Table I

$$2ArCHO + Ar'H \xrightarrow{BF_3} ArCH_2Ar' + ArCO_2H$$

Registry no. ArCHO'	Registry no. Ar'H	Ar	Mol	Ar'	Ml	Method[a]	Aldehyde conversion, %	Diphenylmethane[b] yield, %	$ArCH_2Ar'$ registry no.
100-52-7	71-43-2	C_6H_5	1.89	C_6H_5	400	A	8	85	101-81-5
		C_6H_5	1.89	C_6H_5	400	B	16	91	
		C_6H_5	1.89	C_6H_5	300	C	47	55	
	108-88-3	C_6H_5	1.89	$CH_3C_6H_4$	400	A	16	81	
		C_6H_5	1.89	$CH_3C_6H_4$	400	B	36	82	
		C_6H_5	1.89	$CH_3C_6H_4$	300	C	51	57	
	108-38-3	C_6H_5	1.89	m-$(CH_3)_2C_6H_3$	300	C	53	67	38094-29-0
104-87-0		p-$CH_3C_6H_4$	1.89	C_6H_5	300	C	48	33	620-83-7
104-88-1		p-ClC_6H_4	1.00	C_6H_5	300	C	66	79	14310-22-6

[a] In method A the indicated quantities were refluxed under nitrogen with 25 ml of boron fluoride etherate for 24 hr, method B used 48-hr reflux, and in method C the reaction mixtures were heated for 6 hr at 150° in an autoclave. [b] Based on reacted aldehyde.

ticularly using method B, is simple and product isolation is easily accomplished by distillation.

Experimental Section[7]

Reaction of Benzaldehyde with Toluene (Method B). A mixture of 200 g (1.89 mol) of benzaldehyde, 25 ml of boron fluoride etherate, and 400 ml of toluene was refluxed for 48 hr. After cooling, the reaction mixture ws washed with water (100 ml) and extracted with saturated sodium carbonate solution. The organic layer was dried ($MgSO_4$) and filtered, and the toluene was removed on a 36-in. column. Distillation of the residue through the same column gave 127.3 g (64% recovery) of benzaldehyde, bp 80–82° (20 mm), and 51.1 g (82%) of a mixture of benzyltoluenes, bp 160–164° (18 mm), which was found to contain 42% ortho, 7% meta, and 51% para isomer by glc analysis (150 ft × 0.01 in. Carbowax 20M column programmed from 150 to 200° at 5°/min). The sodium carbonate extracts were filtered, acidified with concentrated HCl, collected on a filter, and air dried to give 5.4 g (13%) of benzoic acid, mp 119–120°, identified by its infrared spectrum.

Reaction of p-Chlorobenzaldehyde with Benzene (Method C). A 1-l. Magnedrive autoclave[9] constructed of Hastelloy C was charged with 140.5 g (1.0 mol) of p-chlorobenzaldehyde, 300 ml of benzene, and 25 ml of boron fluoride etherate. The autoclave was flushed with nitrogen and heated at 150° for 6 hr. After work-up as in method B there was obtained 48.2 g (34%) of unreacted p-chlorobenzaldehyde, bp 98–100° (15 mm), and 52.9 g (79%) of 4-chlorodiphenylmethane, bp 116–117° (3 mm).

Anal. Calcd for $C_{13}H_{11}Cl$: C, 77.04; H, 5.43; Cl, 17.5. Found: C, 76.88; H, 5.35; Cl, 17.4.

Acidification of the sodium carbonate extracts gave 10.3 g (10%) of p-chlorobenzoic acid, mp 232–234°, identified by comparison of the infrared spectrum with that of an authentic sample.

Registry No.—o-Benzyltoluene, 713-36-0.

References and Notes

(1) (a) G. A. Olah, "Friedel-Crafts Chemistry," Wiley, New York, N. Y., 1973, p 51. (b) J. E. Hofmann and A. Schriesheim in "Friedel-Crafts and Related Reactions," Vol. II, G. A. Olah, Ed., Interscience, New York, N. Y., 1964, Part I, p 602.

(2) (a) D. H. Hey, *J. Chem. Soc.*, 72 (1935); (b) H. Ellison and D. H. Hey, *ibid.*, 1847 (1938).

(3) J. Dewar and H. O. Jones, *J. Chem. Soc.*, 212 (1904).

(4) A. Schaarschmidt, L. Herman, and B. Szemzo, *Ber.*, **58B**, 1914 (1925).

(5) P. R. Stapp, *J. Org. Chem.*, **38**, 1433 (1973).

(6) Aromatic aldehydes may be used to prepare diphenylmethanes *via* a three-step procedure involving 1-aryl-2,2,2-trichloroethanes. See, for example, (a) A. B. Galun, A. Kaluszyner, and E. D. Bergmann, *J. Org. Chem.*, **27**, 1426 (1962); (b) A. B. Galun and A. Kalir, "Organic Syntheses," Collect. Vol. V, Wiley, New York, N. Y., 1973, p 130.

(7) The aldehydes and aromatic hydrocarbons were the best commercial grades and were used as received. Boron fluoride etherate was Eastman White Label material and was used as received. Reduction of 4-methylbenzophenone and 2-methylbenzophenone (Aldrich) to p- and o-benzyltoluene was carried out by the Huang-Minlon modification of the Wolff–Kishner procedure.[8] 3-Methylbenzophenone was prepared by reaction of 3-methylphenylmagnesium bromide with benzonitrile followed by reduction to m-benzyltoluene.

(8) Huang-Minlon, *J. Amer. Chem. Soc.*, **68**, 2847 (1946).

(9) Autoclave Engineers, Inc., Erie, Pa.

Reaction of Carbon Disulfide with 4-Hydrazinoquinazoline

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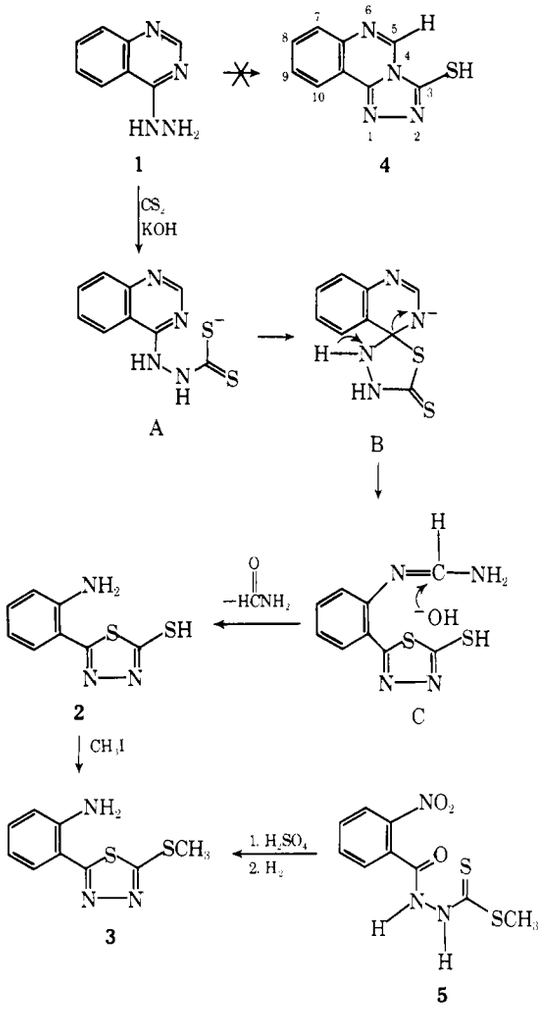
During the course of our studies on quinazolines we observed an unusual reaction between carbon disulfide and 4-hydrazinoquinazoline.



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.

References and Notes

(1) G. Sidhu, S. Naqui, and D. Iyengar, *J. Heterocycl. Chem.*, **3**, 158 (1966).
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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.