crystallized as a hydrochloride. The white, powdery base was dissolved in two volumes of chloroform and could be precipitated with ether; m. p. 150°, yield 50%.

Anal. Calcd. for $C_{25}H_{21}NO_3S$: S, 7.71. Found: S, 7.55.

2-(3,4-Methylenedioxystyryl)-4-acetylamino-6-methoxyquinoline, CC974.—Piperonaldehyde was condensed with 2-methyl-4-amino-6-methoxyquinoline in the presence of acetic anhydride. The deeply-colored condensation product was purified by converting the base to an orange-colored hydrochloride in alcohol; this salt was collected on a filter and again converted to a base. 2-(3,4-Methylenedioxystyryl)-4-acetylaminoquinoline is a tan solid, melting at 234°; it is difficultly soluble in ether, readily in chloroform, and moderately soluble in alcohol.

Anal. Calcd. for $C_{21}H_{16}N_2O_4$: N, 7.73. Found: N, 7.61.

Acknowledgment.—The author wishes to express appreciation to Dr. L. H. Cretcher and to Dr. O. F. Hedenburg for helpful discussion.

DEPARTMENT OF RESEARCH IN PURE CHEMISTRY
MELLON INSTITUTE
PITTSBURGH 13, PENNSYLVANIA

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2-Aminofluorene

BY JOHN R. SAMPEY AND E. EMMET REID

In the Diels[1]–Kuhn[2] method for the preparation of 2-aminofluorene ten times the calculated amount of zinc is used. Conditions have now been found whereby the amount of zinc can be reduced to one-third, or, if the time of reduction is doubled, to one-sixth of this amount.

Procedure.—To a suspension of 30 g. of 2-nitrofluorene in 820 ml. of 95% alcohol and 180 ml. of water are added 10 g. of crystalline calcium chloride in 15 ml. of water, 10 ml. of glacial acetic acid and 50 g. of zinc dust. The mixture is refluxed vigorously for four hours in an oil-bath and, while hot, filtered with suction. The residue is washed with 50 ml. of hot 80% alcohol and the filtrate and washings poured into 2 liters of cold water. The precipitate recrystallized from boiling 50% alcohol (yield 80–90%), melted at 127° (uncor.).

With mossy or 10-mesh granular zinc appreciable amounts of orange-yellow azo and azoxy compounds are formed which are not reduced even after the addition of the required amount of zinc dust.

(1) Diels, *Ber.*, **34**, 1758–1768 (1901).

(2) Kuhn, *Org. Syn.*, **13**, 74–76 (1933).

FURMAN UNIVERSITY
GREENVILLE, SOUTH CAROLINA
BALTIMORE, MARYLAND

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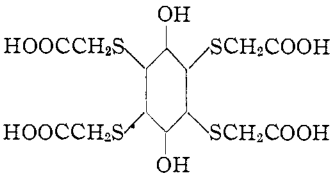
The Interaction of Thiols and Quinones[1]

BY MAXWELL SCHUBERT

In connection with some chemotherapeutic work being carried out at this Laboratory the chemistry of the interaction of quinones and thiols came under consideration. Preliminary experiments led to the isolation of two easily prepared and previously undescribed kinds of compounds. As it is unlikely that this work will be further pursued here, these compounds are now presented and their relation to known compounds pointed out.

If a mole of thioglycolic acid is added to a mole of quinone suspended in water, there results the white crystalline hydroquinone tetrathioglycolic acid, I.



I

This compound on oxidation with nitric acid yields the corresponding red quinone. The quinone on reduction with thioglycolic acid regenerates the hydroquinone. That I represents the structure of the product described is shown by the fact that the same compound results from the action of excess thioglycolic acid on chloranil.

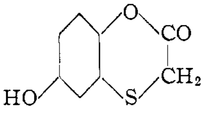
The formation of I from thioglycolic acid and quinone probably results from a sequence of reactions in which quinone adds thioglycolic acid to form a thio substituted hydroquinone which is then oxidized by excess benzoquinone to a thio substituted quinone. This pattern of reaction is repeated until the quinone is completely substituted. The over-all effect is

$$4Q + 4HSR \longrightarrow I + 3H_2Q$$

where R represents —CH_2COOH and Q represents quinone.

Thus, only a quarter of the original quinone could appear in the final product, the other three quarters being used to oxidize the intermediate hydroquinones. On the basis of this scheme, the yield of I recovered after recrystallization was 30%, and the hydroquinone recovered, also after recrystallization, was 63% of that calculated.

Snell and Weissberger[2] in a study of the reaction of thiols and quinones reviewed the older literature. They isolated mono and bis-thio derivatives of quinone and hydroquinone and explained the formation of the bis compounds on the basis of the first steps of the above scheme. Specifically, with thioglycolic acid, they isolated hydroquinone monothioglycolic acid as the lactone.



This compound has also been isolated from our reaction mixture after separation of the hydroquinone derivative, I. Whether the mono or the tetrathioglycolic acid derivative of hydroquinone is formed predominantly seems to depend on the conditions of mixing the components. For example, if a suspension of the quinone in water is added to an aqueous solution of thioglycolic acid,

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(1) The work described in this note was done under a contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and New York University.

(2) Snell and Weissberger, THIS JOURNAL, **61**, 450 (1939).