pension was filtered, and the solid was extracted with 100 ml. of hot (90°) methyl Cellosolve, some insoluble inorganic material being filtered. To the methyl Cellosolve filtrate was added 50 ml. of water and the solution was chilled yielding 1.0 g. (3.6%) of product, m.p. 188–190° (dec.). The solid was crystallized twice from 100 ml. of methanol with the aid of Norit to give 0.80 g. (2.9%) of pure VII, m.p. 190–193° (dec.), which was homogeneous on paper chromatography[8] with R_{Ad} = 1.47, and had $\lambda_{max(\mu)}^{KBr}$ 2.95–3.10 (NH), 5.90 and 6.12 (amide and urea carbonyls), 6.02 (NH_2), 6.48 (NH and C═C), 13.03 and 14.15 (monosubstituted phenyl), and $\lambda_{max(m\mu)}$ 307 (ϵ 12,500) in 95% ethanol.

Anal. Calcd. for $C_{14}H_{16}N_2O_2S$: C, 60.8; H, 5.83; S, 11.6. Found: C, 60.6; H, 5.71; S, 10.6, 10.7.

No effort was made to recover compound I from the filtrate from VII.

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Preparation of Quinone Sulfenimines

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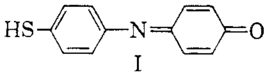
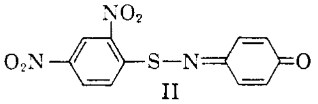
As a part of an investigation of the preparation of compounds of the thio indophenol series, attempts were made to prepare compound I



I

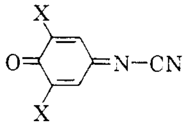
following the procedure of Hirsch[1] by reaction of *N*-chloro-*p*-quinoneimine with aromatic thiols unsubstituted in the para position. The desired compound was not obtained; but instead the reaction took another course to yield quantitatively, quinone sulfenimines. Since this method offers a simple procedure for the preparation of sulfenimines, the results are reported here. Gebauer-Fülnegg and Beatty[2] prepared a metallic complex of 4-chloro-2-nitrophenyl quinone sulfenimine by oxidation of the corresponding sulfenamide with sodium dichromate in acetic acid. By a similar oxidation procedure, Burmistrov and Glazkov[3] reported the preparation of a dinitro sulfenimine (II).



II

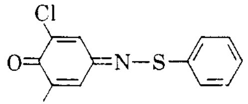
Other workers[4] noted that the reaction of thiols with *N*-chloroquinoneimine yielded colored products which could serve as quantitative estimations of the thiol in solution. Although the formation of quinone sulfenimines was postulated, no attempts were made to isolate or characterize the colored products.

When one equivalent of *N*-chloroquinoneimine was added, with rapid stirring, to the aryl thiol dissolved in sodium carbonate solution, a vigorous reaction occurred yielding a deep red insoluble precipitate. The product was insoluble in dilute alkali and dilute mineral acid and soluble in organic solvents. When treated with alkaline sodium cyanide, the quinone sulfenimine decomposed with the liberation of the thiol which could be detected by odor. Concomitantly, a deep green, unstable water soluble dye was formed, presumably, compound III.



III. X = H, Cl, Br

The infrared spectrum of compound IV



IV

shows absorption maxima at 6.05, 6.45, 6.85 (doublet), 7.85 (doublet), 9.55, 11.1, 12.27, and 13.53μ indicative of quinoid carbonyl and *p*-substituted aromatics. The absence of an absorption peak at 4.0μ due to SH indicates that no free thiol is present.

Similar reactions of *N*-chloroquinoneimines with a variety of thiols such as ethyl potassium xanthate, 2-mercaptobenzothiazole yielded the corresponding sulfenimine (see Table I).

In an attempt to obtain an intramolecular rearrangement of the quinone sulfenimine to the corresponding thio indophenol similar to I, it was found that the reaction was effected by refluxing in glacial acetic acid. Other Lewis acids and bases either cleaved the molecule or had no effect upon it. The course of the rearrangement could be followed by treating sequential aliquots of the glacial acetic acid solution with dilute alkali and noting the appearance of the characteristic blue color of indophenols. The results of these studies will be reported at a later date.

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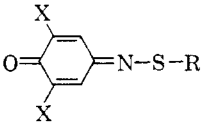
TABLE I

QUINONE SULFENIMINES



				Analysis							
				Calcd.				Found			
X	R	M.P.	Compd.	C	H	N	S	C	H	N	S
H	C_6H_5	97	$C_{12}H_9NOS$	67.0	4.2	6.5	14.9	67.0	4.2	6.8	15.0
Cl	$CH_2C_6H_5$	127–128	$C_{13}H_9Cl_2NOS$	52.4	3.0	4.7	10.7	52.2	3.3	—	10.9
Cl	C_6H_5	208	$C_{12}H_7Cl_2NOS$	50.7	2.5	4.9	11.3	50.7	2.4	5.1	11.9
Cl	2-Acetamidophenyl	243–246	$C_{14}H_{10}Cl_2N_2O_2S$	49.3	2.9	8.2	9.4	48.9	3.0	—	—
Cl	2-Benzimidazolyl	152–154	$C_{13}H_6Cl_2N_2OS_2 . ^1/_2H_2O$	44.6	2.0	8.0	18.3	44.6	2.1	—	18.6
Br	$C_2H_5OC(S)$—	170–173	$C_9H_7Br_2NO_2S_2$	28.1	1.8	3.6	16.6	28.6	1.9	4.1	16.5

EXPERIMENTAL

A solution of 0.01 mole of the appropriate *N*-chloro-*p*-quinoneimine in 3 ml. of dioxane was added to 0 01 mole of thiol in 10% sodium carbonate, cooled in an ice bath. If necessary, a small amount of dioxane was added to the thiol to ensure complete solution. A deep red precipitate immediately formed and was filtered and dried. It was recrystallized from ethanol-water or dioxane-water.

Table I lists the compounds prepared.

One hundredth mole of sulfenimine (2,6-dichloroquinone sulfenimine) was dissolved in 100 ml. of glacial acetic acid and kept at reflux temperature for 30 min. After cooling the solution was poured into ice water and the resulting precipitate was filtered. A portion of the solid thus obtained was treated with 10% sodium carbonate to give a blue-green solution which turned to deep blue on standing.

The infrared spectrum was obtained in a Perkin-Elmer double beam recording spectrophotometer.

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1,2,4-Triphenylbenzene

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1,2,4-Triphenylbenzene has been reported to melt at 109°,[1] 119–120°,[2] 99.5–100° and 119.5–120°,[3] and 101.5–102°.[4] Aside from products obtained in degradative studies, it has been prepared by reaction of 3,4-diphenyl-4-hydroxy-2-cyclopentenone (I) with styrene, decarbonylation and dehydrogenation;[1,3,4] by reaction of I with phenylacetylene;[3] and has been reported to result from trimerization of phenylacetylene in the presence of bis(triphenylphosphino)nickel dicarbonyl.[1]

We have synthesized this compound by the following diene reactions; 3,4-diphenylthiophene-1,1-dioxide and phenylacetylene; 2,5-diphenylthiophene-1,1-dioxide and phenylacetylene; and α-acetoxystyrene with 3,4-diphenylthiophene-1,1-dioxide, as well as by the reported[1] reaction of styrene with I. All gave the same product, m.p. 100°. This was converted to the form melting at 119–120° by seeding a melt with a sample kindly provided by Dr. A. Halleux, as has been observed by other investigators.[2,3]

The trimerization of phenylacetylene[1] was repeated, and produced the substance melting at 109°. Mixed melting point with the 100° compound was 100–107.8°. The infrared spectra of these two compounds were almost identical, with the exception of a strong band at 952 cm.$^{-1}$, a shoulder at 689 cm.$^{-1}$, and several weaker bands shown by the 109°, but not by the 100° compound. The ultraviolet spectra, however, showed marked differences except for a common λ_{max} of 258 mμ, the 109° material showing additional maxima at 280 and 335 mμ and a shoulder at 315 mμ.

These spectral differences suggested the presence of unsaturation in the 109° substance. This was confirmed by rapid decolorization of potassium permanganate in acetone at room temperature; the 100° compound is inert to permanganate in refluxing acetone.

The 109° material thus cannot be 1,2,4-triphenylbenzene. The similarity of the infrared spectra, the ultraviolet spectra, and analysis, however, permit the possibility that it is a complex of 1,2,4-triphenylbenzene with a related phenylacetylene derivative. Its ability to survive chromatographic purification does not eliminate this possibility.

The available evidence confirms the conclusion[2,3] that 1,2,4-triphenylbenzene exists in two crystalline forms, melting at 100° and 119–120°.

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