the preparation of N-(2-nitroisopropyl)-aniline hydrochloride see Fourneau.[6]

2-Butene Product.—2-Chloro-3-nitrobutane: b.p. 45–46° (6 mm.), 8.6 g., n^{25}_{D} 1.4421, d^{25}_{4} 1.1835, MR_D calcd. 30.68, found 31.10; % Cl calcd. 25.59, found 25.47. Derivatives: 2,4-dinitrophenylhydrazone of chemically-reduced product, m.p. 116.5–117°, mixed m.p. with 2,4-dinitrophenylhydrazone of methyl ethyl ketone was 116–117°; benzoyl chloride derivative of catalytically-reduced product, m.p. 72–74°, mixed m.p. with authentic *s*-butylbenzamide 72–73°.

Propene Products.—Propene pseudo-nitrosite: m.p. 135–135.5°, 5 g., % N calcd. 23.72, found 23.58.

1-Nitro-2-chloropropane: b.p. 32–33° (1 mm.), 16.5 g., n^{25}_{D} 1.4388, d^{25}_{4} 1.2338, calcd. MR_D 26.55, mol. wt. 123.5, found, MR_D 26.32; mol. wt. 123.1 (lit.[7] b.p. 172° (749 mm.); d^{15}_{4} 1.2361). Derivatives of 1-nitro-2-chloropropane: N-(2-nitroisopropyl)-aniline hydrochloride, m.p. 139–140°,[6] 2,4-dinitrophenylhydrazone of chemically reduced product, m.p. 142–148°, mixed m.p. with 2,4-dinitrophenylhydrazone of propionaldehyde, m.p. 147–148°. Benzoyl chloride derivative of catalytically reduced product, m.p. 82–83.5°, *n*-propylbenzamide.

Isobutylene Products.—Isobutylene pseudo-nitrosite; m.p. 87–88°, 8.3 g., % N calcd. 21.21, found 19.66 (lit.[8] m.p. 81°).

1-Nitro-2-chloroisobutane: b.p. 35–38° (1 mm.), 6 g., n^{25}_{D} 1.4530 (reported b.p. 35–42° (2 mm.), n^{24}_{D} 1.4530[3d]).

Nitro-*t*-butyl nitrite: m.p. 24.5–25.5°, b.p. 82–83° (1 mm.), 3 g., n^{25}_{D} 1.4599, d^{25}_{4} 1.3022.

Anal. Calcd. for $C_4H_8N_2O_4$: C, 32.43; H, 5.40; N, 18.09; MR_D, 31.91; mol. wt., 148. Found: C, 32.95; H, 5.25; N, 17.35; MR_D, 31.1; mol. wt., 141.1.

The nitrite was converted to isobutyraldehyde (2,4-dinitrophenylhydrazone, m.p. 179–181°) by chemical reduction, with or without prior alkaline treatment. This and the results of the elementary analysis are in accord with the instability ascribed to the nitrite ester function in compounds of this type.[8] Himel[3d] reported only nitro-*t*-butyl chloride as the product of this reaction.

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[6] J. P. Fourneau, *Bull. soc. chim.*, **1**, 603 (1940).

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Nitryl Chloride as a Nitrating Agent[1]

BY CHARLES C. PRICE AND CARLTON A. SEARS

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The ease of preparation of nitryl chloride from nitric acid and chlorosulfonic acid has prompted us to investigate its utility as a nitrating agent for some typical aromatic compounds. The results, summarized in Table I, indicate that its activity as a nitrating agent can be promoted with such acids as hydrogen fluoride, aluminum chloride and boron fluoride, but that its useful application seems to be limited to aromatic substances of intermediate reactivity. Highly reactive aromatics like phenol, anisole, dimethylaniline and naphthalene tend to give oxidative degradation and deactivated aromatics like nitrobenzene, benzoic acid and benzaldehyde are recovered unchanged.

Nitryl Chloride.[2]—Anhydrous nitric acid was prepared by adding 644 g. of fuming sulfuric acid (30% sulfur trioxide content) dropwise, with constant stirring, to 400 g. (5.64 moles) of fuming nitric acid (89% acid content), in a 2-liter three-necked, round-bottomed flask, cooled to 0°, equipped with a dropping funnel, a seal glass stirrer, and attached through a wide bore U-tube to a 500-cc. round-bottomed flask serving as receiver. The receiver was then cooled by a Dry Ice–isopropyl alcohol bath and 370 cc. (5.70 moles) of chlorosulfonic acid (fraction boiling at 149–152° (747 mm.) on redistillation) was added dropwise, with vigorous stirring and continued cooling, over a period of about 12 hours. After all of the chlorosulfonic acid had been introduced the cooling bath was removed from the reaction flask and the mixture stirred for one hour at room temperature; 420 g. (91%) of a dense, pale yellow liquid boiling at −16 to −15° was collected.

TABLE I

REACTION OF NITRYL CHLORIDE WITH VARIOUS AROMATICS

Reactants	Catalyst	Solvent	Product(s)
Benzene	. . .	. . .	Nitrobenzene (27–35%)
Benzene	HF[a]	HF	Nitrobenzene (70%)
Benzene	$AlCl_3$	CS_2	Nitrobenzene (89%)
Toluene	$AlCl_3$	CS_2	*o*-Nitrotoluene (47%) *p*-Nitrotoluene (24%)
p-Bromotoluene	$AlCl_3$	CS_2	2-Nitro-4-bromotoluene (23%) 3-Nitro-4-bromotoluene (16%)
Bromobenzene	$AlCl_3$	CS_2	*p*-Nitrobromobenzene (67%) *o*-Nitrobromobenzene (8%)
m-Dichlorobenzene	$AlCl_3$	CS_2	2,4-Dichloronitrobenzene (31%)
Phenol	$AlCl_3$	CS_2	*p*-Nitrophenol *o*-Nitrophenol (trace of both)
Anisole	$AlCl_3$	CS_2	*o*-Nitrophenol (trace)
Diphenyl ether	$AlCl_3$	CS_2	4-Nitrodiphenyl ether 7% Diphenyl ether 5%
N,N-Dimethylaniline	BF_3	CS_2	Tar
Naphthalene	$AlCl_3$	CS_2	1-Nitronaphthalene 31%
Naphthalene	$AlCl_3$	$C_6H_5NO_2$	1-Nitronaphthalene 26%
Salicylic acid	$AlCl_3$	$C_6H_5NO_2$	Salicylic acid 10% 5-Nitrosalicylic acid 58%
Benzoic acid	$AlCl_3$	CS_2	Benzoic acid (73%)
Benzoic acid	BF_3	CS_2	Benzoic acid (82%)
p-Chlorobenzoic acid	$AlCl_3$	$C_6H_5NO_2$	*p*-Chlorobenzoic acid (92%)
p-Toluic acid	$AlCl_3$	CS_2	*p*-Toluic acid (67%)
Nitrobenzene	$AlCl_3$	CS_2	Nitrobenzene (93%)
Nitrobenzene	BF_3	HF	Nitrobenzene (96%)
p-Nitrotoluene	$AlCl_3$	CS_2	*p*-Nitrotoluene (86%)
Benzaldehyde	$AlCl_3$	CS_2	Benzaldehyde (74%)
Acetophenone	$AlCl_3$	CS_2	Acetophenone (88%)

[a] Benzene (36 g., 0.5 mole) was added to 0.55 mole of nitryl chloride in 250 g. of liquid hydrogen fluoride in a copper beaker.

The Reaction of Benzene with Nitryl Chloride.—Nitryl chloride (0.2 mole) was allowed to distil into 50 cc. of dry benzene slowly at room temperature. The solution became yellow as the inorganic halide was added. After all of the reactant had been added the mixture was heated at reflux for 15 hours, after which the test for escaping inorganic halide was negative. Washing and distillation yielded 8.6 g. (35%) of nitrobenzene.

General Procedure for the Condensation of Nitryl Chloride with an Aromatic Compound.—The reactions were run under anhydrous conditions. The reaction flask was cooled by an ice-bath and a solution of 100 cc. of carbon disulfide and 0.2 mole of the aromatic compound added to the flask. The aluminum chloride (0.25 mole) was then added to this solution with vigorous stirring. Nitryl chloride (0.25 mole) was then allowed to distil into the reaction mixture. After all of the inorganic halide had been added the product was stirred at ice temperature for 1–2 hours, the ice-bath removed, and the reaction stirred at room temperature until inorganic halides were no longer evolved. The product was hydrolyzed by pouring into ice and concentrated hydrochloric acid mixture. The organic layer separated, was washed with water, sodium bicarbonate, again with water, and finally dried. The solvent was re-

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[1] Abstracted from a thesis presented by Carlton A. Sears in partial fulfillment of the requirements for the Ph.D. degree at the University of Notre Dame. This work was presented in part at the 119th National Meeting of the American Chemical Society at Cleveland, Ohio. We are indebted to the Navy Department, Bureau of Ordnance, for a Grant, Contract NOrd 10273, which made this work possible.

[2] K. Dachlauer, German Patent 509,405 (Aug. 30, 1929). We are also indebted to Prof. Harold Shechter, Ohio State University, for some helpful suggestions.

moved by a hot water-bath and the resulting product purified by the conventional means of vacuum distillation, steam distillation or crystallization.

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Some Nuclearly Substituted Catechols and their Acid Dissociation Constants

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In the course of other work, the acid dissociation constants in water of certain nuclearly substituted catechols were required. Such values of the constants[1,2] as appeared in the literature were open to question, so that it was decided to determine them for the entire group. In the preparation of the catechols, difficulties unmentioned by previous authors were encountered, which made it desirable to report some of the synthetic procedures in detail.

The attempt to make 4-nitrocatechol according to Benedikt[3] led, at first, to the isolation of a dinitro derivative, identified *via* its dimethyl ether as 3,4-dinitrocatechol. Reduction in the quantity of nitrosating reagents permitted the desired 4-nitrocatechol to be obtained. Nitration of catechol in ether solution,[4] to produce a mixture of 3- and 4-nitrocatechols, gave evidence of a threshold concentration of reagents, below which no reaction could take place; such a phenomenon has been described by Halberstadt, Hughes and Ingold.[5] After several unsuccessful attempts to isolate 3,4-dihydroxybenzophenone according to the method of Rosenmund and Lohfert,[6] the authors were furnished by Dr. Joseph Corse with a satisfactory modification of that method.[7]

Experimental and Results

3,4-Dinitrocatechol.—A solution of sodium nitrite (16 g., 0.24 mole) and catechol (4.0 g., 0.036 mole) in water (150 ml.) was mixed with sufficient ice to bring the temperature down to 0°. In the course of 3–5 minutes, 75 ml. of 2.5 *M* H_2SO_4 (0.19 mole) was added, along with more ice and with shaking. The solution was then extracted with ether in two portions (150 and 75 ml.). The combined ether extract was twice washed with 100 ml. of water, dried briefly over anhydrous sodium sulfate and evaporated quickly at room temperature under a stream of nitrogen. When the ether had been removed, the oily residue was left under vacuum until it had crystallized; it was then extracted with xylene at 100° and the crystalline product that separated from the cooled xylene solution was collected, washed with petroleum ether and air-dried. This material was recrystallized twice from 15% ethanol–water (8–11 ml./g.), care being taken not to exceed the temperature required for solution. The air-dried dihydrate thus obtained in 24% yield lost two moles of water on drying for several hours at 59° and a pressure of 8 mm. The anhydrous compound was somewhat hygroscopic (m.p. 147–148°).

Anal. Calcd. for $C_6H_4O_6N_2$: C, 36.0; H, 2.0; N, 14.0; mol. wt., 200. Found: C, 35.2; H, 2.39; N, 13.4; mol. wt. (Rast), 197.

In 1 *N* aqueous HCl this compound showed an absorption maximum at 352 mμ, ϵ 7.1 $\times 10^3$, and a minimum at 266 mμ.

3,4-Dinitroveratrole.—Anhydrous 3,4-dinitrocatechol (0.45 g., 0.00225 mole) was mixed with methyl sulfate (0.60 ml., 0.0063 mole) and 1.09 *N* NaOH (4.8 ml., 0.0052 mole) and subjected to vigorous shaking and gentle heating for about five minutes at which time the initially red color of the aqueous phase had been nearly discharged. Additional NaOH solution (3.1 ml., 0.0034 mole) caused reappearance of the red color, which persisted on further heating and shaking. A solid phase soon appeared to take the place of the liquid methyl sulfate layer. The mixture was cooled and extracted with ether. The ether layer was extracted with several portions of a dilute aqueous NaOH solution until the aqueous phase was colorless, then washed twice with water and dried over Na_2SO_4. Evaporation of the ether left a white residue which was recrystallized from methanol–water. The product so obtained was isolated and dried with a stream of air (m.p. 90.5°). Of the four possible dinitroveratroles, all of which are known,[8] only the 3,4-isomer has the m.p. found.

4-Nitrocatechol.[3]—A solution of sodium nitrite (5.5 g., 0.08 mole) and catechol (4.0 g., 0.036 mole) in water (150 ml.) was mixed with sufficient ice to bring the temperature down to 0°. In the course of 3–5 minutes, 25 ml. of 2.5 *M* H_2SO_4 (0.063 mole) was added, along with more ice and with shaking. The solution was then extracted with ether in two portions (150 and 75 ml.). The combined ether extract was twice washed with 100 ml. of water, dried briefly over anhydrous sodium sulfate and evaporated quickly at room temperature under a stream of nitrogen. The residue was subjected to vacuum sublimation at a pressure of 6 mm. The first small fraction, somewhat oily, was removed at a bath temperature of 100–150° and probably consisted mostly of 3,4-dinitrocatechol. The second fraction, removed at a bath temperature of 160–190°, was nearly pure 4-nitrocatechol (m.p. 172–174°); its weight was 1.63 g. (29% yield). When somewhat greater amounts of sodium nitrite (8.25 g., 0.12 mole) and sulfuric acid (37.5 ml., 0.09 mole) were used a yield of 2.11 g. (37%) of 4-nitrocatechol was obtained.

3- and 4-Nitrocatechol.—Previous authors[4] treated a solution of 10 g. of catechol in 500 ml. of ether with 4 ml. of fuming nitric acid, allowed the resulting solution to stand 24 hours, washed the ether solution with water and proceeded with the isolation of 3- and 4-nitrocatechol. The present authors recovered mostly catechol by this procedure. Neither refluxing nor addition of water induced the reaction when the recommended quantity of ether was employed, but distillation of a portion of the ether prior to washing with water caused the desired reaction to take place. When the amount of ether was reduced to 250 ml. the reaction proceeded rapidly and the products were isolated; when 375 ml. of ether was employed, the reaction proceeded in three out of the four times it was tried. When 375 ml. of ether was used, isolation was carried out by evaporation of the washed ether solution, vacuum sublimation of the residue (bath temperature being raised gradually from 100 to 200°), and continuous extraction of the sublimate with 30–60° petroleum ether. The petroleum ether-soluble fraction consisted of nearly pure (m.p. 84°, reported 86°) 3-nitrocatechol, while the residue, consisting mostly of 4-nitrocatechol, was purified (m.p. 176°, reported 174°) by recrystallization from water. The yield of impure mononitrocatechols was approximately 65–70%, the product consisting of 56–62% 3-nitrocatechol and 38–44% 4-nitrocatechol. Variation of the temperature of reaction did not produce significant difference in the ratio of the 3- to 4-isomer. Spectral absorption maxima for 4-nitrocatechol in 1 *M* aqueous HCl occurred at 240 and 346 mμ, while the 3-isomer showed a single maximum at 298 mμ. Isobestic points for the first dissociation of 4-nitrocatechol were found at 229, 252, 280 and 370 mμ, while those of 3-nitrocatechol were found at 268 and 320 mμ.

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(7) Private communication from Dr. Joseph W. Corse of the Western Regional Research Laboratory, Albany, California. A sample of this material was kindly made available to us by Dr. Corse.

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