Anal. Calcd. for $C_{11}H_{16}O_2S_2$: C, 54.08; H, 6.60; S, 26.25. Found: C, 53.94; H, 6.57; S, 25.99.

B. Preparation from *p*-Toluenesulfonyl Iodide.[17]—Silver *t*-butyl mercaptide[18] (3.3 g., 16.7 mmoles) was added slowly to a solution of 4.5 g. (16.0 mmoles) of *p*-toluenesulfonyl iodide[17] in 25 ml. of dry benzene. The suspension was stirred at *ca.* 25° for 30 min. Insoluble material then was removed by filtration and washed with benzene. The combined benzene filtrates were washed twice with 10 ml. of 5% aqueous sodium sulfite and twice with 10 ml. of water and were evaporated under reduced pressure. The amorphous yellow solid left (3.0 g.) was recrystallized from *n*-heptane to give 1.3 g. of thiolsulfonate **5** (34%), m.p. 65–67°, identical with **5** from A (mixture melting point, infrared spectrum).

Reaction of 2-Mercaptoethylamine. A. With the Triisopropylphenyl Thiolsulfonate 3.—Thiolsulfonate **3** (3.0 g., 6 mmoles)[1c] and 2-mercaptoethylamine (0.462 g., 6 mmoles) were stirred in ethanol (250 ml.) for 1 hr. Ethanol was removed, and the residue was suspended in water (150 ml.) and benzene (75 ml.). Iced base (0.40 g. of potassium hydroxide in 30 ml. of water) was added to neutralize the sulfinic acid. The benzene layer was separated, washed with water (100 ml.), and filtered into an iced mixture of 1.7 ml. of 12 *N* hydrochloric acid in 25. ml. of water. Two more benzene extracts of the alkali layer were added to the acid. 2-Aminoethyl 2,4,6-triisopropylphenyl disulfide hydrochloride (**4**) precipitated: m.p. 203–204° dec., yield 1.35 g. (65% conversion; 100% yield based on isolation of 2,4,6-triisopropylphenyl disulfide from the benzene).

Anal. Calcd. for $C_{17}H_{30}ClNS_2$: C, 58.67; H, 8.69; N, 4.03; S, 18.44. Found: C, 58.97; H, 8.72; N, 4.13; S, 18.58.

The attempts to obtain **4** using 2-mercaptoethylamine hydrochloride (**1**) were done using a procedure usually successful for preparing amino disulfides,[4,6–8] *i.e.*, by allowing reaction to occur, then making the mixture alkaline, extracting the free base into organic solvent, and subsequently converting it to the hydrochloride. Only minor conversion to **4** occurred and as much as 74% of thiolsulfonate **3** was recovered.

B. With the *t*-Butyl Thiolsulfonate 5.—A solution of 2.44 g. (10 mmoles) of *t*-butyl *p*-toluenethiolsulfonate (**5**), 1.13 g. (10 mmoles) of 2-mercaptoethylamine hydrochloride (**1**), and 0.56 g. (10 mmoles) of potassium hydroxide in 75 ml. of ethanol was let stand for 3 hr. and then was evaporated under reduced pressure. The residue was dissolved in 25 ml. of water containing 12 mmoles of sodium bicarbonate (to neutralize sulfinic acid) and was extracted with three 25-ml. portions of methylene chloride. The combined organic extracts were washed with 12 mmoles of dilute hydrochloric acid and twice with water. Evaporation of the aqueous extracts under vacuum and washing of the product with absolute ether gave 1.34 g. of 2-(*t*-butyldithio)ethylamine hydrochloride (**6**, 67%), m.p. 195° dec. (lit.[4] m.p. 195° dec.), infrared spectrum identical with that of authentic **6**.[4]

The thiolsulfonate **5** and the thiol salt **1** did not react after 7 days in ethanol (recovery of **5**, 90%). Use of the usual conditions for the reaction[4,6–8] also resulted in only 90% recovery of **5**.

Reaction of Thiolsulfonates with Benzenethiol by Larger Scale Isolation.—The procedure used with phenyl benzenethiolsulfonate also illustrates that used with thiolsulfonates **3** and **5**, as reported in Table IB; all experiments were done at room temperature.

Benzenethiol (1.10 g., 10 mmoles) and 2.50 g. (10 mmoles) of phenyl benzenethiolsulfonate were allowed to react in 25 ml. of dry ether at 25° for 1 hr. Ether and unreacted thiol then were distilled (without heating) at 1 mm. into a Dry Ice chilled trap. Iodine titration of the trap contents showed the presence of 69% of the original benzenethiol. An ether solution of the undistilled residue was washed with aqueous sodium carbonate and evaporated to a solid which, recrystallized, amounted to 1.59 g. of phenyl benzenethiolsulfonate (64% recovery). When 1 molar equiv. of pyridine was used, the undistilled residue proved to be phenyl disulfide, yield (recrystallized) 1.99 g. (91%), m.p. 57–59° (infrared spectrum identical with that of authentic material, m.p. 59–60°); titration of the distillate showed the presence of 1% of benzenethiol.

For isolation of phenyl *t*-butyl disulfide (**7**), the combined undistilled residues from the last three experiments of Table IB were dissolved in ether. The solution was washed with 5% hydrochloric acid and 5% aqueous sodium bicarbonate. Evaporation gave a yellow oil (5.5 g.), which was distilled using a 7 mm. × 21 cm. spinning-band column. The yield of **7** was 3.0 g. (59%, based on benzenethiol consumed); b.p. 106–106.5° (3 mm.), n^{25}_{D} 1.5708, d^{25}_{4} 1.0408, M_D 62.65 (calcd. M_D 60.38[19]; exaltation, 2.27).

Anal. Calcd. for $C_{10}H_{14}S_2$: C, 60.56; H, 7.12. Found: C, 60.59; H, 7.10.

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[17] Based on the procedures of ref. 12 and of D. T. Gibson, C. J. Miller, and S. Smiles, *J. Chem. Soc.*, **127**, 1821 (1925).

[18] Kindly prepared (*cf.* ref. 17) by W. B. Lacefield. Sodium acetate trihydrate (137 g.) and *t*-butyl mercaptan (90 g.) in water (500 ml.) were added to silver nitrate (170 g.) in water (500 ml.). The precipitate was washed with water, ethanol, and ether, and was dried at 0.1 mm.

[19] Calculated using the value of 7.80 for the atomic refraction of divalent sulfur [W. Strecker and R. Spitaler, *Ber.*, **59**, 1775 (1926)].

Thioureas and Isothiuronium Salts. Monomeric Derivatives

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An attempt has been made to characterize N-vinylthiourea. N-(*p*-Vinylphenyl)thiourea and its N′-methyl- and N′,N′-dimethyl derivatives were prepared. Reaction of the thiourea with methyl iodide afforded S-methyl-N-(*p*-vinylphenyl)isothiuronium iodide and its N′-methyl and N′,N′-dimethyl derivatives, respectively.

As part of a program designed to synthesize potential antiradiation agents, it was decided to prepare polymeric derivatives of thioureas and isothiuronium salts containing structural features similar to S-2-aminoethylisothiuronium bromide hydrobromide (AET) or its propyl analog (APT). Both of these compounds are known to possess radiation-protection properties.[2] The usefulness of a drug is closely related to its rate of excretion and rate of metabolism in the body. Placing the functional groups in a polymeric molecule would be expected to lessen these factors.

The only thioureas reported in the literature containing an unsaturated center are those containing allylic groups. However, owing to chain-transfer properties of such moieties, difficulties are normally encountered in preparing such high molecular weight polymers.

Very few unsaturated derivatives of isothiuronium salts have been reported. Cavallito, *et al.*,[3] prepared benzoylvinylisothiuronium chloride by the addition of thiourea to phenyl ethynyl ketone in the presence of

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[1] Taken from a portion of the dissertation submitted to the faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy in chemistry, 1964.

[2] J. X. Khym, D. G. Doherty, and R. Shapira, *J. Am. Chem. Soc.*, **80**, 3342 (1958).

[3] C. J. Cavallito, C. M. Martini, and F. C. Nachod, *ibid.*, **73**, 2544 (1951).

hydrogen chloride. Fischer and Brieger[4] reported the addition of thiourea to the triple bond of phenylpropiolic acid. However, the product, a trisubstituted vinylisothiourea, was unstable and decomposed into a mercaptan and cyanamide.

N-Vinyl derivatives of thioureas have been reported by Welzel.[5a] N-Vinylthiourea, for example, was prepared by the reaction of vinyl isothiocyanate with ammonia. This compound, as well as the other N-vinyl compounds prepared, was found to be unstable in the presence of moisture. In all cases hydrolysis produced acetaldehyde and the parent amino compound.

Results and Discussion

N-Vinylthiourea was desired for reaction with β-bromoethylamine hydrobromide. The product, a derivative of S-2-aminoethylisothiuronium bromide hydrobromide, would be expected to be capable of polymerization.

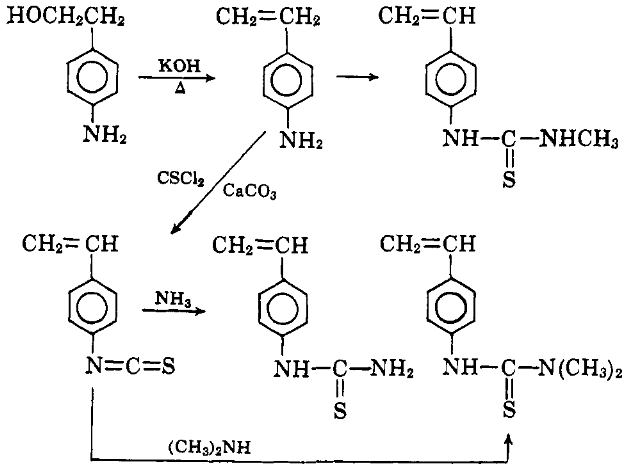
The procedure of Welzel[5] was followed in the preparation of the alleged N-vinylthiourea. However, although the product was reported to melt at 109°, repetition of the procedure yielded a compound melting at 118–120°. Furthermore, precipitation of this product from a tetrahydrofuran or ethyl acetate solution by addition to benzene gave colorless platelets, m.p. 112–115°. The solubility properties of the two compounds were found to be different. A comparison of the infrared spectra revealed large differences which could not be ascribed to polymorphism. There is an indication from the infrared and n.m.r. spectra that these compounds are tautomers but no definite assignments can be made at this time.

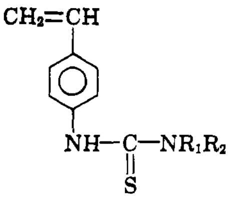
To overcome the possibility of tautomerism, thioureas containing a phenyl group inserted between the vinyl and thiourea linkages were synthesized. Such derivatives would be expected to exhibit a greater degree of stability towards hydrolytic conditions than N-vinylthiourea.

There are two principal methods in which such derivatives may be synthesized. The reaction of *p*-aminostyrene with an isothiocyanate will yield a symmetrically disubstituted thiourea. The mono- or trisubstituted compound may be prepared by reacting *p*-vinylphenyl isothiocyanate with either ammonia or a secondary amine, respectively. A second method[6,7] available for the synthesis of isothiocyanates employs thiophosgene.

p-Aminostyrene reacted with methyl isothiocyanate to yield N-(*p*-vinylphenyl)-N′-methylthiourea (I). The reaction of *p*-vinylphenyl isothiocyanate with ammonia or with dimethylamine yielded N-(*p*-vinylphenyl)thiourea (Ia) or N-(*p*-vinylphenyl)-N′,N′-dimethylthiourea (Ic), respectively. The reactions involving the preparation of the isothiocyanate and the thioureas are outlined in Scheme I.

SCHEME I

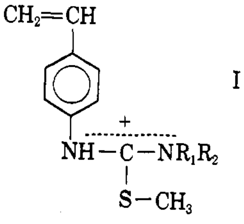




Ia, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = CH_3$
c, $R_1 = R_2 = CH_3$

The vinyl group appeared to have a deactivating effect upon the reactivity of the thioureas towards alkylating agents. When N-(*p*-vinylphenyl)-N′-methylthiourea was treated with benzyl chloride or with *n*-butyl bromide, satisfactory reaction did not take place. Nothing could be isolated from the reaction with β-bromoethylamine hydrobromide. However, reaction of N-phenyl-N′-methylthiourea with the above compounds yielded the desired products in high yield.

Alkylation occurred without difficulty when a more reactive halide was used. The three isothiuronium salts, IIa–c, all stable compounds, were prepared by the reaction of methyl iodide and the corresponding thiourea.



II

IIa, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = CH_3$
c, $R_1 = R_2 = CH_3$

The solubility properties of both the thioureas and isothiuronium salts showed a trend expected of compounds exhibiting hydrogen bonding. As alkylation of the thioureas was increased, the solubilities of these compounds in organic solvents also increased. However, the solubilities of the isothiuronium salts in water increased with decreased alkylation.

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[4] E. Fischer and W. Brieger, *Ber.*, **47**, 2469 (1914).

[5] (a) G. Welzel, Ph.D. Thesis, Albert-Ludwigs Universitat zu Freiberg i. Br. (Germany), 1960; *Makromol. Chem.*, **31**, 230 (1959) (since the manuscript is not readily available, detailed procedures may be obtained on request from the senior author). (b) Experimental details are not to be found in the published manuscript.

[6] "Methoden der Organischen Chemie (Houben-Weyl)," Vol. IX, Georg Thieme Verlag, Stuttgart, 1955, p. 867.

[7] S. J. Assony in "Organic Sulfur Compounds," N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, p. 326 ff.

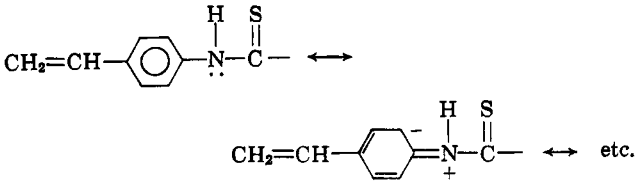
TABLE I

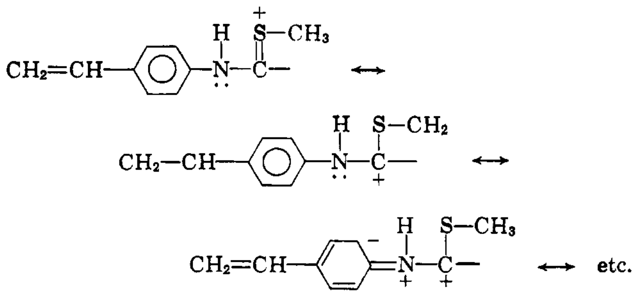
INFRARED[a] AND N.M.R. SPECTRA[b]

Structure	Frequency[c] A	Frequency[c] B	Frequency[c] C	Frequency[c] D	N-CH$_3$[d]	S-CH$_3$[d]
Ia	3450–3000 (vs)	1530 (s)	1623 (s)	1322 (m)	...	...
Ib	3270–3100 (s)	1555 (vs)	1618 (s)	1333 (s)	6.99[e]	...
Ic	3270 (m)	1535 (s)	...	1325 (vs)	6.74[e]	...
IIa	3230–3000 (s)	1600 (vs)	1620 (vs)	...	...	7.22[f]
IIb	3200–2850 (vs)	1600 (vs)	1615 (vs)	...	6.65[f]	7.32[f]
IIc	3100–2870 (m)	1600 (vs)	...	...	6.52[f]	7.63[f]

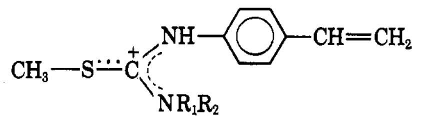
[a] All values given in cm.$^{-1}$. [b] All values given in τ. [c] A = NH stretching frequency, B = NHAr deformation frequency, C = NHR or NH$_2$ deformation frequency, and D = C=S stretching frequency. [d] Singlet. [e] Taken at 26° in acetonitrile as the solvent; tetramethylsilane used as an internal solvent standard. [f] Taken at 126° in deuterium oxide as the solvent; 3-(trimethylsilyl)propanesulfonic acid sodium salt (Eastman Organic Chemicals) used as an internal standard. The trimethylsilyl group was assigned a value of τ 10.

In the infrared region of the spectrum the change in absorption for the NH deformation when going from the thiourea to the isothiuronium salt should be noted. This change is due chiefly to changes in π-electron structure.[8] The shift to higher frequency in comparing the thiourea with the isothiuronium salt appears to be slight for the NH-alkyl (or NH$_2$) as opposed to the change for the NHAr (see Table I). This is understandable when one considers the electronic structure of the compounds involved.[9] There is π-overlap between the nitrogen atom and the aryl group in the thiourea, thereby giving rise to a positively charged nitrogen atom, as illustrated below. However, if in the isothiuronium salt this same overlap is developed, a high-energy species resulting from the two positive charges on adjacent atoms will result. Therefore, resonance interaction between the nitrogen atom and the aryl group is greatly diminished and the change in the NHAr deformation relative to the NH-alkyl is not as great as that for the corresponding thioureas.





A trend may also be noted in the n.m.r. spectra of the isothiuronium salts. As methylation of the nitrogen atom was increased, the S-methyl group showed an increased degree of shielding. This may be taken as an indication that the isothiuronium cation has its positive charge delocalized over the sulfur atom as well as the two nitrogen atoms with the carbon atom in between. This is illustrated below. It should be recalled that Lecher[10] had suggested that such an electron distribution should be considered. The trend may be explained in the following way. When R$_1$ = H and R$_2$ = CH$_3$, the electropositive nature of the methyl group should, to a small degree, aid in lessening the positive charge on the carbon atom. Thus, the electrons on the sulfur atom could be capable of offering a correspondingly greater degree of shielding for the S-methyl protons. This could take place to an even greater degree if both R$_1$ and R$_2$ are methyl.



Experimental[11,12]

Vinyl Isothiocyanate.—The procedure of Welzel[5a] was followed. From 87.8 g. (0.43 mole) of β-bromoethylamine hydrobromide in aqueous ethylene chloride solution and 100 g. (0.87 mole) of thiophosgene was obtained 52.4 g. (75.0%) of β-bromoethyl isothiocyanate, b.p. 97–100° (11–12 mm.), $n^{25.5}\text{D}$ 1.5608 (lit.[5a] 81.2%, b.p. 93–94° at 12 mm. by the same procedure).

From 137 g. (0.83 mole) of this product and 83.5 g. (0.83 mole) of triethylamine to which had been added 6 g. of dinitrobenzene was obtained 43 g. (61%) of vinyl isothiocyanate, b.p. 48° (100 mm.), $n^{26}\text{D}$ 1.5175 (lit.[5a] 61%, b.p. 46–47° at 100 mm. by the same procedure).

N-Vinylthiourea.—The procedure of Welzel[5a] was followed. Vinyl isothiocyanate (6 g., 0.06 mole) was added to 100 ml. of anhydrous ether. The solution was cooled in an acetone bath kept at −50° with Dry Ice. Anhydrous, gaseous ammonia was passed into the stirred solution causing precipitation of a white powder after about 10 min. of reaction. The addition of ammonia was continued for an additional 5 min.

The solution was allowed to reach room temperature causing the crystals that had previously appeared to redissolve in the solution. Evaporation of the major portion of the solvent afforded crystals of a substance analyzing correctly for N-vinylthiourea. The crystals were washed with cold petroleum ether and dried *in vacuo* over potassium hydroxide to yield material melting at 100–120°. The best melting point obtained for this compound was 118–120° (lit.[5a] m.p. 109° by the same procedure).

Anal. Calcd. for $C_3H_6N_2S$: C, 35.27; H, 5.92; N, 27.42; S, 31.39. Found: C, 35.50; H, 6.03; N, 27.64; S, 31.20.

Precipitation of an ethyl acetate or tetrahydrofuran solution of the compound from benzene gave a substance of different physical properties. The melting point was lowered to 112–115°. All attempts to recrystallize the compound were unsuccessful.

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(8) W. Kutzelnigg and R. Mecke, *Spectrochim. Acta*, **17**, 530 (1961).

(9) The authors wish to thank a referee for his helpful comments.

(10) H. Z. Lecher and K. Gubernator, *J. Am. Chem. Soc.*, **75**, 1087 (1953).

(11) All melting points are uncorrected.

(12) Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

p-Aminostyrene.—p-Aminostyrene was prepared by the dehydration of p-aminophenylethyl alcohol, using the procedure of Sabetay and Tchang,[13] in a yield of 46 g. (77.3%), b.p. 80° (2.5 mm.), $n^{21}\text{D}$ 1.6297 (lit.[13] b.p. 98–100° at 4 mm., $n^{21.5}\text{D}$ 1.6250).

Anal. Calcd. for C_8H_9N: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.61; H, 7.76; N, 11.75.

An ultraviolet absorption spectrum of the compound indicated values of λ_{max} 274 mμ (ϵ 16,490).

An n.m.r. spectrum of the compound was taken of the neat liquid calibrated against tetramethylsilane as an internal standard. The values (τ) indicated were as follows[14]: NH_2, 6.60 (singlet); H_a, 5.07 (doublet); H_b, 3.52 (quadruplet); H_c, 4.62 (doublet); J_{ab} = 10.3 c.p.s., J_{bc} = 1.66 c.p.s.; aromatic protons, 6.58 (center of A_2X_2 type quadruplet); $J_{\alpha\beta}$ = 8.3 c.p.s.

p-Vinylphenyl Isothiocyanate.—p-Aminostyrene (11.9 g., 0.1 mole), calcium carbonate (15 g., 0.15 mole), and dinitrobenzene (0.1 g.) were added to the flask containing 1,2-dichloroethane (75 ml.) and water (15 ml.). Thiophosgene (11.5 g., 0.1 mole) was added dropwise to the rapidly stirred mixture. The solution, cooled in an ice bath, was stirred for 5 hr. Filtration of the mixture yielded two layers. The organic phase was dried over anhydrous magnesium sulfate, stripped of solvent, and vacuum distilled to yield p-vinylphenyl isothiocyanate, an off-white liquid, in a yield of 6 g. (37.3%), b.p. 129–130° (12 mm.), 77° (0.25 mm.), $n^{25}\text{D}$ 1.6792.

Anal. Calcd. for C_9H_7NS: C, 67.05; H, 4.38; N, 8.69; S, 19.89. Found: C, 67.21; H, 4.67; N, 8.53; S, 19.76.

An infrared spectrum of the compound showed very heavy, broad absorption at 2110 cm.$^{-1}$ (—N=C=S). An ultraviolet absorption spectrum of the compound indicated values of $\lambda_{max}^{CH_3CN}$, mμ (ϵ): 299 (28,720), 286 (33,290), 281 (sh) (26,970), 274 (sh) (23,450), 238 (15,360), 221 (24,150), 214 (26,970). An n.m.r. spectrum of the compound was taken of the neat liquid calibrated against tetramethylsilane as an internal standard. The values (τ) indicated were as follows[14]: H_a, 5.05 (doublet); H_b, 3.77 (quadruplet); H_c, 4.72 (doublet); J_{ab} = 9.5 c.p.s., J_{bc} = 15.2 c.p.s.; aromatic protons, 3.35 (center of quadruplet); $J_{\alpha\beta}$ = 7.6 c.p.s.

N-(p-Vinylphenyl)thiourea (IIa).—p-Vinylphenyl isothiocyanate (5.0 g., 0.03 mole) was added to *ca.* 25 ml. of ether. Ammonia was bubbled into the solution at a moderate rate for about an hour. The ether was evaporated and the thiourea was collected as an impure solid, m.p. 134–138°, yield 4.0 g. (72.3%). Recrystallization to constant melting point from benzene yielded an analytical sample, m.p. 138.5–140°.

Anal. Calcd. for $C_9H_{10}N_2S$: C, 60.64; H, 5.65; N, 15.72; S, 17.99. Found: C, 60.36; H, 5.88; N, 15.49; S, 18.20.

An ultraviolet absorption spectrum of the compound indicated values of λ_{max}^{EtOH}, mμ (ϵ): 280 (17,080), 255 (sh) (14,170).

N-(p-Vinylphenyl)-N′-methylthiourea (IIb).—p-Aminostyrene (18 g., 0.15 mole) was dissolved in 25 ml. of methanol. To the solution was added methyl isothiocyanate (11.0 g., 0.15 mole). The solution was refluxed with stirring for a period of 15 min. Upon cooling, 23.5 g. (81.0% yield) of colorless crystals, m.p. 124–128°, was isolated. The thiourea was recrystallized to a constant melting point of 132–133.5° from benzene.

Anal. Calcd. for $C_{10}H_{12}N_2S$: C, 62.46; H, 6.29; N, 14.57; S, 16.68. Found: C, 62.78; H, 6.40; N, 14.42; S, 16.52.

An ultraviolet absorption spectrum of the compound indicated values of λ_{max}^{EtOH}, mμ (ϵ): 272 (29,440).

N-(p-Vinylphenyl)-N′,N′-dimethylthiourea (IIc).—p-Vinylphenyl isothiocyanate (6 g., 0.03 mole) was dissolved in 25 ml. of ether. The solution, cooled in an ice bath, was treated with anhydrous, liquid dimethylamine (15 g., 0.33 mole). Vigorous reaction took place immediately. The slurry was stirred for 0.5 hr. affording a quantitative yield of the thiourea, m.p. 156–161°. Recrystallization of the compound from benzene yielded an analytical sample, m.p. 159.5–161°.

Anal. Calcd. for $C_{11}H_{14}N_2S$: C, 64.04; H, 6.84; N, 13.58; S, 15.54. Found: C, 64.00; H, 7.09; N, 13.57; S, 15.38.

An ultraviolet absorption spectrum of the compound indicated values of λ_{max}^{EtOH}, mμ (ϵ): 256 (22,400), 283 (sh) (11,980).

N-(p-Vinylphenyl)-S-methylisothiuronium Iodide (IIIa).—N-(p-Vinylphenyl)thiourea (3.6 g., 0.02 mole) was treated with methyl iodide (2.8 g., 0.02 mole) in 25 ml. of benzene. Hydroquinone (0.1 g.) was added as a polymerization inhibitor. The solution was refluxed with stirring for 15 min. Upon cooling to room temperature, 5.5 g. (85.9% yield) of the crude salt, m.p. 148–158°, was isolated. Difficulties were encountered in attempts to recrystallize the compound from a variety of organic solvents. The salt was purified by the following procedure. The yellow solid, in powder form, was leached with refluxing benzene for about 5 min. Filtration of the mixture afforded a light cream-colored solid, m.p. 154–159°. The salt was further purified by dissolution in a small quantity of warm chloroform, making certain that solution was complete. Benzene, in a quantity of about 4–5 times the amount of chloroform used, was then added to the solution. The resultant solution was evaporated until faint turbidity appeared. It was then allowed to cool slowly to room temperature. The crystals thus isolated had a melting point of 156.5–159°. Recrystallization of this compound from chloroform gave an analytical sample, m.p. 163.5–164.5°.

Anal. Calcd. for $C_{10}H_{13}IN_2S$: C, 37.51; H, 4.09; N, 8.75; S, 10.01. Found: C, 37.43; H, 4.10; N, 8.85; S, 10.22.

When the reaction was carried out in isopropyl alcohol, crude material, m.p. 155–175°, was isolated which defied purification. An ultraviolet absorption spectrum of the compound indicated values of λ_{max}^{EtOH}, mμ (ϵ): 274 (33,660).

N-(p-Vinylphenyl)-N′,S-dimethylisothiuronium Iodide (IIIb).—N-(p-Vinylphenyl)-N′-methylthiourea (4.8 g., 0.025 mole) was treated with methyl iodide (3.6 g., 0.025 mole) in 40 ml. of benzene. Hydroquinone (0.1 g.) was added as a polymerization inhibitor. The solution was refluxed with stirring for 15 min. The salt separated as an oil. Upon cooling, the salt solidified to an off-white precipitate, yield 8.0 g. (95.5%), m.p. 151–161°. An analytical sample, m.p. 162–163.5°, was obtained by repeated recrystallization from ethanol.

Anal. Calcd. for $C_{11}H_{15}IN_2S$: C, 39.53; H, 4.52; N, 8.38; S, 9.59. Found: C, 39.78; H, 4.62; N, 8.31; S, 9.88.

An ultraviolet absorption spectrum of the compound indicated values of λ_{max}^{EtOH}, mμ (ϵ): 274 (18,600).

N-(p-Vinylphenyl)-N′,N′,S-trimethylisothiuronium Iodide (IIIc).—N-(p-Vinylphenyl)-N′,N′-dimethylthiourea (4.0 g., 0.02 mole) was treated with methyl iodide (2.8 g., 0.02 mole) in 25 ml. of isopropyl alcohol. Hydroquinone (0.1 g.) was added as a polymerization inhibitor. The solution was refluxed with stirring for 15 min. Within minutes of the start of the reaction, a precipitate developed. The yield of the product was 6.5 g. (95.6%), m.p. 163–171°. Repeated crystallizations of the compound from ethanol yielded an analytical sample, m.p. 172–173.5°.

Anal. Calcd. for $C_{12}H_{17}IN_2S$: C, 41.39; H, 4.92; N, 8.04; S, 9.21. Found: C, 41.53; H, 4.99; N, 8.12; S, 9.50.

An ultraviolet absorption spectrum of the compound indicated values of λ_{max}^{EtOH}, mμ (ϵ): 303 (1505), 274 (sh) (1136).

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