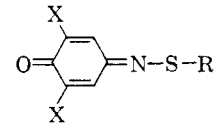
TABLE I

QUINONE SULFENIMINES



X	R	M.P.	Compd.	Analysis Calcd. C	H	N	S	Found 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	$C_{13}H_6Cl_2N_2OS_2 \cdot {}^1/_2H_2O$	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°.

(1) J. D. Rose and F. S. Statham, *J. Chem. Soc.*, 69 (1950).
(2) A. Halleux and C. Hoogzand, private communication (1957).
(3) W. Herz and E. Lewis, *J. Org. Chem.*, **23**, 1646 (1958).
(4) T. L. Jacobs and M. H. Goodrow, *J. Org. Chem.*, **23**, 1653 (1958).

EXPERIMENTAL[5]

1,2,4-Triphenylbenzene. Preparation from 3,4-diphenylthiophene-1,1-dioxide. A mixture of 1.0 g. (0.0037 mole) 3,4-diphenylthiophene-1,1-dioxide[6] and 1.0 g. (0.0098 mole) of phenylacetylene was slowly heated to 135°, at which point a sudden vigorous evolution of sulfur dioxide occurred. After 1 hr. at 140–150° excess phenylacetylene was removed under reduced pressure, the residue dissolved in 1:1 benzene–petroleum ether (b.p. 30–60°) and passed through a column of activated alumina. Solvent was removed, the product dissolved in petroleum ether, chromatographed on alumina, and eluted with 1:4 benzene–petroleum ether The oily product was taken up in a small quantity of petroleum ether, from which it crystallized very slowly. After 19 days, 71.5 mg. (6.3%) of white granules, m.p. 97.5–98.5°, were collected. After two recrystallizations from methanol, fine white needles were obtained, m.p. 99.1–99.6°.

A very low yield of the same compound was obtained by refluxing 1.07 g. (0.0040 mole) 3,4-diphenylthiophene-1,1. dioxide and 0.71 g. (0.0044 mole) α-acetoxystyrene[7] in 5 ml. xylene for 4 hr., acidification, and repeated chromatographic purification.

1,2,4-Triphenylbenzene. Preparation from 2,5-diphenylthiophene-1,1-dioxide. A mixture of 0.461 g. (0.00172 mole) 2,5-diphenylthiophene-1,1-dioxide,[8] and 1.06 g. (0.0104 mole) phenylacetylene were heated in a xylene vapor bath for 11 hr.; sulfur dioxide was evolved. The solution was diluted with petroleum ether, chromatographed on alumina and eluted with 1:4 benzene–petroleum ether. Solvent removal left 0.238 g. (45.3%) of white needles, m.p. 100°.

The infrared spectra of these three materials, as well as those of a sample prepared from styrene and 3,4-diphenyl-4-hydroxy-2-cyclopentenone[1] and a sample of the 119° form supplied by Dr. A. Halleux, were identical. The principal absorption bands in carbon tetrachloride solution were at 3040, 3010, 1940(w), 1875(w), 1800(w), 1750(w), 1670(w), 1600, 1575(w), 1490, 1472(s), 1440, 1385, 1177(w), 1072, 1027, 1008, 911, 895, 837, and 698(vs) cm.$^{-1}$ A supercooled melt showed, in addition, bands at 779, 756, and 742 cm.$^{-1}$ The ultraviolet spectrum in cyclohexane showed a minimum at 229 mμ (log ε 4.31), λ_{max} 248 mμ (log ε 4.54), an inflection at 270 mμ (log ε 4.39), and very low absorbance beyond 320 mμ.

Phenylacetylene trimer (?) The procedure of Rose and Statham[1] gave the 109° material in 1.4% yield; chromatographic purification of the residues, using the same procedure as used for 1,2,4-triphenylbenzene, provided an additional 7.1%. The infrared spectrum showed all of the bands of 1,2,4-triphenylbenzene at somewhat lower absorbance, except for a stronger 1490 cm.$^{-1}$; in addition, it absorbed strongly at 952 and 689 cm.$^{-1}$ and had weak bands at 1298, 1260, 1098, and 981(vw) cm.$^{-1}$ The ultraviolet spectrum in cyclohexane showed λ_{max} 248 mμ (log ε 4.40),[9] 280 mμ (log ε 4.32), and 335 mμ (log ε 3.90), with minima at 232 mμ (log ε 4.28), 266 mμ (log ε 4.30), and 333 mμ (log ε 3.89) and an inflection at 315 mμ (log ε 4.11).

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(5) All melting points are corrected. Infrared spectra were determined on a Perkin-Elmer Model 21 instrument with sodium chloride prism and ultraviolet spectra on a Carey Recording Spectrophotometer, Model 11.

(6) H. J. Backer, C. C. Bolt, and W. Stevens, *Rec. trav. chim.* **56,** 1063 (1937), modified by use of peroxyacetic acid in place of peroxybenzoic acid.

(7) W. M. Quattlebaum and C. A. Noffsinger, Brit. Pat. **615,521,** Jan. 7, 1949.

(8) J. L. Melles and H. J. Backer, Rec. trav. chim., **72,** 319 (1953).

(9) Assuming molecular weight 306.

Pyrido[3,2-b][1,4]benzothiazine (1-Azaphenothiazine)

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Due to the importance of phenothiazine and its derivatives in medicinal chemistry it seemed of interest to synthesize the phenothiazine nucleus incorporating a nitrogen atom in one of the benzenoid rings. A recent publication by Yale and Sowinski[2] describes the preparation of 1-azaphenothiazine (I) by the Smiles rearrangement of 2′-(3-nitro-2-pyridylthio) acetanilide. Other 3- or 4-aza[3,4] and 4,6-diazaphenothiazines[5] are known. This paper is concerned with the direct thionation[6] of 2-anilinopyridine (II) to give I.

Heating II with sulfur in the presence of iodine catalyst affords a rapid method for obtaining I. Attempts to obtain I using other cyclization methods analogous to those reported for phenothiazine, such as: heating phenol and 2-aminopyridine with sulfur and iodine[7] or aluminum chloride; the thionation of II with aluminum chloride catalyst[8]; or directly with sulfuryl chloride[9] failed.

With picric acid I forms a *mono*picrate but a hydrochloride of definite composition could not be isolated. Oxidation of I with hydrogen peroxide in an attempt to form the 5-oxide or 5,5-dioxide regenerated II. Acylation with acetic anhydride gives the 10-acetyl derivative (III).

Preliminary attempts to alkylate I by the usual methods employed for phenothiazine (alkyl halide preceded by treatment with sodamide in a hydrocarbon solvent) were not successful. The only identifiable product obtained was II, which could arise by dethionation of I. Since dethionation of phenothiazine (with copper powder) leads to the formation of carbazole,[10] the product derived from I in such a case should be 9-pyrid[2,3-*b*]indole (α-carboline).[11] This compound was not identified in the reaction products of I with sodamide or copper. Raney nickel has been reported to remove the

(1) This study was initiated by a grant from the Institute for Muscle Research, New York, N.Y.

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(3) T. Takahashi and E. Yoshi, *Pharm. Bull. (Tokyo)*, **2,** 382 (1954).

(4) (a) T. Takahashi and Y. Maki, *Yakugaku Zasshi*, **77,** 485 (1957); *Chem. Abstr.*, **51,** 14738a (1957). (b) V. A. Petrow and E. L. Rewald, *J. Chem. Soc.*, 591 (1945).

(5) Y. Maki, *Yakugaku Zasshi*, **77,** 862 (1957); *Chem. Abstr.*, **52,** 1174b (1958).

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(7) Swiss patent **204,521**; *Chem. Abstr.*, **35,** 2338 (1941).

(8) F. Ackermann, D. R. P. **222,879**; *Chem. Abstr.*, **5,** 210 (1911).

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(10) A. Goske, *Ber.*, **20,** 232 (1887).

(11) R. Robinson, *J. Chem. Soc.*, 629 (1924).