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Substituent effects on the spectral behavior and synthesis of mercury 1,5-diarylthiocarbazonates

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Symmetric and unsymmetric substituted 1,5-diarylthiocarbazones, and their mono- and bismercury complexes, were synthesized for spectral analysis. The first singlet-singlet transition of the mercury complexes was determined and the spectral shift produced by trifluoromethyl substitution was compared with that caused by different substituents in similar complexes. The large magnitude of the hypsochromic shift produced by the trifluoromethyl substituent can be explained by concerted steric and inductive effects, while the smaller bathochromic shift induced by the methoxy substituent is a result of opposing steric and electronic effects. In the trifluoromethyl substitution, a hypsochromic shift caused by steric influences was found to be 500 cm^{-1} in the photochromic unactivated state, and 250 cm^{-1} in the photochromic activated state. A similar shift caused by inductive influences was found to be 750 cm^{-1} in the photochromic activated state, and 600 cm^{-1} in the photochromic activated state. The smaller spectral shift observed in the photochromic activated state is consistent with the elucidated structure of the unsymmetric 1,5-diarylthiocarbazone, 6d, which was shown that the trifluoromethyl substitution was on the phenylazo portion of the molecule by chemical and spectral studies.

NORI Y. C. CHU, STEVEN A. GOLDSTEIN et PHILIP M. KEEHN. Can. J. Chem. 59, 679 (1981).

En vue d'en faire une analyse spectrale, on a synthétisé des diaryl-1,5 thiocarbazones substituées de façon symétrique et non symétrique ainsi que leurs mono et bis complexes de mercure. On a déterminé la première transition singulet-singulet des complexes de mercure et on a comparé les déplacements produits dans les spectres par le substituant trifluorométhyle avec ceux provoqués par d'autres substituants dans des complexes semblables. On peut expliquer l'ampleur du déplacement hypsochrome provoqué par le substituant trifluorométhyle en se basant sur des effets inductifs et stériques concertés alors que la valeur plus faible du déplacement bathochrome induite par le substituant méthoxy serait le résultat d'effets électronique et stérique opposés. Dans le cas du substituant trifluorométhyle, on a trouvé que le déplacement hypsochrome provoqué par des influences stériques est de 250 cm⁻¹ dans l'état photochrome activé. On a trouvé qu'un déplacement semblable provoqué par des influences inductive est de l'ordre de 750 cm⁻¹ dans l'état photochrome inactivé et de 600 cm⁻¹ dans l'état photochrome activé. Les déplacements plus faibles observés dans l'état photochrome activé sont en accord avec la structure trouvée pour la diaryl-1,5 thiocarbazone non symétrique (6d) pour laquelle des études chimiques et spectrales on montré que le substituant trifluorométhyle se trouve sur la portion phénylazo de la molécule.

[Traduit par le journal]

Introduction

The photochromic properties of mercury bis-(1,5-diphenylthiocarbazonate) (1) were discovered independently by Irving *et al.* (1) and Webb *et al.* (2). Benzene or chloroform solutions of 1 are orange, and show absorption maxima at 485 nm ($\epsilon \sim 7 \times 10^4$), 320 nm (sh, $\epsilon \sim 1.5 \times 10^4$), and 270 nm



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($\varepsilon \sim 4 \times 10^4$). When irradiated by sunlight, solutions develop an intense blue color which changes back to orange when solutions are placed in the dark. The color change upon irradiation is due to a new absorption centered at 606 nm ($\varepsilon \sim 4 \times 10^4$), and to decreased absorption at 485 nm. The photochromic change is minimized in hydroxylic solvents, organic acids, and bases, and is most dramatic in dry, nonpolar solvents (3).

The absorption of 1 in the visible region of the spectrum can be attributed to the ligand since a solution of 1,5-diphenylthiocarbazonate ion (2b) exhibits a single strong absorption maximum at 470 nm ($\varepsilon \sim 2 \times 10^4$). 1,5-Diphenylthiocarbazone (2a), however, shows well defined bands at 450 and 620 nm.

The effect of substitution in the benzenoid rings of the ligands on the spectral properties of mercury

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CAN. J. CHEM. VOL. 59, 1981

	Ortho		Meta		Para	
Substituent	λ_{max} (nm)	З	λ_{max} (nm)	З	λ_{max} (nm)	ε
Н	485	63 700	485	63 700	485	63 700
C ₂ H ₅	475 ^b	44 100	<u> </u>	c	498	70 700
F	485	52 800	485	63 200	485	56 800
C1	485	49 000	485	60900	495	e
CH ₂ O	510	46 100	490	64200	510	72000
CF ₃	445	53 000	485^{d}	57 000 ^d	485 ^d	55 900 ^d

TABLE 1. Effect of substituents on the absorption maximum of mercury bis(1,5-diarylthiocarbazonates) in methylene chloride^a

Data obtained from ref. 5 except as noted. The adsorption peak for a CH₃ substituent at the *ortho* position is at 475 nm.

Compound not prepared.

⁴Present work. Sample too insoluble.

bis(1,5-diarylthiocarbazonates) has been documented by Coleman et al. (5) (Table 1). They reported that meta substituents produced only small effects on the position of the absorption maxima and molar absorptivities, while large spectral changes were produced by ortho substituents. They attributed the decrease in the molar absorptivity caused by most ortho substituents, and the spectral blue shifts induced by 2-ethyl and 2-trifluoromethyl groups to steric influences.



Closer examination of the spectral blue shifts produced by ortho substituents reveals that only relatively bulky substituents at this position cause a spectral shift. Steric influences cannot, however, explain the large spectral blue shift produced by 2-trifluoromethyl substituents in comparison with 2-ethyl substituents. This is demonstrated spectrally in mercury bis[1,5-di(2'-methylphenyl)thiocarbazonate], which shows an absorption maximum at 475 nm (as does the 2-ethyl substituted material), since the size of a methyl group is about the same as a trifluoromethyl group.

In order to explain the large spectral shift produced by 2-trifluoromethyl substitution, an investigation of the spectral behavior of symmetric and unsymmetric mercury 1,5-diarylthiocarbazonates with trifluoromethyl substitution has been undertaken.

Synthesis of Diarylthiocarbazones

Methods for synthesis of symmetric 1,5-diarylthiocarbazones have been described by Fischer (6) and Bamberger (7). In the Bamberger method, Scheme 1, 2 mol of aryldiazonium salt are coupled with 1 mol of nitromethane at pH \sim 5 to form nitro(bisarylazo)methane (4). Reduction of 4 with ethanolic ammonium sulfate affords 1,5-diarylthiocarbazide (5), which is oxidized in alkaline solution to form 1,5-diarylthiocarbazone (6).

The coupling of aryldiazonium salts with nitromethane is strongly pH dependent (7). At low pH (~ 1) , 1 mol of aryldiazonium salt couples with 1 mol of nitromethane to form 1-(nitromethylene)-2-arylhydrazine (3), while at higher pH (\sim 5), 2 mol of aryldiazonium salt react with 1 mol of nitromethane to form 4. Pupko and Pelkis (8, 9) have utilized the pH dependence of coupling to synthesize a number of unsymmetric 1,5-diarylthiocarbazones.

Employing the method of Bamberger, with modifications to improve yields, symmetric and unsymmetric trifluoromethyl substituted 1,5diphenylthiocarbazones were synthesized. We observed that, at low pH (~ 1), 2-trifluoromethylphenyldiazonium salts predominantly reacted with nitromethane to give 1-(nitromethylene)-2-(2'-trifluoromethylphenyl)hydrazine (3, $R_1 = CF_3$), in 90-95% yield. In contrast, the coupling reaction of unsubstituted phenyldiazonium salts (3, $R_1 = H$) was not efficient, yields were less than 30%, and obtaining the pure product required numerous recrystallizations.

Structure Determination of 1-(2'-Trifluoromethylphenyl)-5-phenylthiocarbazone

Two isomeric products, 6d and 6e, could have been obtained in the synthesis of 1-(2'-trifluoromethylphenyl)-5-phenylthiocarbazone from oxidation of 5d. The absorption properties of these two isomers, and their mercury complexes, would be different. Therefore, it was important to establish whether the isolated product was a mixture of 6d and 6e, or one favored product. This was of particular importance since it had previously been demonstrated by X-ray analysis (10) that the azo and hydrazo functions in the symmetric 1,5-

CHU ET AL.



Isomer	R	R ₁
	2'-CF ₃	2'-CF3
Ь	3'-CF,	3'-CF ₃
С	4'-CF3	4'-CF ₃
d	Н	2'-CF3
е	2'-CF3	н
f	Н	Н
	Scurve 1	

Scheme 1

diphenylthiocarbazone showed no localized single or double bonds in the 6e as shown in Scheme 2. Structural analysis

S ∥ N—N—C—N—N– chain and tautomerism would interconvert 6d and 6e as shown in Scheme 2. Structural analysis identified the product as 6d, with the 2-trifluoromethyl substituted aryl ring bound to the azo portion of the thiocarbazone group. CAN. J. CHEM. VOL. 59, 1981



The structure determination, Scheme 3, was achieved by employing the reported (11) reaction of thiocarbazones with phosgene to give 1,3,4-thiodiazol-5-ones. Phosgene reacts with the hydrazo portion of thiocarbazone to afford a relatively stable 1,3,4-thiodiazol-5-one (7d-f). Subsequent reduction (12) by zinc of the thiodiazolone produces an arylamine (9d-f) and a thiosemicarbazide (10d-f). If the isolated thiocarbazone product were a mixture of 6d and 6e, then this sequence of reactions would yield amines 9d and 9e, and thiosemicarbazides 10d and 10e as products of reduction. Isolation of a single amine and thiosemicarbazide pair (9d and 10d or 9e and 10e) would indicate that a single thiocarbazone product had been isolated. Further, if a single amine and thiosemicarbazide pair were produced, the position of the substituted aryl ring relative to the azo or hydrazo function of the thiocarbazone product would be established by the presence of the trifluoromethyl substituent on either the aryl amine (azo portion) or thiosemicarbazide (hydrazo portion).

When the reaction sequence was performed on



SCHEME 3

CHU ET AL.

1,5-diphenylthiocarbazone (6f), aniline (9f) was obtained from reduction of 2-phenylazo-4-phenyl-1,3,4-thiodiazol-5-one (7f), as identified by gas chromatographic and infrared spectral analyses (11). Reaction of the isolated thiocarbazone product (6d and/or 6e) with phospene afforded a single orange crystalline product with elemental analysis $(C_{15}H_9F_3N_4OS)$ and spectral properties suggesting a thiodiazolone structure. Reduction of the thiodiazolone with zinc and NaOH afforded two major products, a solid and a liquid. Infrared and gas chromatographic analyses of the liquid, when compared with a known standard, demonstrated the presence of 2-trifluoromethylaniline (9d) exclusively; no aniline was observed at the limit of detection sensitivity. The solid product melted at 198-200°C, and its infrared spectrum was identical to 1-phenyl-3-thiosemicarbazide (10d).² The isolated thiocarbazone product was therefore a single tautomer, 6d, with the 2-trifluoromethyl substituted aryl ring bound to the azo portion of the thiocarbazone group.

Spectral Properties of Mercury Complexes of 1,5-Diarylthiocarbazones

A toluene solution of mercury bis(1,5-diphenylthiocarbazonate) (1) shows an intense absorption with a maximum at 485 nm. Upon irradiation the intensity of this band decreases, while a new absorption band appears at 606 nm, Fig. 1. Substitution of the benzenoid rings with 2-trifluoromethyl groups causes a blue shift in these maxima to 445 nm and 560 nm, Fig. 2. No spectral shift is observed when trifluoromethyl substituents are on either the meta or para positions. These results and the spectral properties of mercury complexes of 1,5-diphenylthiocarbazones with other substituents in the benzenoid rings obtained by Coleman et al. (5) are given in Table 1. It is observed that monosubstitution at the meta or para position does not change the position of the absorption greatly though a large spectral shift is induced by a relatively bulky ortho substituent or a trifluoromethyl group.

The spectral shifts produced by *ortho* substituents can be explained by steric and inductive effects. X-ray crystallography (13) shows that the atoms of both ligands in mercury bis(1,5-diphenylthiocarbazonate) exist primarily in a planar configuration. This configuration maximizes the interaction of π -electrons of the benzenoid rings and the

-N=N-C=S

²Stadler Research Laboratories, Inc., mp 198–200°C.



FIG. 1. The absorption spectrum of mercury bis(1,5-diphenylthiocarbazonate) (1) in toluene. The solid curve shows the spectrum before and the dashed curve after irradiation.



FIG. 2. The absorption spectrum of mercury bis[1,5-di(2' trifluoromethylphenyl)thiocarbazonate] (14) in toluene. The solid curve shows the spectrum before and the dashed curve after irradiation.

chain. It seems likely that 2-methyl or 2-ethyl substituents will force the benzenoid rings out of the

plane and increase the energy required for photochromic activation, causing the observed blue shift. This explanation is consistent with the observation that fluorine or chlorine in the *ortho* position does not cause spectral shifts (while 2-methyl substitution does) since these substituents are smaller than methyl. However, the large spectral shift caused by methoxyl and trifluoromethyl substituents cannot be accounted for by steric effects alone, as asserted by Coleman *et al.* (5).

Mercury complexes with a single 1,5-diphenylthiocarbazone ligand, e.g., phenylmercuric 1,5diphenylthiocarbazonate (11), show absorption maxima at 470-475 nm, which is blue shifted by

683

	Unactivated			Activated			
Compound	λ_{max} (nm)	v_{max} (cm ⁻¹)	$\Delta v (cm^{-1})$	λ_{max} (nm)	v_{max} (cm ⁻¹)	$\Delta v (cm^{-1})$	
$Hg[DZ(1)]_2 (1)$	485	20619	0	606	16 502	0	
ϕ HgDZ(1) (11)	473	21141	522	596	16778	276	
$Hg[DZ(2)]_{2}$ (12)	467	21413	794	584	17 123	621	
ϕ HgDZ(2) (13)	457	21 882	1263	577	17331	829	
$Hg[DZ(3)]_{2}$ (14)	445	22 472	1853	560	17857	1355	

TABLE 2. The spectral properties of ϕ HgDZ(1), ϕ HgDZ(2), Hg[DZ(1)]₂, Hg[DZ(2)]₂, and Hg[DZ(3)]₂^{a,b}

^aHDZ(1) = 1,5-diphenylthiocarbazone (6f), HDZ(2) = 1-(2'-trifluoromethylphenyl)-5-phenylthiocarbazone (6d), HDZ(3) = 1,5-di(2'-trifluoromethyl)thiocarbazone (6a).^bSpectra were measured in toluene.

10-15 nm relative to bis-complexes, (e.g., 1), Table 2. This small hypsochromic shift may result from purely steric effects. Since the Hg—S—C bond angle is likely to be the same as in the bis-complex, the azo-benzenoid ring is twisted out of the chromophoric plane due to the presence of the phenyl group.

In order to assess the individual contributions of the steric and inductive effects, 1,5-diphenylthiocarbazones with a trifluoromethyl substituent in only one of the benzenoid rings, and the mono- and bismercury complexes of these ligands, were studied, Table 2. From these data, one can infer the magnitude of the blue shift produced by steric effects to be about 500 cm^{-1} in the unactivated state, and about 250 cm⁻¹ in the activated state, assuming that the blue shift observed in phenylmercuric 1.5diphenylthiocarbazonate (11) is only due to steric effects. The magnitude of the blue shift induced by the inductive effect of the trifluoromethyl group is about 750 cm⁻¹ in the unactivated state, and about 600 cm^{-1} in the activated state, if we assume the blue shift observed in mercury bis[1-(2'-trifluoromethylphenyl)-5-phenylthiocarbazonate], 12, is solely due to inductive effects. The observed blue shift produced by the electron-withdrawing trifluoromethyl group is adequately explained in this manner.

The bathochromic shift, 1000 cm^{-1} , observed in mercury bis[1,5-di-(2'-methoxyphenyl)thiocarbazonate], Table 1, is most likely the result of opposing steric and electronic effects. Assuming steric hindrance is responsible for a blue shift of about 500 cm⁻¹, as above, the actual electronic effect of the two methoxyl groups in this complex can be estimated to be 1500 cm^{-1} . Along these lines, the observed spectrum of mercury bis[1,5-di-(2'methylphenyl)thiocarbazonate] is consistent with the very weak electron donating power of methyl groups.

It is interesting to note that inductive and steric effects in the activated form, e.g., phenylmercuric 1-(2'-trifluoromethylphenyl)-5-phenylthiocar-

bazonate (13), are smaller than those in the unactivated form. This is consistent with the proposed photochromic mechanism which involves a cis-trans isomerization of the azomethine group and a rate determining proton shift (4). Since the main chromophore responsible for absorption is on the phenylazo portion of the molecule which, upon activation, is changed to hydrazo bonding whose contribution to the observed absorption is much smaller. The benzenoid ring with the trifluoromethyl substituent is no longer conjugated with the absorbing chromophore upon activation, and the inductive and steric effects of the trifluoromethyl group are reduced.

Experimental Section

General

The absorption spectra of the mercury complexes were recorded on a Cary 14 spectrophotometer. The infrared source, a General Electric CPR tungsten lamp having a color temperature of 3075 K, of the spectrophotometer was used to irradiate the photochromic solutions and the absorption spectrum of the equilibrium mixture between the activated and unactivated forms was measured. Infrared spectra were recorded on Perkin-Elmer 567 and 180 spectrophotometers. Analytical gasphase chromatography was performed using a Varian Aerograph Model 920 chromatograph, with a 6 ft by 1/4 in. SS 10% Carbowax 1540, 40% Chromosorb P/W PAW 80–100 mesh column. Melting points were determined on either a Thomas-Hoover capillary or Fischer-Johns melting point apparatus. Elemental analyses were determined by Galbraith Laboratories, Inc., Knoxville, TN.

Trifluoromethylanilines were purchased from Aldrich Chemical Co., Milwaukee, WI. All other chemicals were reagent grade and used without further purification.

Synthesis

(1) Preparation of 1,5-Di(2'-trifluoromethylphenyl)thiocarbazone (6a) and 1-(2'-Trifluoromethylphenyl)-5phenylthiocarbazone (6d)

(A) Nitrobis(2-trifluoromethylphenylazo)methane (4a)

2-Trifluoromethylaniline (50 g) in concentrated HCl (250 mL) was diazotized with a solution of NaNO₂ (23 g) in H₂O (50 mL). NaOAc (100 g) in H₂O (330 mL), and an alkaline solution of nitromethane, prepared by slowly adding nitromethane (10 g) to a stirred cold solution of NaOH (50 g) in H₂O (300 mL) and EtOH (150 mL), were added to the filtered diazotized solution, maintaining $T < 10^{\circ}$ C. The pH of the mixture was about 5.

A maroon precipitate was filtered and purified by two recrys-

CHU ET AL.

TABLE 3. Melting points and elemental analyses of nitrobis(trifluoromethylphenylazo)methane derivatives (4) $C_{15}H_9F_6N_5O_2$

Compound			Experimental ^a (%)					
	Mp (°C)	С	Н	F	Ν	Ob		
Ortho Meta Para	152–154 149–150 159–160	44.39 44.37 44.50	2.20 2.17 2.13	28.31 28.35 28.21	17.22 17.06 17.17	(7.88) (8.05) (7.99)		

^aCalculated: C 44, 46, H 2.24, F 28.13, N 17.28, O 7.90. ^bOxygen cannot be analyzed in the presence of F. The numbers in the parentheses are the difference of 100 and the percentage sum of the other elements.

TABLE 4. The prominent ir bands of nitrobis(trifluoromethylphenylazo)methane derivatives (4)

Compound	Infrared bands (KBr), cm ⁻¹
Ortho	1584, 1550, 1454, 1372, 1334, 1312, 1270, 1220, 1166, 1132, 1116, 1052, 1032, 996, 850, 790, 766, 753
Meta	1594, 1550, 1464, 1366, 1324, 1294, 1282, 1216, 1194, 1170, 1134, 1094, 1062, 1012, 896, 820, 810, 798
Para	1610, 1554, 1510, 1418, 1354, 1318, 1278, 1226, 1172, 1130, 1100, 1062, 1004, 846, 838

TABLE 5. The melting points and prominent ir bands of 1,5-di(trifluoromethylphenyl)thiocarbazones, C15H10F6N4S

Compound	Mp (°C)	Infrared bands (KBr), cm ⁻¹
Ortho	>85	3200, 1620, 1580, 1524, 1494, 1462, 1400, 1318, 1280, 1214, 1202, 1178, 1106, 1050, 1032, 754
Meta	113–114	3200, 1618, 1600, 1540, 1502, 1470, 1448, 1332, 1278, 1248, 1208, 1168, 1124, 1092, 1064, 790
Para	121–122	3200, 1620, 1522, 1468, 1426, 1410, 1322, 1252, 1210, 1160, 1120, 1060, 1008, 832

tallizations from 400 mL of boiling EtOH, yielding 60 g 4a. Meta and *para* derivatives (4b, 4c) were prepared in a similar fashion. Elemental analyses and prominent infrared bands are reported in Table 3 and Table 4, respectively.

1-(Nitromethylene) - 2-(2' - trifluoromethylphenyl)hydrazine (3a) was similarly prepared, except the pH of the final solution was about 1. For 3a: mp 71-72°C; ir(KBr): 3280, 3120, 1620, 1578, 1548, 1480, 1456, 1348, 1325, 1282, 1202, 1150, 1114, 770 cm⁻¹.

Anal. calcd. for C₈H₆F₃N₃O₂: C 41.21, H 2.60, F 24.45, N 18.03, O 13.72; found: C 41.09, H 2.63, F 24.65, N 18.03.

(B) Phenylazo(2'-trifluoromethylphenylazo)nitromethane (4d) Aniline (40 g) in concentrated HCl (200 mL) was diazotized with NaNO₂ (28 g) in H_2O (60 mL). A solution of 3a (94 g) in EtOH (600 mL), solid NaOAc (170 g), and the diazotized aniline solution were mixed at $T < 10^{\circ}$ C. The mixture was stirred for 1 h. A maroon precipitate was filtered, washed with H₂O, and purified by recrystallization from boiling EtOH (1 L): mp 131-132°C, ir(KBr): 1590, 1542, 1454, 1354, 1312, 1290, 1264, 1226, 1170, 1156, 1116, 1050, 1030, 774, 760 cm⁻¹.

Anal. calcd. for C₁₄H₁₀F₃N₅O₂: C 49.85, H 3.00, F 16.90, N 20.77, O 9.49; found: C 49.70, H 2.98, F 16.73, N 20.86.

(C) Conversion to Thiocarbazone

Nitrobis(2'-trifluoromethylphenylazo)methane (4a) (20 g) was suspended in EtOH (400 mL), treated with (NH₄)₂S solution (60 mL), and stirred until the solid dissolved. The mixture was poured into 2 L of ice water, the light yellow thiocarbazide, 5a, was filtered and dissolved in 2% aqueous NaOH (600 mL) with heating. After cooling the solution in an ice-water bath, it was titrated with 1 N HCl to pH 5. A green precipitate (6a) was

filtered and purified by repeated dissolution and titration. Meta and para derivatives (6b, 6c) were similarly prepared. The prominent infrared bands and melting points are tabulated in Table 5

Compound 4d was converted to unsymmetric thiocarbazone in the same fashion to compound 6d: mp 112-114°C; ir(KBr): 3200, 1602, 1586, 1524, 1496, 1464, 1442, 1320, 1276, 1220, 1198, 1166, 1104, 1054, 1032, 752 cm⁻¹.

(2) Preparation of Mercury Complex of Thiocarbazones

The mercury complexes were prepared by reacting thiocarbazone with equal molar amounts of either phenylmercuric chloride or mercuric chloride to form mono- or bis-complex, respectively, in a CH₂Cl₂/H₂O (1:1) mixture. The organic layer was separated and the complex was precipitated out by the addition of MeOH.

The elemental analyses and melting points for the biscomplexes are tabulated in Table 6 with the infrared spectral bands in Table 7. For compound 13: mp 177-178°C ir(KBr): 3302, 3056, 1606, 1588, 1530, 1460, 1374, 1320, 1282, 1260, 1162, 1150, 1128, 1110, 1050, 1028, 750 cm⁻¹.

Anal. calcd. for C₂₀H₁₅F₃N₄SHg: C 39.96, H 2.52, F 9.48, N 9.32, S 5.33, Hg 33.37; found: C 39.86, H 2.63, F 9.28, N 9.19, S 5.61, Hg 33.50.

(3) 2-Phenylazo-4-phenyl-1,3,4-thiodiazol-5-one (7f)

1,5-Diphenylthiocarbazone (6f) (10 g, 0.039 mol), dissolved in a minimum of benzene, was added to a stirred solution of phosgene (5 g, 0.05 mol) in toluene (25 mL) at 0°C. The reaction mixture was stirred for 1 h, washed with $H_2\mathrm{O}$ until no further evolution of HCl gas, and followed with NaHCO₃, but kept acidic. After drying with MgSO4 and evaporating the solvent,

685

CAN. J. CHEM. VOL. 59, 1981

TABLE 6. Melting points and elemental analyses of bismercury complexes of 1,5-di(trifluoromethylphenyl)thiocarbazone (14) and of 1-(2'-trifluoromethylphenyl)-5-phenylthiocarbazone (12)

Compound		Experimental ^a (%)					
	Mp (°C)	С	Н	N	F	S	Hg
Ortho Meta Barra	217–218 ^b 216–217 248, 2400	36.70	1.95	11.56	22.98	6.58	20.23
DZ(2)	254-255	39.74	2.49	13.08	13.32	7.43	23.61

^aCalculated (a) for ortho, meta, and para: C 36.64, H 1.85, N 11.40, F 23.19, S 6.52, Hg 20.40; (b) for DZ(2): C 39.69, H 2.38, N 13.23, F 13.45, S 7.57, Hg 23.67. ^aLiterature reported value is 215-216°C (8).

'Insufficient material for elemental analysis.

 TABLE 7. The prominent ir bands of bismercury complexes of 1,5-di(trifluoromethylphenyl)thiocarbazone (14) and of 1-(2'-trifluoromethylphenyl)-5-phenylthiocarbazone (12)

Compoun	d Infrared bands (KBr), cm ⁻¹
Ortho	3260, 1608, 1590, 1528, 1462, 1380, 1326, 1322, 1286, 1260, 1170, 1156, 1100, 1052, 1030, 752
Meta	3260, 1616, 1596, 1534, 1486, 1468, 1448, 1366, 1330, 1276, 1170, 1130, 1092, 1062, 898, 794
Para	3260, 1612, 1530, 1502, 1470, 1422, 1364, 1320, 1266, 1164, 1128, 1106, 1062, 1010, 838
DZ(2)	3332, 3064, 1608, 1590, 1532, 1500, 1462, 1380, 1322, 1284, 1264, 1160, 1126, 1054, 1030, 758

10.3 g (92%) of 7*f* was obtained (mp 138–141°C). Trituration with MeOH, and recrystallization from toluene/MeOH, afforded golden needles: mp 142–143°C (lit. mp 140°C) (6); ir(CHCl₃): 1700, 1679, 1590, 1529, 1489, 1458, 1329, 1257, 1191, 1160, 1149 cm⁻¹.

Compound 7*d* was similarly prepared: mp 128–129°C; ir(CHCl₃): 1703, 1682, 1598, 1542, 1487, 1457, 1414, 1316, 1270, 1151, 1112, 1092, 1050 cm⁻¹.

Anal. calcd. for $C_{15}H_9F_3N_4OS$: C 51.42, H 2.59, N 16.00, F 16.27, S 9.15, O 4.57; found: C 51.26, H 2.57, N 15.90, F 16.34, S 9.36.

(4) Zinc Reduction of 4-Phenyl-1,3,4-thiodiazol-5-one

2-Phenylazo-4-phenyl-1,3,4-thiodiazol-5-one, 7f, (1 g, 0.0034 mol) was dissolved in MeOH/20% NaOH (100 mL v/v). Zinc (0.5 g, 0.0076 mol) was added to the deep red solution and the mixture heated under reflux until no color change on exposure to air (10 min). The reaction mixture was extracted with CH_2Cl_2 and 0.05 μ L of the organic extract was injected into the gas chromatograph. Two peaks were observed whose retention times matched that for solvent and aniline 9f. The organic layer was evaporated and the residue triturated with ether. The triturate was evaporated, affording a brown oil and an ir spectrum identical to that of commercial aniline.

Similarly, 2-(2'-trifluoromethylphenyl)azo-4-phenyl-1,3,4thiodiazol-5-one, 7d, was dissolved in MeOH/20% NaOH and reduced. Gas chromatograms of the reaction mixture, the mixture with added 2-trifluoromethylaniline (9d), and the mixture with added aniline (9f), are shown respectively in Fig. 3 a, b, c. When the reaction mixture was analyzed, the instrument was set at its highest sensitivity and no aniline was detected. Only 2-trifluoromethylaniline (9d) was observed, identified by a retention time identical to that of supplemented commercial 2-trifluoromethylaniline.



FIG. 3. Gas chromatograms of the organic layer of the zinc reduction of 7*d*. (*a*) Reaction mixture neat, (*b*) reaction mixture with added 2-trifluoromethylaniline (9*d*), and (*c*) reaction mixture with added aniline (9*f*).

The organic layer was evaporated and the residue washed with CS_2 . The resultant residue was crystallized from benzene/EtOH and afforded white crystalline flakes, mp 198-200°C. The infrared spectrum and the mp were identical to a reported² infrared spectrum and mp for 1-phenyl-3-thiosemicarbazide (**10***d*).

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686

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