carbon tetrachloride in excess, phosgene and the nitrating agent are formed. Aromatic compounds are nitrated by this system under column-chromatographic or batch conditions. A reaction sequence involving trichloromethyl nitrate, phosgene, nitryl chloride, carbonyl nitrate, and dinitrogen pentoxide is proposed.

While chromatographing *trans*-stilbene on AgNO₃-silicic acid, we attempted to elute with carbon tetrachloride. The result was complete destruction of the stilbene with formation of some 4,4'-dinitrostilbene.¹ We have observed nitration of several other aromatic compounds under these conditions, but none of these reactions occurs in the absence of carbon tetrachloride.^{1,2} Carbon tetrachloride is generally considered inert to silver nitrate in homogeneous solution.³ Petrenko-Kritschenko and Opotsky⁴ reported 3% reaction with 0.2 *N* silver nitrate in 95% ethanol at 90° in 12

hr; the products were not examined. We were thus interested to attempt identification of the reactions involved.

Results

Static batch experiments with benzene and anisole are summarized in Table I. The basic experimental results drawn from there and the Experimental Section follow. (1) Neither benzene nor anisole is nitrated by AgNO₃-silicic acid alone (expt 8, 18). Both are nitrated in high yield by AgNO₃-silicic acid in the presence of CCl₄ (expt 16, 17). (2) The nitration reaction involves specifically Ag⁺, NO₃⁻, CCl₄, and the silicic acid surface (expt 6, 8, 9; ref 4). (3) The nitration reaction is independent of illumination and the presence of air (expt 3, 4, 11, 12). (4) Phosgene is formed in quantity. Two independent determinations

(1) J. E. Gordon, *J. Chromatogr.*, **48**, 532 (1970).

(2) E. Wenkert, D. J. Watts, and L. L. Davis [*Chem. Commun.*, 1317 (1969)], have recently reported nitration of phenols by AgNO₃-silicic acid alone. This appears to depend upon the presence of the acidic OH group.

(3) See, *e.g.*, R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley & Sons, Inc., New York, N. Y., 1956, p 136 ff.

(4) P. Petrenko-Kritschenko and V. Opotsky, *Ber.*, **59**, 2131 (1926).

TABLE I
 NITRATION OF BENZENE AND ANISOLE

Expt	C ₆ H ₆ , mmol	C ₆ H ₅ OCH ₃ , mmol	CCl ₄ , mmol	AgNO ₃ , mmol	Solvent ^a	Other conditions	—Reaction time, hr—		Limiting ^b reagent	Yield, mmol of ArNO ₂ /mmol of limiting reagent
							CCl ₄ + AgNO ₃	CCl ₄ + AgNO ₃ + ArH		
1	2.74		c	4.26	CCl ₄		2.8	2.8	AgNO ₃	0.042
2	2.74		c	4.70 ^d	CCl ₄ -C ₆ H ₁₄		2.8	2.8	AgNO ₃	0.060 ± 0.005 ^d
3	2.74		c	4.6	CCl ₄ -C ₆ H ₁₄	Bubbled N ₂	2.8	2.8	AgNO ₃	0.14
4	2.74		c	4.6	CCl ₄ -C ₆ H ₁₄	Bubbled air	2.8	2.8	AgNO ₃	0.14
5	220		c	4.39	CCl ₄ -C ₆ H ₆		3.5	3.5	AgNO ₃	0.0
6	2.74		0	4.72	CHCl ₃		11	11	AgNO ₃	0.0
7	2.74		c	4.71	CCl ₄ -CHCl ₃		22	22	AgNO ₃	0.0
8	c		0	4.49	C ₆ H ₆			24	AgNO ₃	0.0
9	2.74		c	5.92	CCl ₄ -C ₆ H ₁₄	NaNO ₂ , not AgNO ₃	24	24	AgNO ₃	0.0
10	2.74		c	4.70 ^e	CCl ₄ -C ₆ H ₁₄		24	24	AgNO ₃	0.41 ± 0.02 ^e
11	2.74		c	4.79	CCl ₄ -C ₆ H ₁₄		48	48	AgNO ₃	0.48
12	2.74		c	5.04	CCl ₄ -C ₆ H ₁₄	Dark	48	48	AgNO ₃	0.51
13	2.74		c	2.63	CCl ₄ -C ₆ H ₁₄		91	91	AgNO ₃	0.51
14	2.74		c	4.02	CCl ₄ -C ₆ H ₁₄		97	97	AgNO ₃	0.47
15	2.74		c	5.01	CCl ₄ -C ₆ H ₁₄		90	90	AgNO ₃	0.52
16	2.68		c	6.12	CCl ₄ -C ₆ H ₁₄		144	144	C ₆ H ₆	1.01
17		2.25	c	4.68	CCl ₄ -C ₆ H ₁₄		21	21	C ₆ H ₅ OCH ₃	0.71 ^f
18		2.82	0	5.34	C ₆ H ₁₄		70	70	AgNO ₃	0.0
19		9.1	0.975	6.49	C ₆ H ₁₄		1.2	58	CCl ₄	0.38
20		9.1	0.975	5.86	C ₆ H ₁₄		1.0	18	CCl ₄	0.25
21		9.1	0.975	5.83	C ₆ H ₁₄		5.0	18	CCl ₄	0.71
22		9.1	0.975	5.92	C ₆ H ₁₄		10	18	CCl ₄	0.20
23		9.1	0.975	12.8	C ₆ H ₁₄		5.0	18	CCl ₄	1.32 ^g

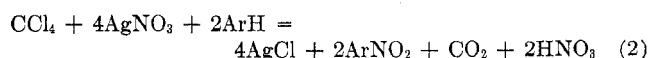
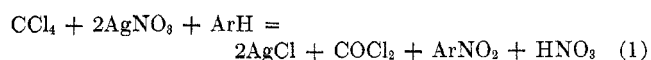
^a Volume ratios of mixed solvents: CCl₄-C₆H₁₄, 1:2; CCl₄-C₆H₆, 1:1; CCl₄-CHCl₃, 1:1. ^b Based on eq 1 or 2. ^c Large excess. ^d Mean of two experiments. ^e Mean of three experiments. ^f Isomer composition: 21% *ortho*, 79% *para*. ^g Isomer composition: 20% *ortho*, 80% *para*.

yielded 0.27 and 0.24 mol COCl₂/mol of AgNO₃ (CCl₄ in excess). Phosgene production is complete in 2 hr. (5) Dinitrogen tetroxide appears in the AgNO₃-silicic acid-CCl₄ reaction mixture after a few hours in the absence, but not in the presence of aromatic substrate. (6) Mass spectrometric observation of the AgNO₃-silicic acid-CCl₄ reaction mixture reveals only phosgene, CCl₄, and traces of CO₂ when CCl₄ is in excess, but, when CCl₄ is in deficiency, CO₂ is present in quantity. (7) No chlorobenzene could be detected in the AgNO₃-silicic acid-CCl₄-C₆H₆ reaction product. (8) With AgNO₃ as the limiting reagent, the ArNO₂ yield levels off after 48 hr (room temperature) at a limiting ArNO₂:AgNO₃ ratio of 0.50 ± 0.02 (expt 2, 10, 11, 13-15). (9) The stoichiometry with respect to CCl₄ could not be accurately determined owing to the slowness of the AgNO₃-CCl₄ reaction when CCl₄ is limiting, so that decomposition of the nitrating agent becomes competitive. Also, inhibition of the AgNO₃-CCl₄ reaction by ArH (see 12 below) was so severe with CCl₄ in deficiency that reasonable yields could be obtained only by allowing the AgNO₃-CCl₄ reaction to proceed for some hours, using a large excess of AgNO₃-silicic acid, then adding excess ArH. The ArNO₂ yield passes through a maximum as the CCl₄-AgNO₃ reaction time increases (expt 20-22), and the maximum ArNO₂:CCl₄ ratio observed is 1.32 (expt 23). (10) The nitrating agent cannot be eluted from AgNO₃-silicic acid with CCl₄. (11) The *ortho/para* ratio in the nitration of anisole is 0.25 with CCl₄ in excess or deficiency (expt 17, 23). (12) Aromatic substrates inhibit the CCl₄-AgNO₃-silicic acid reaction (expt 5, expt 19 vs. 21; see Experimental Section.) (13) Substitution of alumina for silicic acid in expt 11 reduces

nitrobenzene production from 0.48 to 0.02 mol/mol of AgNO₃.

Discussion

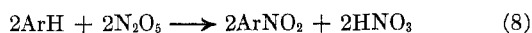
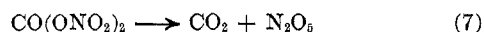
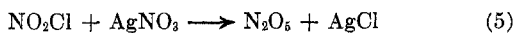
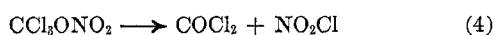
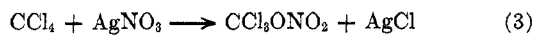
We believe that eq 1 and 2 give the simplest description of these reactions which is capable of rationalizing all of the observations. When the observed nitro-



benzene production in presence of excess CCl₄ (0.50 ± 0.02 mol/mol of AgNO₃) is corrected for the slow nitration of benzene by the nitric acid formed according to eq 1 and 2, the net yield becomes 85-90% of the theoretical yield for these processes. The formation of 0.25 mol COCl₂/mol AgNO₃ implies parallel occurrence of eq 1 and 2, *i.e.*, competition between CCl₄ and COCl₂ for the available AgNO₃ such that some COCl₂ remains when the AgNO₃ is exhausted. When CCl₄ is the limiting reagent, eq 2 should apply alone. The difficulties in establishing the stoichiometry under these conditions have been described. Correcting the maximum ArNO₂:CCl₄ ratio observed (1.32) for nitration by the nitric acid formed according to eq 2 gives a net value of 1.0. Since we know that the nitrating agent is decomposing with time and that side-reaction products are formed in the nitration step, the experimental results require a ArNO₂:CCl₄ stoichiometry >1:1.

The detailed course of reactions 1 and 2 has not been rigorously established. However, both can be ac-

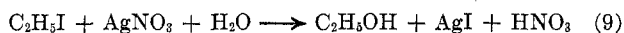
counted for by individual steps which are in accord with our observations and for which reasonable precedents are available. The sum of eq 3–8 is eq 2; eq 1 is the sum



of eq 3–5 and half of eq 8. The trichloromethyl nitrate of eq 3 is not known, but trichloromethyl perchlorate can be prepared from CCl_4 and solid AgClO_4 in the presence of AgCl , and it decomposes to phosgene.⁵ Trichloromethanol is unknown; it decomposes to phosgene and HCl .⁶ Equation 5 is a known reaction.⁷ Acyl chlorides react with AgNO_3 to give acyl nitrates in analogy with eq 6.⁸ The acyl nitrates undergo facile thermal disproportionation to N_2O_5 and carboxylic anhydride in analogy with eq 7.⁸ Dinitrogen pentoxide is known to nitrate benzene instantly in CCl_4 solution at 20°; in nitration by benzoyl nitrate, N_2O_5 is the actual nitrating agent.⁹ Dinitrogen pentoxide also decomposes thermally to NO_2 – N_2O_4 + O_2 in the gas phase and in solution with a half-life of a few hours at room temperature.¹⁰

Anisole is nitrated by N_2O_5 (or by $2\text{ArCOONO}_2 \rightleftharpoons (\text{ArCO})_2\text{O} + \text{N}_2\text{O}_5$) predominantly in the *ortho* position, whereas the CCl_4 – AgNO_3 –silicic acid reagent gives the predominance of *para* nitration characteristic of nitronium ion nitrations.¹¹ However, it has been shown that the second-order nitration by molecular N_2O_5 in CCl_4 is replaced in the presence of HNO_3 by higher order processes catalyzed by HNO_3 and involving solvated nitronium ion as the nitrating agent.¹² There is physical evidence that drying at 120–180° removes all of the adsorbed water from the silicic acid surface,¹³ but treatment of such material with dichlorodimethylsilane produces hydrolysis products of $(\text{CH}_3)_2\text{SiCl}_2$.¹⁴ In view of this and because the dried AgNO_3 –silicic acid samples used in this work were not handled in a strictly anhydrous atmosphere, it is most likely that some hydrolysis of N_2O_5 occurs; the orientation pattern observed is therefore reasonable.

The origin of the surface catalysis of eq 3 is of some interest. This is very likely catalysis by AgCl . The reaction of CCl_4 with solid AgClO_4 requires initiation by a small amount of HCl .⁵ Also, it has recently been shown that the familiar reaction 9 proceeds simulta-



(5) L. Birckenbach and J. Goubeau, *Naturwissenschaften*, **18**, 530 (1930); *Ber.*, **64B**, 218 (1931).

(6) K. Elbs and K. Kratz, *J. Prakt. Chem.*, **55** [2], 502 (1897).

(7) Odet and Vignon, *C. R. Acad. Sci., Paris*, **69** [II], 1142 (1869).

(8) F. Francis, *Ber.*, **39**, 3798 (1906).

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

(10) F. Daniels and E. H. Johnston, *J. Amer. Chem. Soc.*, **43**, 53 (1921); H. Eyring and F. Daniels, *ibid.*, **52**, 1472 (1930).

(11) P. B. D. de la Mare, and J. H. Ridd, "Aromatic Substitution. Nitration, and Halogenation," Butterworth and Co. (Publishers) Ltd., London, 1959, p 51 ff.

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

(13) J. J. Wren, *J. Chromatogr.*, **4**, 173 (1960); G. J. Young, *J. Colloid Sci.*, **13**, 67 (1958).

(14) K. F. Ebert, *Monatsh. Chem.*, **88**, 275 (1957).

neously by homogeneous and heterogeneous paths; AgI is a good surface catalyst and the reaction is auto-catalytic.¹⁵ Inhibition of the CCl_4 – AgNO_3 reaction by benzene is difficult to account for in homogeneous solution because the formation constant for $\text{C}_6\text{H}_6 \cdot \text{Ag}^+$ is small.¹⁶ However, if Ag^+ adsorbed on an initially small amount of AgCl ¹⁷ is the active reagent, this might be susceptible to more complete complexation by C_6H_6 . The comparatively poor performance of AgNO_3 –alumina may stem from a smaller surface area.

We have given elsewhere some examples of nitrations by CCl_4 – AgNO_3 –silicic acid under chromatographic conditions.¹ Should this system ever be used to deliberately nitrate small samples, limitations of solubility in CCl_4 would be encountered with many compounds, since most other solvents except saturated hydrocarbons react with the reagent. We investigated the possibility of nitrating 2,4-dinitrophenol, which is poorly soluble in carbon tetrachloride, by stirring a suspension with CCl_4 – AgNO_3 –silicic acid. This produced a clean reaction mixture and 49% picric acid in 24 hr at room temperature, along with 45% recovered starting material.

Experimental Section

General.—All reactions were conducted at $24 \pm 2^\circ$. Product analyses, except where otherwise stated, were *via* gas chromatography using silicone QF-1 columns (20% on acid-washed Chromosorb W) in a F & M 700 instrument with a thermal conductivity detector. Peak areas from duplicate 20- μl samples were planimetrically compared with those from standard solutions prepared from Fisher Certified Reagent or Eastman White Label materials and chromatographed before and after the unknown. Linearity of detector response was verified over the concentration range employed. Nitrobenzene was chromatographed at 150°, the nitroanisoles at 200°. The analytical precision was ~1%.

Melting points were determined by hot stage microscopy and are uncorrected. Mass spectra were measured on a GEC-AEI MS-12 instrument. Infrared and electronic spectra were recorded on Perkin-Elmer Model 337 and 202 instruments.

Silver Nitrate Impregnated Silicic Acid and Aluminum Oxide.—Mallinckrodt chromatographic silicic acid (6.1% water loss at 150°), 56.1 g, was slurried with 160 ml of methanol and added to a solution of 14.00 g of silver nitrate in 60 ml of 50% aqueous methanol. The resulting slurry was evaporated at 40–55° and 15 Torr in a rotary evaporator to yield a white powder which was lightly ground in a Pyrex mortar. The product was dried to constant weight at 150° just before use, and the resulting samples thus contained 1.24 mmol of AgNO_3/g . Material which was dried to constant weight at 120° possessed the same chemical properties. Impregnated alumina was prepared in the same way, using Merck acid-washed chromatographic alumina and a nominal 15 wt % loading rather than the above 20%; the dried product contained 0.932 mmol of AgNO_3/g .

Observations on CCl_4 – AgNO_3 –Silicic Acid Mixtures.—(a) A 50 mg sample of AgNO_3 –silicic acid was covered with CCl_4 ; after 1 hr it was frozen, evacuated, and allowed to warm until a vapor pressure of *ca.* 10^{-4} Torr resulted. The vapor was then observed mass spectrometrically, using an exciting potential of 70 eV. After subtracting the lines due to CCl_4 , the following peaks remained: *m/e* (relative abundance) 36 (25), 38 (10), 44 (92), 63 (100), 64 (1.2), 65 (36), 98 (9.3), 100 (5.4), 102 (1.1). A similar experiment using CCl_4 adsorbed on an excess of AgNO_3 –silicic acid gave the following spectrum: 30 (2.6), 35 (4.9), 36 (0.5), 37 (1.4), 38 (0.1), 44 (100), 45 (2.4), 46 (1.1), 63 (18),

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(16) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, p 90 ff.

(17) K. Fajans and K. von Beckerath, *Z. Physik. Chem.*, **97**, 47 (1921).

65 (5.0), 69 (0.4), 70 (0.6), 72 (0.5), 98 (0.4), 100 (0.1), 121 (0.6), 131 (0.2).

(b) A tightly stoppered sample of AgNO_3 -silicic acid covered with CCl_4 was allowed to stand for 24 hr. A 1 ml sample of the liquid phase was transferred to a 10-cm path length fused-quartz cell. The uv-visible spectra were recorded using a slit-cell geometry which placed only the vapor above the CCl_4 solution in the light path. The observed spectrum, consisting of ca. 40 narrow lines superimposed on broad maxima centered near 340 and 400 $\text{m}\mu$, was that reported for NO_2 - N_2O_4 .¹⁸

(c) A 3.868-g (4.80 mmol AgNO_3) sample of AgNO_3 -silicic acid was placed in a small chromatographic column arranged to deliver effluent into a solution containing 15 ml of CCl_4 and 1.6 ml of aniline. Flow of carbon tetrachloride through the column was begun, and within 2 min a white precipitate appeared in the magnetically stirred receiver solution. Three fractions were collected using fresh aniline- CCl_4 solutions: effluent volumes in ml (flow times in min) 30 (20), 30 (35), and 65 (110). Each fraction was filtered, and the white solid was washed with water and dried, yielding 230, 34, and 15 mg of carbanilide respectively (total 279 mg, 1.32 mmol, 0.274 mmol COCl_2 /mmol AgNO_3). The combined material was recrystallized (78% recovery) from ethanol, mp 243.5-244°, mmp [with authentic carbanilide (mp 243.5-244°)] 243-243.5°. If the elution is conducted with 10% of benzene in the CCl_4 , very little phosgene is produced.

(d) In a similar experiment benzene replaced the aniline of experiment c. The effluent was stirred for 48 hr; analysis by glpc revealed no nitrobenzene.

(e) A 2.336-g (2.89 mmol AgNO_3) sample of AgNO_3 -silicic acid was covered with CCl_4 in a vessel connected to a vacuum line by way of a small trap cooled in liquid N_2 . Over a period of 2.5 hr, all of the volatile material was slowly distilled into the trap. The trapped material was warmed to $\sim -50^\circ$ and 11 ml of a solution prepared by dissolving 5.07 g of NaOH in 50 ml of water was added. The mixture was allowed to come to room temperature, the phases were equilibrated and separated, and a water wash of the CCl_4 phase was added to the aqueous phase which was then acidified with nitric acid. Gravimetric determination of Cl^- then produced 0.234 g (1.38 mmol) of silver chloride corresponding to 0.69 mmol of COCl_2 or 0.24 mmol of COCl_2 /mmol of AgNO_3 .

Nitration of Benzene (Expt 1-16).—To the freshly dried AgNO_3 -silicic acid (or alumina) sample (weight in Table I) was added 10 ml of CCl_4 -hexane (1:2). After 1-15 min, 250 μl (214 mg, 2.74 mmol) of benzene was injected and the mixture was agitated and allowed to stand for the specified time. It was then transferred to a small chromatography column and eluted with ether to provide one or two (depending on the amount of silicic acid used) 25.0-ml product solutions which were analyzed by gas chromatography.

(18) T. C. Hall, Jr., and F. E. Blacet, *J. Chem. Phys.*, **20**, 1745 (1952).

Nitration of Anisole (Expt 17-23).—Nitration with excess CCl_4 (expt 17) was done as in the preceding paragraph, substituting anisole for benzene. Nitration with CCl_4 as limiting reagent (expt 19-23) was done by adding 10-20 ml of hexane to the dry, 5-10-g AgNO_3 -silicic acid sample, injecting 100 μl (150 mg, 0.975 mmol) of CCl_4 , and stirring magnetically for the specified time (Table I). Anisole (1.0 ml, 990 mg, 9.1 mmol) was injected and the mixture was stirred for 1 hr, then allowed to stand for 17 hr; work-up was as in the preceding paragraph. The *o*- and *p*-nitroanisole peaks in the gas chromatogram were $\sim 75\%$ resolved, and the isomer ratio was calculated by integration in comparison with standard mixtures.

Nitration by HNO_3 -Silicic Acid.—To a slurry of 3.18 g of dry (130-140° overnight) silicic acid in 10 ml of hexane- CCl_4 (2:1) was added 50 μl (73 mg, 1.28 mmol) of white, fuming nitric acid. The mixture was stirred magnetically for 5 min, and 125 μl (107 mg, 1.37 mmol) of benzene was added. The mixture was worked up and analyzed as in the reaction with CCl_4 after 48 (96) hr to give 0.15 (0.17) mmol, 11 (13%), of nitrobenzene.

Application of this procedure to 6.67 g of silicic acid, 16.5 ml of hexane, 73 mg (0.96 mmol) of nitric acid, and 1.0 ml (9.1 mmol) of anisole gave, after 18 hr, 0.29 mmol (31%) of nitroanisoles.

Nitration of 2,4-Dinitrophenol.—A suspension of 500 mg (2.72 mmol) of 2,4-dinitrophenol (mp 112.5-113.5°) in 15 ml of CCl_4 was vigorously stirred with 4.687 g (5.81 mmol AgNO_3) of AgNO_3 -silicic acid for 24 hr. The suspension was filtered and the solid was washed with ether and methanol. The residue from evaporation of the filtrate was dissolved in 25 ml of methylene chloride and extracted with 150 ml of pH 4.4 citrate buffer. The buffer was washed with three 25-ml portions of methylene chloride and the combined organic phases were evaporated to 223 mg (1.21 mmol, 45%) of recovered 2,4-dinitrophenol. The aqueous phase was acidified with 8 ml of sulfuric acid and extracted with four 25-ml portions of methylene chloride which gave on evaporation 306 mg (1.33 mmol, 49%) of picric acid, mp 120-122°, mmp [with authentic material (mp 121-122.5°)] 121-122°; the infrared spectra were identical.

Registry No.—Benzene, 71-43-2; anisole, 100-66-3; silver nitrate, 7761-88-8; carbon tetrachloride, 56-23-5.

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