Iyengar, Naqui, and Sidhu[1] reported that the treatment of 1-hydrazinoisoquinoline with carbon disulfide in the presence of base led to the formation of 3-mercapto-*s*-triazolo[3,4-*a*]isoquinoline. When 4-hydrazinoquinazoline (1) was allowed to react with carbon disulfide under the same conditions, we observed that the expected [4,3-*c*]triazoloquinazoline (4) was not formed. Instead, 2-(2-aminophenyl)-5-mercapto-1,3,4-thiadiazole (2) was isolated as indicated by the presence of $-NH_2$ absorptions at 3410 and 3300 cm^{-1} in the infrared and by the absence of the expected proton in the 5 position of 4 in the nmr.

As the mechanism of the formation of 2 under these conditions, we stipulate the first intermediate to be A, which should be formed by a nucleophilic attack of the hydrazino group of carbon disulfide. An intramolecular attack of the dithiocarbazate anion may then occur at the 4 position and the spiro intermediate B is formed. Following the abstraction of a proton from the solvent, the quinazoline ring opens and C is produced. This, in turn, is attacked by hydroxide ion to produce 2 with concomitant loss of formamide.

The structure of 2 was also confirmed by the independent synthesis of 3. Using the procedure of Young and Wood,[2] 2-nitrobenzoylhydrazide was treated with carbon disulfide in the presence of potassium hydroxide followed by alkylation of the intermediate with methyl iodide to form methyl-3-(2-nitrophenyl)dithiocarbazate (5) in 25% yield (mp 174–178°). Compound 5 cyclized in concentrated sulfuric acid to 5-methylmercapto-2-(2-nitrophenyl)1,3,4-thiadiazole in 85% yield (mp 90–93°), which was then hydrogenated over palladium on carbon at 3.5 atm to 3 in 28% yield. All physical constants and spectra were identical with those of 3 isolated by the previous route.

Experimental Section[3]

Melting points were determined on a Thomas-Hoover Unimelt apparatus and are uncorrected. All compounds gave satisfactory elemental analyses and their spectra (ir, obtained on Perkin-Elmer Models 257 and 457 spectrophotometers, and nmr, on Varian Models A-60 and T-60) were in full accord with the proposed structures.

2-(2-Aminophenyl)-5-mercapto-1,3,4-thiadiazole (2). A mixture of 10.0 g of 4-hydrazinoquinazoline,[4] 10 ml of carbon disulfide, 3.6 g of potassium hydroxide (85%), and 30.0 g of water in 200 ml of ethanol was refluxed for 3 hr. All insoluble materials were filtered from the reaction mixture and the solvent was removed under reduced pressure. To the residue was added 200 ml of 5% potassium hydroxide solution and any insoluble material was filtered off. The resulting solution was neutralized with 50% aqueous acetic acid, and the yellow precipitate was filtered and washed well with water. Recrystallization from ethanol furnished 6.1 g (48%) of 2, mp 214–216°.

Anal. Calcd for $C_8H_7N_3S_2$: C, 45.9; H, 3.4; N, 20.1. Found: C, 45.5; H, 3.4; N, 19.8.

2-(2-Aminophenyl)-5-methylmercapto-1,3,4-thiadiazole (3). To a solution of 2 in 125 ml of 1 *N* potassium hydroxide was added 2.2 ml of methyl iodide. The mixture was stirred at 25° for 30 min (precipitation occurred after 5 min). The resulting precipitate was filtered and recrystallized from ether to yield 6.0 g (87%) of 3, mp 91–92°.

Anal. Calcd for $C_9H_9N_3S_2$: C, 48.4; H, 4.1; N, 18.8. Found: C, 48.3; H, 4.1; N, 18.6.

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Registry No.—1, 36075-44-2; 2, 51805-88-0; 3, 51805-89-1; carbon disulfide, 75-15-0.

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Oxidation of Hydrocarbons. V. Oxidation of Naphthalenes by Ruthenium Tetroxide[1]

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It is known that ruthenium tetroxide will readily oxidize aromatic rings to yield either mono- or dicarboxylic acids.[2-5] This ability has found particular application in the degradation of steroids.[6] Ruthenium tetroxide is an attractive reagent for these processes, since it is a vigorous oxidant which is soluble in a variety of organic solvents.[5] Furthermore it is not costly, since it can be used catalytically in conjunction with inexpensive cooxidants such as aqueous sodium hypochlorite (household bleach). Despite these advantages little was known about the directive effect of ring substituents in fused polyaromatic systems prior to this study.

From the data contained in Table I it can be seen that the substituents exert a substantial directive effect on the oxidation of substituted naphthalenes. In those cases where the substituent is electron donating it activates the ring and increases the yield of phthalic acid. When electron-withdrawing groups are present the overall reaction time is increased, the substituted ring is protected, the observed yield is reduced, and a mixture of products is obtained. The application of these observations to organic synthesis is straightforward; if it is desirable to use this reaction in an oxidative degradation procedure, the introduction of an activating group such as hydroxy or methoxy will greatly increase the rate of oxidation, thus preventing side reactions. Conversely, an aromatic ring may be protected simply by introduction of an electron-withdrawing group such as nitro.

In the case of methyl-substituted naphthalenes no evidence could be found for side-chain oxidation. In this respect ruthenium tetroxide differs in its reactions from those of several other common oxidants, particularly aqueous sodium dichromate, which is known to attack side chains preferentially.[7]

Experimental Section

All successful reactions were carried out using a two-phase system composed of carbon tetrachloride and water along with catalytic amounts of ruthenium dioxide and an excess of cooxidant. [Several experiments which were performed using stoichiometric amounts of ruthenium tetroxide were found to give extremely low yields (<10%) possibly because of absorption of the organic products on the resulting inorganic product, ruthenium dioxide.]

A typical reaction was initiated by combining 50 ml of carbon tetrachloride and 100–200 ml of bleach (enough cooxidant to ensure that phthalic acid would be the product). Then 0.01 g of $RuO_2 \cdot 2H_2O$ was added while stirring. When all of the black ruthenium dioxide had been converted to yellow ruthenium tetroxide, 0.5 g of the particular naphthalene was added. The reaction mixture was well stirred and allowed to react until no further ruthenium tetroxide was generated. Typically this time varied from hours for activated naphthalenes to several days for those compounds with electron-withdrawing groups present.

The products were separated by ether extractions and identified by glc (after esterification), ir, and tlc.

Table I
Products from Ruthenium Tetroxide Oxidation of Substituted Naphthalenes

Compd[a]	Registry no.	Reaction time[b]	Products	Yield, %
Naphthalene (3)	91-20-3	60 hr	Phthalic acid	70
α-Naphthol (3)	90-15-3	1 hr	Phthalic acid	82
β-Naphthol (2)	135-19-3	1 hr	Phthalic acid	60
1-Methylnaphthalene (7)	90-12-0	24 hr	Phthalic acid	24
			3-Methylphthalic acid	6
2-Methylnaphthalene (5)	91-57-6	24 hr	Phthalic acid	50
			4-Methylphthalic acid	5
1-Methoxynaphthalene (3)	2216-69-5	4 days	Phthalic acid	85
2-Methoxynaphthalene (1)	93-04-9	4 days	Phthalic acid	72
			4-Methoxyphthalic acid	6
2,3-Dimethylnaphthalene (2)	581-40-8	3 days	Phthalic acid	25
1,4-Dimethylnaphthalene (2)	571-58-4	3 days	Phthalic acid	10
			3,6-Dimethylphthalic acid	15
2-Chloronaphthalene (2)	91-58-7	5 days	Phthalic acid	7
			4-Chlorophthalic acid	70
1-Fluoronaphthalene (3)	321-38-0	3 days	Phthalic acid	44
			3-Fluorophthalic acid	11
1-Nitronaphthalene (4)	86-57-7	7 days	Phthalic acid	7
			3-Nitrophthalic acid	63
1-Naphthoic acid (2)	86-55-5	36 hr	Phthalic acid	38
			1,2,3-Tricarboxybenzene	16
2-Naphthoic acid (3)	93-09-4	48 hr	Phthalic acid	28
			1,2,4-Tricarboxybenzene	24
2-Naphthaldehyde (2)	66-99-9	48 hr	Phthalic acid	29
			1,2,4-Tricarboxybenzene	29
			2-Naphthoic acid	2
Tetralin (6)	119-64-2	60 hr	Adipic acid[c]	36
3-Hydroxy-2-naphthoic acid (2)	92-70-6	48 hr	Phthalic acid	85

[a] Numbers in parentheses indicate number of trials. [b] The reaction time can be reduced if more $RuO_2 \cdot 2H_2O$ is used, but this causes large decreases in yields. [c] Large amounts of tars present.

All materials were available commercially; the substituted naphthalenes were purified prior to use by crystallization and/or sublimation.

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Registry No.—Ruthenium tetroxide, 20427-56-9.

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Dominance of an Ionic Mechanism over a Cyclic Concerted Process in a Hydrocarbon Solvent

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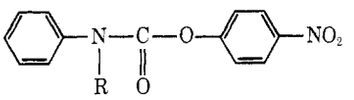
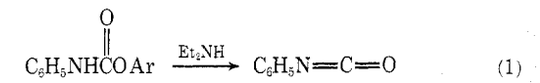
We have investigated the mechanism for the aminolysis of *p*-nitrophenyl *N*-phenylcarbamate (Ia) in toluene.[2] As will be shown below, Ia reacts in the nonpolar solvent through an ionic mechanism to the exclusion of a cyclic six-center process that generates little or no charge.



Ia, R = H
b, R = CH_3

The observed rate constant (as measured by *p*-nitrophenol release) for the reaction of 0.053 *M* diethylamine with 8.7×10^{-5} *M* Ia in toluene at 25.0° was found to equal 1.50×10^{-3} sec^{-1}. This is at least 10^4 faster than that between diethylamine and Ib.[3] If the amine attacked the carbamate carbonyl (to eject *p*-nitrophenol and form a urea *via* a BAC2 mechanism), then Ia and Ib would not differ so widely in their rates.[4] The requirement of an N proton for a facile reaction demands that Ia eliminate to give an isocyanate intermediate (eq 1).[5,6] The intermediate subsequently reacts with amine to produce a urea.



(1)

Formation of the isocyanate in toluene could conceivably occur by one of three mechanisms.

(1) Six-membered cyclic concerted process