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Synthesis of Some New Substituted Thioureas

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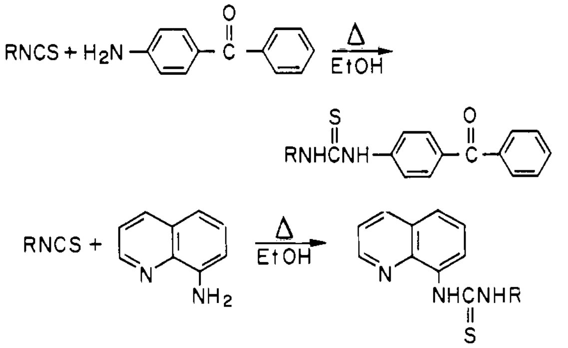
New thiourea derivatives have been synthesized by reacting aryl isothiocyanates with 4-aminobenzophenone and with 8-aminoquinoline.

THE TECHNICAL literature concerned with thiourea and its derivatives is extensive (*4*). These compounds have proven useful in numerous chemical and biological applications (*2*). Of the many preparative methods which have been used for substituted thioureas (*3*), one of the most common involves the direct reaction of isothiocyanates with amines.

During an investigation in this laboratory of the synthesis of new fungicides containing the thiocarbonyl group, two series of previously unreported substituted thioureas have been prepared by reacting aromatic and substituted-aromatic isothiocyanates with 4-aminobenzophenone and with 8-aminoquinoline. Thioureas having structures I and II, respectively, were obtained; this was confirmed by elemental analysis and infrared spectroscopy. The new compounds are listed in Tables I and II.



I

II

The electronic absorption spectra, in the near ultraviolet region, of compounds 1 to 10 were measured; the relevant peak wavelengths and molar extinction coefficients are shown in Table III. These data are relevant to the photostabilities of thiourea and its derivatives (*2*), as well as to the possible photoprotectiveness of these compounds (*5*).

The fungistatic effectiveness of the compounds listed in the tables against the microorganisms *A. niger* and *C. globosum* was the following: Compd. 1, 2, 4, and 8: 1000 p.p.m. (*C. g.*); Compd. 7: 10 p.p.m. (*C. g.*), 1000 p.p.m. (*A. n.*). None of the other compounds was fungistatic at concentrations of 1000 p.p.m. or less.

Table I. 1-(4-Benzoylphenyl)-3-(Substituted) Thioureas (I)

Compd. No.	*R*	M.P., ° C.	Yield, %	Molecular Formula[a]
1	1-naphthyl	165[b]	89	$C_{24}H_{18}N_2OS$
2	2-naphthyl	169[b]	80	$C_{24}H_{18}N_2OS$
3	*m*-nitrophenyl	181[c]	95	$C_{20}H_{15}N_3O_3S$
4	*p*-nitrophenyl	204[d]	90	$C_{20}H_{15}N_3O_3S$
5	phenyl	168[c]	85	$C_{20}H_{16}N_2OS$

[a] Analysis of all compounds for C, H, N, and S was within 0.24% of the calculated values. These data have been deposited as Appendix A with the ASIS National Auxiliary Publications Service. [b] Recrystallized from benzene–*n*-hexane. [c] Recrystallized from acetone-water. [d] Recrystallized from *p*-dioxane–water.

Table II. 1-(8-Quinolyl)-3-(Substituted) Thioureas (II)

Compd. No.	*R*	M.P., ° C.	Yield, %	Molecular Formula[a]
6	1-naphthyl	176[b]	75	$C_{20}H_{15}N_3S$
7	2-naphthyl	175[c]	90	$C_{20}H_{15}N_3S$
8	*m*-nitrophenyl	180[d]	89	$C_{16}H_{12}N_4O_2S$
9	*p*-nitrophenyl	200[d]	79	$C_{16}H_{12}N_4O_2S$
10	phenyl	161[e]	91	$C_{16}H_{13}N_3S$

[a] Analysis of all compounds for C, H, N, and S was within 0.30% of the calculated values. These data have been deposited as Appendix A with the ASIS National Auxiliary Publications Service. [b] Recrystallized from benzene. [c] Recrystallized from acetone-water. [d] Recrystallized from dimethylformamide-water. [e] Recrystallized from ethanol.

EXPERIMENTAL

Melting points were determined using a Fisher-Johns apparatus, and have been corrected. Elemental analyses were performed at the microanalytical laboratory of Weiler and Strauss in Oxford.

The infrared spectra were obtained from KBr pellets with a Model 21 Perkin-Elmer spectrophotometer over the frequency range 3500 to 650 cm.$^{-1}$. The ultraviolet spectra

Table III. Electronic Spectra of Substituted Thioureas

Compd. No.	Absorption Band Maxima, mμ [Molar Extinction Coefficients × 10^{-3}]			
1[a]	293[22.7]	307[25.1]	323[25.1]	
2[a]		319[29.6]		
3[b]		304[14.8]		
4[b]		320[26.9]		
5[a]		315[28.6]		
6[b]	313[14.4]	323[14.1]	355[14.8]	
7[a]	243[40.9]	263[36.1]	332[11.3]	
8[b]	307[13.0]	323[15.8]	338[11.1]	357[5.2]
9[b]	271[17.8]	323[15.7]	342[16.9]	
10[a]	244[33.8]	270[22.9]	332[9.2]	

[a] Measured in ethanol. [b] Measured in *p*-dioxane.

were measured on a Beckman DK-1 recording instrument.

The antimicrobial effectiveness of the compounds listed in Tables I and II were evaluated, at concentrations of 10, 100, and 1000 p.p.m., by the tube dilution method (*1*). The test organisms used in these screening experiments were *Aspergillus niger*, strain USDA 215-5373.16, and *Chaetomium globosum*, strain USDA 1-42.4. The criterion of effectiveness was the absence of growth after a 48-hour (*A. niger*) or a two-week (*C. globosum*) incubation period.

The aryl isothiocyanates, the 8-aminoquinoline, and the 4-aminobenzophenone were the purest grades obtainable from commercial sources, and were used without further purification.

Preparation of 1-(4-Benzoylphenyl)-3-(Substituted)-2-Thioureas (I). A solution of 4-aminobenzophenone (0.01 mole) in absolute ethanol (50 ml.) was added dropwise with stirring to a warm solution of aryl isothiocyanate (0.01 mole) in absolute ethanol (50 ml.). The resulting mixture was heated gently on the steam bath for 2 hours; water was then added until the onset of precipitation. The precipitate which formed during subsequent cooling to room temperature was collected, washed with cold 50% aqueous ethanol, and recrystallized to constant melting point.

The following major characteristic infrared bands (cm.$^{-1}$) were common to the spectra of compounds 1 to 5: 3360–3300, m (NH stretch); 1655–1635, s (C=O stretch) ; 1605–1600, s (phenyl ring stretch); 1535, s, 1325, s (NH deformation and CN stretch); 1080, w (NCN stretch, some C=S stretch); 800–795, m (C=S stretch).

Preparation of 1-(8-Quinolyl)-3-(Substituted)-2-Thioureas (II). To a warm solution of an aryl isothiocyanate (0.01 mole) in absolute ethanol (50 ml.) was added, with stirring, 8-aminoquinoline (0.01 mole) in absolute ethanol (50 ml.). The resulting mixture was refluxed for one-half hour. The precipitate which formed on cooling was collected, washed with cold absolute ethanol, and recrystallized to constant melting point.

The following important specific absorptions (cm.$^{-1}$) were observed in the infrared spectra of compounds 6 to 10: 3200–3180, s (NH stretch); 1630–1600, m (aromatic ring stretch); 1550, vs, 1325–1310, m (NH deformation and CN stretch); 1090, m (NCN stretch, some C=S stretch); 805–795, s (C=S stretch).

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Preparation of *p*-bis(Dinitromethyl)benzene

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The application of the ter Meer reaction to the synthesis of aromatic substituted *gem*-dinitromethyl compounds is reported. The preparation of *p*-bis(dinitromethyl)benzene by this method is given.

THE SYNTHESIS of aliphatic *gem*-dinitro compounds from 1-nitro-1-haloalkanes by the displacement of halogen with nitrite ion in basic media is well known (*1, 2, 4*). The application of the ter Meer reaction to the synthesis of aromatic substituted *gem*-dinitromethyl compounds is now reported for the first time.

$$ArCH(NO_2)X \xrightarrow[2)\ H^+]{1)\ NO_2^-} ArC(NO_2)_2H$$

Gem-dinitromethyl aromatic compounds have been prepared by the oxidation and nitration of benzaldoximes (*3, 6*) and nitration of phenylnitromethane (*7, 8*) with dinitrogen tetroxide. In the present work, the ter Meer reaction was used to prepare the first aryl bis-*gem*-dinitromethyl compound.

Treatment of α,α′-dibromo-*p*-xylene (I) with sodium nitrite in dimethylformamide or silver nitrite in dichloromethane gave α,α′-dinitro-*p*-xylene (II). A second product, α-nitro-*p*-tolualdehyde (IV), was isolated from this reaction after sulfuric acid treatment. This compound probably originated from the decomposition of the expected by-product, nitrite ester (III). Bromination of II yielded *p*-bis(bromonitromethyl)benzene (V). Initial efforts to convert V to the dipotassium salt of *p*-bis(dinitromethyl)benzene (VI) using the usual ter Meer conditions or potassium nitrite