collisions of the hot iodine atoms with molecules as a whole[8] or with radicals produced by the neutrons, beta rays and gamma rays in the system. It is to be expected that a variety of fragments would be formed by such a process and that by careful fractionation experiments the organically bound iodine might be found to be in several different compounds rather than as a single organic iodide.

Although the elemental iodine solutions used in our tests were in all cases at a concentration below the solubilities reported in the literature,[18] a slowly forming iodine-like deposit was observed on the walls of the bombardment tube in a majority of the cases. If, as this might indicate, the iodine actually is present as much larger aggregates than I_2, it would be expected that there would be a high probability that the hot atoms from the (n, γ) process would lose their energy to atoms in the parent aggregate before escaping into the hydrocarbon medium. This may possibly account for the lower organic yield when iodine is used as the solute than when ethyl iodide is used. A perhaps more probable explanation is that elemental iodine both reduces the concentration of organic radicals in the system and exchanges with thermalized hot atoms to fix them in inorganic combination.

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MADISON 6, WIS.

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[18] (a) J. H. Hildebrand and C. A. Jenks, THIS JOURNAL, **42**, 2180 (1920); (b) W. Jaok, *Rocz. Chem.*, **6**, 501 (1926); (c) G. R. Negishi, L. H. Donnally and J. H. Hildebrand, THIS JOURNAL, **55**, 4793 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, MICHIGAN COLLEGE OF MINING AND TECHNOLOGY]

Reactions of 2,4-Dinitrobenzeneselenenyl Bromide with Alcohols and Amines[1]

BY WENDELL S. COOK AND ROBERT A. DONIA[2]

2,4-Dinitrobenzeneselenenyl bromide was condensed with a series of alcohols in the presence of silver acetate to form alkyl 2,4-dinitrobenzeneselenenates. The aromatic amines, aniline, *p*-bromoaniline and *p*-toluidine reacted with the bromide giving N-aryl 2,4-dinitrobenzeneselenenamides whereas 1- and 2-naphthylamine formed aminonaphthyl 2,4-dinitrophenyl selenides.

The recent interest in sulfenic acid derivatives, particularly the reactions of nitrobenzenesulfenyl halides,[3] and the enhanced stability of selenenic acids and derivatives over that of the corresponding sulfenic acid type suggested the present study of 2,4-dinitrobenzeneselenenyl (hereafter abbreviated as DNBSe) bromide.

The principal investigators of selenenic acids have been Behaghel and co-workers[4] who isolated 2-nitrobenzene, 2,4-dinitrobenzene-, and 1-anthraquinoneselenenic acids; they also used corresponding selenenyl halides in the synthesis of selenenyl acetates, cyanides, selenenamides and diaryl selenides. Recently, Foss[5] prepared selenothio compounds by reaction of 2-nitrobenzeneselenenyl bromide with potassium salts of several thio acids and Rheinboldt and Giesbrecht[6] studied the preparation and properties of aromatic selenenyl selenocyanates. We have found that 2,4-DNBSe bromide reacts readily with alcohols to produce alkyl 2,4-dinitrobenzeneselenenates; likewise, aniline, *p*-bromoaniline and *p*-toluidine condense with the bromide, giving the corresponding N-aryl selenenamides. However, 1- and 2-naphthylamines form diaryl selenides instead of selenenamides.

Reaction of 2,4-DNBSe Bromide with Alcohols.—Selenenic acids are amphoteric and esterification with either an acid [reaction (a)] or an alcohol (b) is anticipated; for example

$$C_6H_5SeOH + CH_3COOH \longrightarrow C_6H_5SeOOCCH_3 \text{ (benzeneselenenyl acetate)} \quad (a)$$

$$C_6H_5SeOH + CH_3OH \longrightarrow C_6H_5SeOCH_3 \text{ (methyl benzeneselenenate)} \quad (b)$$

Behaghel and Müller[4d] reported the formation of aryl selenenyl acetates as shown in (c) and (d)

$$ArSeBr + CH_3COOAg \xrightarrow{CH_3OH} ArSeOOCCH_3 + AgBr \quad (c)$$

(Ar = 2-nitrophenyl, 4-nitrophenyl and 2,4-dinitrophenyl)

$$1\text{-}C_{14}H_7O_2Se(OH) \text{ (or Br)} + CH_3COOAg \xrightarrow{CH_3COOH} 1\text{-}C_{14}H_7O_2SeOOCH_3 + AgBr \quad (d)$$

($1\text{-}C_{14}H_7O_2$ = 1-anthraquinonyl)

Selenenate esters (b) could not be prepared according to these investigators for they observed that treatment of 2-nitrobenzeneselenenyl bromide with sodium ethylate produced a mixture of the diselenide, selenenic acid and perhaps some selenophenol. Furthermore, in the sulfenic acid series, direct esterification with an alcohol has been successful only with 1-anthraquinonesulfenic acid or chloride.[7]

In repeating the work of Behaghel and Müller[4d] on reaction (c) using 2,4-DNBSe bromide, we

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[1] From the thesis of W. S. Cook in partial fulfillment of the requirements for the M.S. degree, December, 1948.

[2] The Upjohn Company, Kalamazoo, Michigan.

[3] N. Kharasch, S. J. Potempa and H. L. Wehrmeister, *Chem. Revs.*, **39**, 269 (1946); N. Kharasch, N. L. Wehrmeister and H. Tigerman, THIS JOURNAL, **69**, 1612 (1947); N. Kharasch and C. M. Buess, *ibid.*, **71**, 2724 (1949); H. Rheinboldt and E. Giesbrecht, *ibid.*, **71**, 1740 (1949); N. Kharasch, G. I. Gleason and C. M. Buess, *ibid.*, **72**, 1796 (1950); C. M. Buess and N. Kharasch, *ibid.*, **72**, 3529 (1950); H. Rheinboldt and E. Giesbrecht, *Ann.*, **568**, 198 (1950).

[4] (a) O. Behaghel and H. Seibert, *Ber.*, **65**, 812 (1932); (b) *ibid.*, **66B**, 708 (1933); (c) O. Behaghel and W. Müller, *ibid.*, **67B**, 105 (1934); (d) *ibid.*, **68B**, 1540 (1935); (e) O. Behaghel and K. Hofmann, *ibid.*, **72B**, 582, 697 (1939).

[5] O. Foss, THIS JOURNAL, **69**, 2236 (1947).

[6] H. Rheinboldt and E. Giesbrecht, *ibid.*, **72**, 866 (1950).

[7] K. Fries, *Ber.*, **45**, 2965 (1912).

found that our product is not 2,4-DNBSe acetate as reported by them, but rather is methyl 2,4-dinitrobenzeneselenenate. The methyl ester was obtained in reactions performed at room temperature or under reflux conditions. The type reaction

$$2,4\text{-}(NO_2)_2C_6H_3SeBr + ROH + CH_3COOAg \longrightarrow 2,4\text{-}(NO_2)_2C_6H_3SeOR(I) + AgBr + CH_3COOH \quad (e)$$

was extended to different alcohols with formation of a series of alkyl 2,4-dinitrobenzeneselenates (Table I). That silver acetate serves principally to remove hydrogen bromide is indicated by failure of a large excess of this reagent to alter the course of the reaction; in the absence of silver acetate the reaction produced a mixture of I and starting material. Other silver salts as benzoate or propionate were also effective as hydrogen bromide acceptors. The substitution of acetic acid for the alcohol in (e) gave a compound which agrees analytically with 2,4-DNBSe acetate and depresses the melting point of the alkyl selenenates. The 2,4-DNBSe acetate did not undergo alcoholysis during two hours in refluxing methanol. While the discrepancy between our results and those of Behaghel and Müller are not explained by these experiments, it does appear that formation of an intermediate acetate is unlikely.

Reaction of 2,4-DNBSe Bromide with Aromatic Amines.—Although the preparation of selenenamides and diaryl selenides has been reported[4b,4c,4d] we wished to investigate specifically the action of 2,4-DNBSe bromide on primary aromatic amines. Previous work[8] on sulfenyl halide–primary aromatic amine reactions indicates the possibility of condensation with the attachment of sulfur to either nitrogen or an activated nuclear position.

When 2,4-DNBSe bromide reacted with aniline, *p*-bromoaniline or *p*-toluidine the product was the corresponding N-aryl 2,4-dinitrobenzeneselenenamide (Table I)

$$2,4\text{-}(NO_2)_2C_6H_3SeBr + 2ArNH_2 \longrightarrow 2,4\text{-}(NO_2)_2C_6H_3SeNHAr(II) + ArNH_3Br \quad (f)$$

The selenenamide structure was established by hydrogen chloride cleavage and isolation and identification of the amine hydrochloride. However, under comparable reaction conditions 1- and 2-naphthylamine condensed on the activated nuclear positions giving 1-(4-aminonaphthyl) 2,4-dinitrophenyl selenide and 1-(2-aminonaphthyl) 2,4-dinitrophenyl selenide, respectively (Table I). These red selenides, isomeric with N-naphthylselenenamides, formed unstable yellow hydrochloride salts on treatment with hydrogen chloride and there was no indication of cleavage. This is similar to the behavior of the known compound, 2-nitrophenyl 4-dimethylaminophenyl selenide.[4b]

Reaction of 2,4-DNBSe Bromide with Phenolic Compounds.—The formation of hydroxyaryl sulfides from sulfenyl halides and phenols is well known. Preliminary experiments on the condensation of 2,4-DNBSe bromide with phenol and resorcinol at 120–140° gave only 2,4-dinitrophenyl diselenide (55 and 100%, respectively) and copious evolution of hydrogen bromide.

TABLE I

PROPERTIES OF SELENENATES, SELENENAMIDES AND SELENIDES FROM 2,4-DNBSe BROMIDE

Compound	Color	M.p.,[a] °C.	Nitrogen, % Calcd.	Nitrogen, % Found	Mol. wt.[b] Calcd.	Mol. wt.[b] Found
Alkyl 2,4-dinitrobenzeneselenenates ($2,4\text{-}(NO_2)_2C_6H_3SeOR$)						
R = methyl	Yellow	131–133	10.11	10.30	277.1	281.8
ethyl	Orange	128–129	9.62	9.52	291.1	294.9
isopropyl	Yellow	92–93	9.18	9.16	305.2	308.2
s-butyl	Yellow	79–81	8.78	8.82	319.2	323.0
benzyl	Yellow	147–148.5	7.93	8.01	353.2	348.2
N-Aryl 2,4-dinitrobenzeneselenenamides ($2,4\text{-}(NO_2)_2C_6H_3SeNHAr$)						
Ar = phenyl	Dk. red	144–146.5	12.43	12.42	338.2	331.2
p-tolyl	Dk. red	173–175	11.93	12.02	352.2	347.9
p-bromophenyl	Dk. red	172–173	10.08	10.24	417.1	408.1
Aminonaphthyl 2,4-dinitrophenyl selenides ($H_2NC_{10}H_6SeC_6H_3(NO_2)_2\text{-}2,4$)						
4-(1-aminonaphthyl)	Dk. red	215–216	10.82	10.76	388.2	[c]
1-(2-aminonaphthyl)	Dk. red	209–210	10.82	10.81	388.2	[c]

[a] Uncorrected. [b] Cryoscopic method in benzene. [c] Low solubility precluded this determination.

Experimental

Alkyl 2,4-Dinitrobenzeneselenenates (II, R = Methyl, Ethyl, Isopropyl, *s*-Butyl).—A mixture of 3.26 g. (0.01 mole) of 2,4-DNBSe bromide[9] and 25 ml. of the alcohol (absolute) in which was suspended 1.84 g. (0.011 mole) of silver acetate was refluxed for two hours. The precipitate of silver bromide was filtered from the hot solution and the filtrate was cooled to 0°, whereupon the selenenate ester crystallized. Yields of nearly pure esters were 84, 76, 71 and 63%, respectively. Recrystallization from methanol revealed a very small amount of red methanol-insoluble product; this turned yellow at 220°, melted at 263°.[10] The formation of methyl 2,4-dinitrobenzeneselenenate was also achieved by stirring the reactants in 25 ml. of methanol for five hours at room temperature. The mixture was filtered and the precipitate washed with 100 ml. of ether. The combined filtrates were concentrated *in vacuo* to 25 ml. Long golden yellow needles precipitated; m.p. 132–134°; yield 68%. A mixed melting point with an authentic sample was not depressed.

In the preparation of the ethyl ester, substitution of silver acetate by an equimolar amount of propionate or benzoate gave almost the same result. In another experiment, the quantity of silver acetate was increased to 0.044 mole and methanol reduced to 5 ml. Again, results were comparable to those obtained in the standard procedure.

Benzyl 2,4-Dinitrobenzeneselenenate.—A mixture of 6.52 g. (0.02 mole) of 2,4-DNBSe bromide, 2.23 g. (0.02 mole) of benzyl alcohol and 3.5 g. (0.02 mole) of silver acetate in 100 ml. of chloroform was refluxed for six hours. After filtration of the silver bromide, the filtrate was evaporated to dryness. The residue was recrystallized from chloroform; yield 4.63 g. (61%).

2,4-Dinitrobenzeneselenenyl Acetate.—A suspension of 3.26 g. (0.01 mole) of 2,4-DNBSe bromide and 1.84 g. (0.011 mole) of silver acetate in 50 ml. of glacial acetic acid was refluxed for two hours. The solution was filtered and the filtrate diluted with 100 ml. of water. The canary yellow product which precipitated was collected by filtration, dried and then recrystallized three times from 3:1 acetic acid–water; m.p. 128–129°; N, calcd. 9.18, found, 9.22. A mixed melting point of this product with I (R = CH_3 or C_2H_5) was depressed to 106°.

N-Aryl 2,4-Dinitrobenzeneselenenamides (II, R = Phenyl, *p*-Bromophenyl, *p*-Tolyl).—A solution of 0.02 mole of 2,4-DNBSe bromide and 0.04 mole of the amine in 250 ml. of chloroform was allowed to stand for 24 hours. Rapid

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(8) (a) T. Zincke and S. Lenhardt, *Ann.*, **400**, 1 (1913); (b) T. Zincke and H. Röse, *ibid.*, **406**, 103 (1914); (c) M. L. Moore and T. B. Johnson, THIS JOURNAL, **57**, 1517 (1935); *ibid.*, **58**, 1091 (1936); (d) J. H. Billman and E. O'Mahoney, *ibid.*, **61**, 2340 (1939); (e) J. H. Billman, J. Garrison, R. Anderson and B. Wolnak, *ibid.*, **63**, 1920 (1941).

(9) Prepared as described by O. Behaghel and W. Müller.[4b]

(10) This agrees well with the behavior of 2,4-dinitrobenzeneselenenic acid observed by Behaghel and Müller.[4d]

precipitation of the amine hydrobromide was observed. The reaction mixture was filtered and the filtrate evaporated to dryness at room temperature. The residue was triturated twice in hot water to dissolve amine salts and then recrystallized from chloroform keeping heat at the minimum compatible with recrystallization requirements. The selenenamides were formed in 72, 64 and 70% yields.

1-[4(and 2)-Aminonaphthyl] 2,4-Dinitrophenyl Selenides.—The same method as described for preparation of N-aryl selenenamides was used in the reaction of 1- and 2-naphthylamines with 2,4-DNBSe bromide. These compounds were much less soluble in chloroform than the selenenamides.

Hydrogen Chloride Cleavage of N-Aryl 2,4-Dinitrobenzeneselenenamides.—Dry hydrogen chloride was bubbled through cold chloroform solutions of each selenenamide for 10 minutes. The solution changed from red to yellow and a white precipitate formed. The melting point of the precipitate was found in each case to agree with that of the corresponding amine hydrochloride.

Hydrogen Chloride Treatment of 1-[4(and 2)-Aminonaphthyl] 2,4-Dinitrophenyl Selenides.—Dry hydrogen chloride was bubbled through solutions of about 50 mg. of each selenide in 20 ml. of cold chloroform. The color changed from orange to light yellow; the original color slowly returned on standing. Attempts to isolate hydrochloride salts of the selenides by evaporation of the chloroform in air or *in vacuo* led only to recovery of the original selenide. The latter were identified by the mixed melting point technique. No evidence was observed for the presence of a naphthylamine hydrochloride based on precipitation or water extraction.

HOUGHTON, MICHIGAN RECEIVED JULY 24, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Ortho Esters, Imidic Esters and Amidines. II. Disproportionation Reactions of Nitrophenyl-, Chlorophenyl- and Tolyl-substituted Formimidates and Formamidines

BY ROYSTON M. ROBERTS, ROBERT H. DEWOLFE, AND JOSEPH H. ROSS

The study of acid-catalyzed disproportionations which may occur during syntheses involving imidic esters and amidines is continued. Reactions involving *p*-nitroaniline, *o*- and *p*-chloroaniline and *o*-toluidine derivatives are described. It is shown that the occurrence and course of the reaction are highly dependent on acid concentrationa nd are influenced more by steric and statistical factors than by the relative basicity of the amino groups involved, as has been suggested. The mechanisms of the reactions are discussed. Several new unsymmetrical N,N'-diarylformamidines are reported and some are correctly reported for the first time.

In a previous publication[1] we described an acid-catalyzed disproportionation which may occur during the preparation of N-phenyl-N'-*p*-tolylformamidine, and we mentioned that similar results were encountered in the preparation of N-phenyl-N'-*p*-nitrophenylformamidine. The purpose of this paper is to give the experimental data related to the latter compound and also to the analogous compounds derived from *o*- and *p*-chloroaniline and *o*-toluidine.

p-Nitroaniline reacts with ethyl N-phenylformimidate less readily than does *p*-toluidine and, at the higher temperatures employed, there was always some disproportionation resulting in the formation of N,N'-diphenylformamidine and N,N'-di-*p*-nitrophenylformamidine as well as the expected N-phenyl-N'-*p*-nitrophenylformamidine, even when precautions were taken against the presence of traces of acids. Because of the large differences in the solubilities of these compounds, it was feasible to separate them and identify each of them directly from reaction mixtures, which was not the case with the analogous *p*-tolyl derivatives. The ultraviolet absorption spectra of these three compounds are shown in Fig. 1.

The unsymmetrical nitro-substituted formamidine could be "disproportionated" by heating it in ethanol in the presence of an acid catalyst, producing a mixture containing the two corresponding symmetrical formamidines as well as the original substance; the more insoluble N,N'-di-*p*-nitrophenylformamidine was isolated from such a mixture. Another component of the mixture is *p*-nitroaniline. This result can be explained reasonably by reference to Fig. 1 of the preceding paper[1] of this series. The large amount of ethanol required to dissolve N-phenyl-N'-*p*-nitrophenylformamidine displaces the equilibria set up between the three formamidines and ethanol on the one hand and the two aromatic amines and two N-arylformimidates on the other in favor of a high concentration of the latter substances. When, in a second experiment, the ethanol was slowly removed from the reaction mixture by distillation, N,N'-di-*p*-nitrophenylformamidine was isolated; this is in accord with the expectation of shifting (by the removal of ethanol) the equilibria toward completeness of reaction of aromatic amines with N-arylformimidates producing the three formamidines.

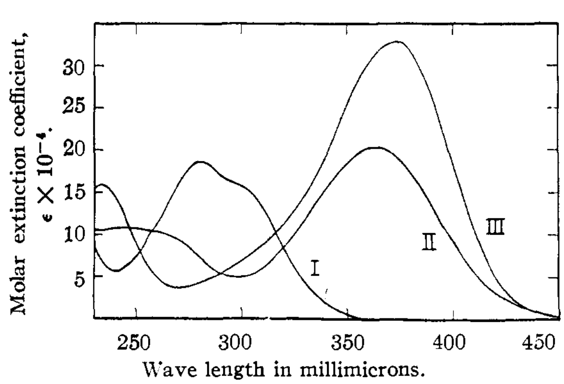

Fig. 1.—Ultraviolet absorption spectra in isopropyl alcohol: I, N,N'-diphenylformamidine; II, N-phenyl-N'-*p*-nitrophenylformamidine; III, N,N'di-*p*-nitrophenylformamidine.

The reverse of the above changes was effected by heating N,N'-diphenylformamidine and N,N'-di-*p*-nitrophenylformamidine with ethanol in nitrobenzene solution containing a trace of acid. The unsymmetrical formamidine was produced and could

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[1] R. M. Roberts, THIS JOURNAL, **72**, 3603 (1950).