2-Fluorenylmethyl bromide. The carbinol (2.17 g., 0.011 mole) was added gradually to a solution of 3 ml. of phosphorus tribromide in 20 ml. of benzene. The mixture was shaken until the solid dissolved and then left several days at room temperature. Probably this long reaction time is not necessary. The benzene solution was poured slowly with stirring into a mixture of ether and water. The organic phase was extracted 3 times with water, filtered, and dried over anhydrous sodium sulfate. It was then evaporated to dryness under vacuum. A yield of 2.6 g. (90.7%) of cream colored solid was obtained. This material had m.p. 94–97° (lit.[2] 95°). When stored sealed at 0° for 1 week, the m.p. was lowered to 90–96°. The best preparation obtained showed m.p. 95–100° and all recrystallizations lowered this value, especially if done from aqueous solvents.

Diethyl (2-fluorenylmethyl)acetamidomalonate. A solution containing 0.24 g. of sodium (0.0104 mole) and 2.22 g. of diethyl acetamidomalonate (0.0104 mole) in 150 ml. of anhydrous ethanol (distilled from sodium and diethyl phthalate) was prepared. This was treated with a solution of 2.59 g. of the bromide (0.01 mole) in benzene-ethanol. Little or no heat was evolved and the mixture was refluxed for 16 hr. Acetic acid (5 ml.) was added and the mixture was distilled to a small volume under vacuum. It was then steam distilled for 0.5 hr. An orange oil was left in aqueous suspension and this crystallized on cooling and standing. This product was recrystallized once from aqueous acetone and dried. It weighed 3.5 g. or 88.6%. For purification, the ester was recrystallized from aqueous acetone and from ether-petroleum ether, m.p. 149.5–150.5°.

Anal. Calcd. for $C_{23}H_{25}NO_5$: C, 69.87; H, 6.33. Found: C, 69.64; H, 6.12.

DL-*β-(2-Fluorenyl)alanine hydrochloride.* Hydrolysis and decarboxylation of the ester required long refluxing with hydrochloric acid, or some ester or intermediate product was recovered. The best procedure found is described. A solution of 8.64 g. of the ester in 150 ml. of glacial acetic acid was heated to boiling under reflux and 125 ml. of concentrated hydrochloric acid was slowly added while maintaining reflux. The mixture was refluxed for 6 days and then evaporated to dryness under vacuum. The residue was repeatedly extracted with boiling 3*N* hydrochloric acid and the extracts filtered while above 90°. Storage of the combined filtrates at 0° overnight produced a crystalline deposit which was filtered, washed, and dried. The filtrates were boiled to a small volume and further crops taken. The combined yield of hydrochloride was 5.35 g. or 84.5%. The salt was decolorized in ethanol-benzene solution with Norit and then recrystallized from this solvent 5 times. Recrystallization from boiling dilute hydrochloric acid was less effective in purification. On heating, the hydrochloride sintered and discolored above 230° and melted 240–258° with decomposition, forming an orange-brown melt.

Anal. Calcd. for $C_{16}H_{16}NO_2Cl$: C, 66.32; H, 5.53. Found: C, 66.41; H, 5.35.

DL-*β-(2-Fluorenyl)alanine.* The amino acid hydrochloride was digested with a mixture of equal volumes of concentrated ammonium hydroxide and water on the steam bath until solution was obtained. The hot solution was filtered and the filtrate boiled down to concentrate the solution and to eliminate ammonia. Crystallization of the free amino acid began in the heated solution and was completed on cooling overnight on ice. It was then filtered, washed with water, and dried. From 1.37 g. of hydrochloride, 1.13 g. of amino acid were obtained or 94.3%. The amino acid formed a white powder which could be recrystallized by repeating the solution in hot dilute ammonia and concentrating. The analytical sample was vacuum dried for analysis.

Anal. Calcd. for $C_{16}H_{15}NO_2$: C, 75.89; H, 5.93. Found: C, 76.28; H, 6.06.

On heating, the amino acid begins to discolor (light orange-brown) at 210–215° and melts at 225–233° to a brown liquid with decomposition. On further recrystallization of the analytical sample, the melting point was lowered. This amino acid was nearly insoluble in boiling water, but dissolved in hot, dilute acids and alkalies, more readily in the latter. When boiled in suspension in dilute aqueous acetic acid with ninhydrin, the insoluble particles became purple and the liquid light brown, while with excess amino acid the liquid became greenish-brown. No change in appearance of the compound was observed during storage for 2 years.

*N-Benzenesulfonyl-*DL-*β-(2-fluorenyl)alanine.* This derivative was made by acylation of the fluorenylalanine dissolved in an excess of *N* potassium hydroxide, by stirring vigorously with an ether solution of benzenesulfonyl chloride. After several hours stirring, the mixture was filtered and the insoluble potassium salt washed with ether and dried. It was dissolved in hot water and acidified with an excess of dilute hydrochloric acid. The suspension of product was cooled in ice for some time and then filtered, washed with water, and dried. It was recrystallized a number of times from ether, m.p. 184–186°.

Anal. Calcd. for $C_{22}H_{19}NSO_4$: C, 67.18; H, 4.83. Found: C, 67.64; H, 5.14.

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[COMMUNICATION NO. 1969 FROM THE KODAK RESEARCH LABORATORIES]

Dithiocarbamates. I. Quaternary Ammonium Dithiocarbamates

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Received June 23, 1958

A series of dithiocarbamates containing tertiary amine groups has been alkylated to give quaternary ammonium or pyridinium dithiocarbamates. Proof of the structure of these products is based largely on their ultraviolet absorption spectra. The ultraviolet spectra of various thiono and dithiocarbamates are compared.

A number of dithiocarbamates have been prepared which contain a tertiary amine group; these have been quaternized to give water-soluble quaternary ammonium or pyridinium dithiocarbamates. The synthesis of the intermediate bases was carried out by an adaptation of the well known metathetical reaction between the alkali metal salt of a dithiocarbamate and an alkyl halide,[1] either or both moieties containing the tertiary

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[1] M. Kulka, *Can. J. Chem.*, **34**, 1093 (1956); G. Nachmias, *Ann. Chim.* (Paris), **7**, 584 (1952).

TABLE I

DIALKYLDITHIOCARBAMIC ESTERS WITH TERTIARY AMINE AND QUATERNARY AMMONIUM FUNCTIONS

R_2NCS_2R' ("S" refers to the quaternary salts as indicated)

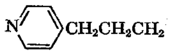
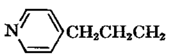
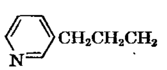
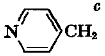
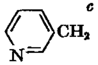
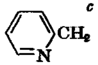
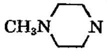
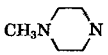
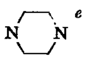
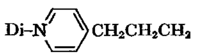
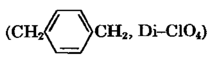
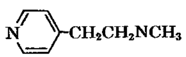
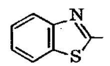
No.	R_2N Amine	R′	% Yield	M.P., °C. and Solvent or B.P., °C. and n_D^{25}	Formula	Analysis Calculated C	H	N	S	Found C	H	N	S	Ultraviolet Absorption Spectra[a] λ_{max}	$\epsilon \cdot 10^{-3}$	λ_{max}	$\epsilon \cdot 10^{-3}$
I	$(CH_3)_2N$		79	62–64 (hexane-chloroform)	$C_{11}H_{16}N_2S_2$	55.0	6.7	11.6		55.0	6.7	11.6		249	12.3	276	9.8
I-S		$(CH_3$, PTS)	70	109.5–111 (acetone)	$C_{19}H_{26}N_2O_3S_3$	53.6	6.1	6.6	22.5	53.8	6.0	6.7	22.8	250	14.2	275	9.8
II	$(C_2H_5)_2N$		60	177 (0.2 mm.); 1.5935[b]	$C_{13}H_{20}N_2S_2$	58.1	7.5	10.4		58.2	7.2	10.0		251	12.3	280	10.8
II-S		(CH_3, ClO_4)	73	101–102 (acetone water)	$C_{14}H_{23}ClN_2O_4S_2$			7.3	16.7			7.2	16.6	254	15.5	279	10.8
III	$(CH_3)_2N$		65	178 (0.4 mm.); 1.6130[b]	$C_{11}H_{16}N_2S_2$	55.0	6.7	11.6		54.7	6.8	11.2		249	11.9	270	11.7
III-S		(CH_3, ClO_4)	50	75–76.5 (acetone)	$C_{12}H_{19}ClN_2O_4S_2$	40.6	5.4	7.9	18.0	40.0	5.4	7.7	18.3	249	10.6	273	12.9
IV	$(CH_3)_2N$	 [c]	59	67.5–69 (hexane-chloroform)	$C_9H_{12}N_2S_2$	51.0	5.7	12.7		51.4	6.0	12.6		247	12.3	276	9.7
IV-S		$(CH_3$, PTS)	89	93–94 (acetone)	$C_{17}H_{22}N_2O_3S_3$			7.0				6.8		242	12.1	269	11.3
V	$(CH_3)_2N$	 [c]	68	149–151 (0.2 mm.); 1.6459	$C_9H_{12}N_2S_2$	51.0	5.7	12.7		51.0	5.3	12.3		248	11.8	272	11.5
V-S		$(CH_3$PTS)	87	161–162.5 (methanol acetone)	$C_{17}H_{22}N_2O_3S_3$	51.3	5.6	7.0		51.1	5.9	6.7		243	11.2	270	12.1
VI	$(CH_3)_2N$	 [c]	81	148–149 (0.25 mm.); 1.6432[b]	$C_9H_{12}N_2S_2$	51.0	5.7	12.7		51.3	5.6	13.1		250	11.0	271	12.5
VI-S		$(CH_3$, PTS)	53	146–147 (dec.) (acetone methanol)	$C_{17}H_{22}N_2O_3S_3$	51.3	5.6	7.0		51.5	5.7	7.0		240	9.5	270	14.1
VII	$(CH_3)_2N$	$(CH_3)_2NCH_2CH_2$[c]	80	88 (0.15 mm.); 1.5733	$C_7H_{16}N_2S_2$	43.6	8.4	14.5		43.4	8.3	14.3		247	8.9	276	10.1
VII-S		$(CH_3$, PTS)	82	153–154.5 (abs. ethanol)	$C_{15}H_{26}N_2O_3S_3$	47.6	6.9	7.4		47.8	6.9	7.2		251	8.5	275	10.2
VIII	 [d]	$C_6H_5CH_2$		Not isolated													
VIII-S		$(CH_3$, PTS)	52 (yield for 2 steps)	199–200.5 (methanol)	$C_{21}H_{28}N_2O_3S_3$	55.6	6.2	6.2		55.8	6.5	6.2		254	14.0	280	10.5
IX			54	*ca.* 24 (ethyl acetate)	$C_{14}H_{21}N_3S_2$	56.8	7.1	14.2		56.9	7.1	13.9		253	12.7	279	10.9

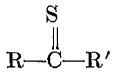
TABLE I (*Continued*)

No.	R_2N Amine	R′	% Yield	M.P., °C. and Solvent or B.P., °C. and n^{25}_{D}	Formula	Analysis Calculated C	Analysis Calculated H	Analysis Calculated N	Analysis Calculated S	Analysis Found C	Analysis Found H	Analysis Found N	Analysis Found S	Ultraviolet Absorption Spectra[a] λ_{max}	Ultraviolet Absorption Spectra[a] $\epsilon \cdot 10^{-3}$	Ultraviolet Absorption Spectra[a] λ_{max}	Ultraviolet Absorption Spectra[a] $\epsilon \cdot 10^{-3}$
IX-S	Very hygroscopic	Di(CH_3, PTS)	50	50.5–52.5 (acetonitrile)	$C_{30}H_{41}N_3O_6S_4$	53.9	6.2	6.3		53.6	6.6	5.9		254	15.7	281	8.8
X	 [e]		63	131–134 (acetone)	$C_{22}H_{28}N_4S_4$	55.4	5.9			55.6	5.4			255	27.8	281	25.0
X-S	[f]	Di(CH_3, PTS)	62	183–185 (abs. ethanol)	$C_{38}H_{48}N_4O_6S_6$	53.8	5.7	6.6		53.6	5.3	6.7		256	34.5	281	24.8
XI	$(C_6H_5CH_2)_2N$	$(CH_3)_2NCH_2CH_2$	74	Undist. oil 1.6187[b]	$C_{19}H_{24}N_2S_2$	66.3	7.0	8.1	18.6	66.7	6.9	7.8	18.7	254	11.7	282	11.3
XI-S		(CH_3, PTS)	87	143.5–145 (acetone)	$C_{27}H_{34}N_2O_3S_3$	61.1	6.5	5.3		61.4	6.5	4.9		250	13.6	282	14.0
XI-S′	[g]		69	159–160 (acetone (methanol)	$C_{46}H_{56}Cl_2N_4O_8S_4$	55.7	5.7	5.6	12.9	55.8	5.8	5.6	12.9				
XII		$C_6H_5CH_2$	71	87.5–89 (methanol)	$C_{16}H_{18}N_2S_2$	63.6	6.0	9.3	21.2	63.9	6.1	9.6	21.2	252	15.6	279	10.3
XII-S	[h]	(CH_3, ClO_4)	82	120–121.5 (acetone)	$C_{17}H_{21}ClN_2O_4S_2$	48.9	5.1	6.7	15.4	48.6	5.3	6.3	15.5				
XIII	$(CH_3)_2N(CH_2)_3NCH_3$	$C_6H_5CH_2$		Not isolated													
XIII-S		(CH_3, PTS)	30 (Yield for 2 steps)	178–179.5 (methanol)	$C_{22}H_{32}N_2O_3S_3$	56.4	6.9	6.0	20.5	56.2	7.2	5.8	20.6				
XIV	$(CH_3)_2N$	$C_6H_5CH_2CH_2$	73	47 (methanol)	$C_{11}H_{15}NS_2$	58.7	6.7	6.2		58.5	6.7	5.9		249	10.8	276	10.1
XV	$(CH_3)_2N$	$CH_3SCH_2CH_2$[c]	87	114 (0.3 mm.); 1.6192	$C_6H_{13}NS_3$	36.9	6.7	7.2	49.2	37.2	6.1	7.2	49.6	248	10.6	276	10.1
XVI[i]	$(C_2H_5)_2N$			78–79.5 (methanol)	$C_{12}H_{14}N_2S_3$			9.9	34.1			9.8	33.9			276	20.1
XVII	Di$(C_2H_5)_2N$	—$(CH_2)_6$—	43	76–78 (methanol)	$C_{16}H_{32}N_2S_4$	50.5	8.5		33.7	50.5	8.3		33.7	252	19.7	278	21.2

[a] In methanol. For published spectra of dithiocarbamates, see A. D. Ainley, W. H. Davies, H. Gudgeon, J. C. Harland, and W. A. Sexton, *J. Chem. Soc.* (London), 147 (1944); J. R. Robinson *et al.*, *Can. J. Res.*, **34,** 1596 (1956); H. P. Koch, *J. Chem. Soc.* (London), 401 (1949). See also: K. Kanamaru, T. Takada, and T. Taniguchi, *J. Soc. Chem. Ind.* (Japan), **42,** 47 (1939); J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Nature*, **177,** 1042 (1956). [b] Purified chromatographically. [c] Intermediate chloride obtained from Aldrich Chemical Co. [d] 1-Methylpiperazine used; courtesy of Carbide and Carbon Chemicals Co. [e] Disodium *N,N′*-piperazinebis(carbodithioate), prepared according to R. Damiens and R. Delaby, *Compt. rend.*, **236,** 931 (1953). [f] The reactants were refluxed in chloroform for 15 min. [g] *p*-Xylylene dibromide and two equivalents of the base (XI) were refluxed in ether for 12 hr., then in methanol for 4 hr. and the product was dissolved in a large volume of 50% aqueous methanol and treated with sodium perchlorate. [h] The base XII was refluxed in methanol for 15 min. with methyl *p*-toluenesulfonate. [i] Prepared according to W. W. Levis, Jr., U. S. Patent **2,697,098** (1954): *Chem. Abstr.*, **49,** 15975 (1955).

TABLE II

MISCELLANEOUS THIOCARBAMATES

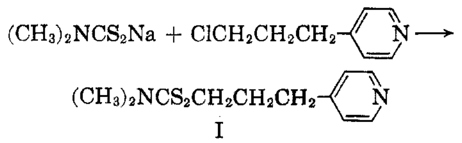


$$R\text{—}\overset{\overset{\displaystyle S}{\|}}{C}\text{—}R'$$

No.	R	R′	% Yield	M.P., °C. and Solvent or B.P., °C. and n_D^{25}	Ultraviolet Absorption Spectra[a]			
					λ_{max}	$\epsilon \cdot 10^{-3}$	λ_{max}	$\epsilon \cdot 10^{-3}$
XVIII[b]	CH_3CONH	C_2H_5S	..	123 (benzene)	259	13.7	310	11.7
XIX[c]	CH_3CONH	C_2H_5O	..	100–101 (ligroin)	261	12.6	...	...
XX[d]	$(C_2H_5)_2N$	C_2H_5O	68	49–50 (0.3 mm.); 1.4940	249	14.2	...	...
XXI[e]	$NHCH_2CH_2NH$	Di-CH_3S	..	105–107 (benzene)	...	..	270	21.4
XXII[f]	$(CH_3)_2N$	$(CH_3)_2N\overset{\overset{S}{\|}}{C}SS$	..	150.5–151.5 (benzene)			280	11.6
XXIII[g]	$(CH_3)_2N$	$(CH_3)_2N\overset{\overset{S}{\|}}{C}S$	..	107.5–108.5 (benzene)			279	16.3
XXIV	$(C_2H_5)_2N$	$(C_6H_5)_2\overset{\overset{S}{\|}}{P}S$	77	130–132.5 (benzene-ligroin)			275–6	9.9
XXV[h]	NH_2NH	$C_6H_5CH_2S$		125 (benzene)	274	13.2	299	14.8

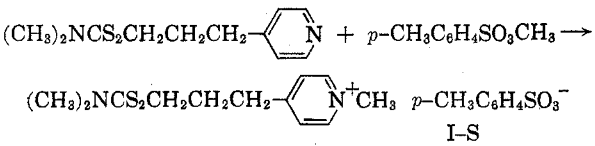
[a] Absorption spectra run in methanol. [b] H. L. Wheeler and H. F. Merriam, *J. Am. Chem. Soc.*, **23,** 290 (1901). [c] G. S. Skinner and H. C. Vogt, *J. Am. Chem. Soc.*, **77,** 5440 (1955); H. L. Wheeler and T. B. Johnson, *Am. Chem. J.*, **24,** 189 (1900). [d] A. Hantzsh, *Ber.*, **64,** 661 (1931). [e] Anal. Calcd. for $C_6H_{12}N_2S_4$: C, 30.0; H, 5.0; N, 11.6, Found: C, 30.1; H, 5.1; N, 12.0. [f] Eastman Chemical No. P-2089, recrystallized from benzene; Beilstein, m.p. 146°. [g] Eastman Chemical No. P-6255, recrystallized from benzene; Beilstein, m.p. 104°. [h] M. Busch and M. Starke, *J. prakt. Chem.*, **93,** 59 (1916). The authors are grateful to Dr. M. Baron, formerly of these Laboratories, for this sample.

amine group. The reaction of γ-3-chloropropylpyridine with sodium dimethyldithiocarbamate (see Experimental) to give 3-(γ-pyridyl)propyl dimethyldithiocarbamate (I) is illustrative of this reaction.



I

The resulting basic esters are listed in Table I, along with products of their quaternization. The reaction of I with methyl *p*-toluenesulfonate is illustrative of the quaternization reaction. A few

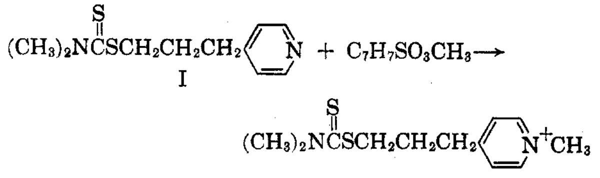


I-S

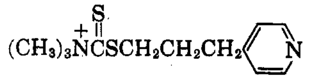
related compounds pertinent to the discussion are shown in Table II.

The quaternization of these compounds was accomplished with methyl *p*-toluenesulfonate in ether solution. In those instances of sluggish reaction, methanol was employed. Extended boiling in methanol produced by-products which made subsequent purification difficult. Extensive decomposition also occurred when the reactants were heated on the steam bath without a solvent.

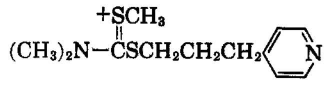
Because of the presence of three basic groups (two nitrogen atoms and one unsaturated carbon sulfur link), the quaternization step is ambiguous. Quaternization of I, for example, might lead to any of the three products shown (I-S, XXVI, or XXVII).



I-S $C_7H_7SO_3^-$



XXVI $C_7H_7SO_3^-$



XXVII $C_7H_7SO_3^-$

The correctness of the assignment of a I-S type of structure to these compounds is evident from the following considerations:

(1) Attempts to form a salt from β-phenethyl dimethyldithiocarbamate (XIV) with methyl *p*-toluenesulfonate were unsuccessful. Furthermore,

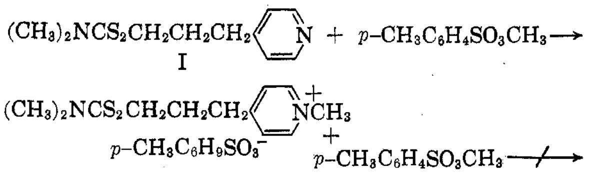
$$\underset{\text{XIV}}{(CH_3)_2NCS_2CH_2CH_2C_6H_5} + p\text{-}CH_3C_6H_4SO_3CH_3 \not\longrightarrow$$

attempts to react I with *two* moles of methyl *p*-toluenesulfonate were unsuccessful. Only I-S was isolated.

TABLE III

COMPARISON OF ULTRAVIOLET SPECTRA OF MONO- AND DITHIOCARBAMATES

No.	Structure	$\lambda_{max(10^{-3}\epsilon)}$	Res. Contr. Involved	$\lambda_{max(10^{-3}\epsilon)}$	Res. Contr. Involved
XIV	$(CH_3)_2N\overset{S}{\overset{\|}{C}}SCH_2CH_2C_6H_5$	249 (10.8)	XXVIIIa	276 (10.1)	XXVIIIb
XX	$(C_2H_5)_2N\overset{S}{\overset{\|}{C}}OC_2H_5$	249 (14.2)	XXIXa	...	...
XVIII	$CH_3\overset{O}{\overset{\|}{C}}NH\overset{S}{\overset{\|}{C}}SC_2H_5$	259 (13.7)	XXVIIIa	310 (11.7)	XXVIIIb
XIX	$CH_3\overset{O}{\overset{\|}{C}}NH\overset{S}{\overset{\|}{C}}OC_2H_5$	261 (12.6)	XXIXa	...	...



This showed that the dimethylthiocarbamate moiety is inert under the conditions of quaternization employed.

(2) The infrared spectrum of the free base (I) has a peak at 6.25 mμ, while the salt absorbs at 6.1 mμ; both are characteristic of a pyridine base and its quaternary salt.[2]

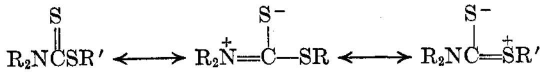
(3) The ease of quaternization (insofar as reaction time and temperature are concerned) paralleled that of the basic group involved, *i.e.*, pyridine in the case of I.

(4) The ultraviolet spectra, which are discussed presently, also are in agreement with a I-S type of structure.

Attempted quaternization of the basic dithiocarbamate esters with bismethanesulfonates or bis-p-toluenesulfonates was unsuccessful since, at the higher temperatures required for quaternization with these reagents, extensive decomposition occurred. The only successful synthesis of a true bisquaternary dithiocarbamate was effected by the use of p-xylylene dibromide to give XI-S′ (Table I).

Attempts to form a sulfonium salt analogous to the quaternary salts by heating β-(methylmercapto)ethyl dimethyldithiocarbamate (XV) with methyl p-toluenesulfonate, with or without a solvent, were unsuccessful. Similarly, 2-benzothiazolyl diethyldithiocarbamate (XVI) was not quaternized successfully.

Ultraviolet spectra. The resonance contributors for dialkyldithiocarbamates are as shown, the uncharged XXVIII being selected as the ground state.

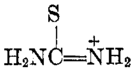


$$R_2N\overset{S}{\overset{\|}{C}}SR' \longleftrightarrow R_2\overset{+}{N}{=}\overset{S^-}{\overset{|}{C}}{-}SR \longleftrightarrow R_2N\overset{S^-}{\overset{|}{C}}{=}\overset{+}{S}R'$$

XXVIII XXVIIIa XXVIIIb

The ultraviolet spectrum of a dithiocarbamate is thus expected to show two peaks, representing the electronic transitions to XXVIIIa and XXVIIIb.[3] Inspection of Table I shows this to be the case.

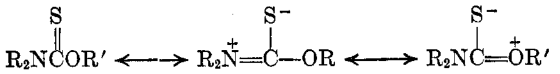
The ultraviolet peak at lower energy (higher λ_{max}) is assigned to XXVIIIb, while that at higher energy level (lower λ_{max}) is assigned to XXVIIIa. This is in agreement with the spectrum of thiourea which shows the transition to



$$H_2N\overset{S}{\overset{|}{C}}{=}\overset{+}{N}H_2$$

at about 255 mμ.[3]

This assignment has also been confirmed by the spectra of thionocarbamates (XXIX) (work done in these Laboratories). Since oxygen does not participate in electronic transitions as readily as sulfur, a structure such as XXIXb is not expected



$$R_2N\overset{S}{\overset{\|}{C}}OR' \longleftrightarrow R_2\overset{+}{N}{=}\overset{S^-}{\overset{|}{C}}{-}OR \longleftrightarrow R_2N\overset{S^-}{\overset{|}{C}}{=}\overset{+}{O}R'$$

XXIX XXIXa XXIXb

to absorb in the quartz ultraviolet region. The peak related to XXIXa, however, should and does correspond to that caused by XXVIIIa. These facts are clearly illustrated by the data presented in Table III.

The acyldithiocarbamate (XVIII) and the acylthionocarbamate (XIX) absorb at a different wave length from that of the corresponding dialkyl analogs because of their different structure. The similarity of absorption in each series, however, is significant and lends support to the theory.

The ultraviolet spectra of the three sulfides (XXII, XXIII, and XXIV) show broad, less distinct peaks than the dithiocarbamate esters and for this reason are difficult to interpret. The broad peaks may be a fusion of several peaks which normally would be resolved. In any case, the three sulfides show an apparent single absorption at 275–280 mμ.

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[2] Unpublished observations of Thelma Davis, of these Laboratories.

[3] H. P. Koch, *J. Chem. Soc.*, 401 (1949).

The discussion of the possible electronic transitions of the dithiocarbamates can presumably be extended to include the dithiocarbazates. In accord with the theory, benzyl dithiocarbazate (XXV), the only such compound available, showed absorption maxima at 274 mμ and 299 mμ.

EXPERIMENTAL[4]

A detailed description of the steps leading to γ-[3-(dimethyldithiocarbamato)propyl]-*N*-methylpyridinium *p*-toluenesulfonate (I-S) is illustrative of the methods used in the preparation of these compounds. Significant variations in the procedures are noted subsequently or in the tables, and all the data of value in the characterization of the compounds are collected in Tables I and II.

In those cases in which the intermediate dithiocarbamate bases were oils, it was sometimes necessary (as noted in Table I) to purify them further, after distillation. This was done by passing an ether solution of the distillate through a short column (*ca.* 1 × 10 in.) of activated alumina and elution with fresh ether. Removal of the solvent by warming *in vacuo* produced the pure product.

Occasionally, the *p*-toluenesulfonate salts were hygroscopic, in which event they were converted to the perchlorates by an excess of aqueous sodium perchlorate.

γ-3-Chloropropylpyridine. Thionyl chloride (90 g.) was added dropwise to 68.5 g. of 4-pyridinepropanol (Eastman Kodak Co. No. P5702) in 250 ml. of chloroform over a 25-min. period. When the initial exothermic reaction had ceased, the solution was heated at reflux temperature for 1 hr. The black reaction mixture was poured onto ice, the aqueous layer was made basic to litmus by the addition of 50% KOH solution, and, after thorough shaking in a separatory funnel, the chloroform layer was removed. The aqueous layer was extracted with 150 ml. of chloroform, and the combined chloroform extracts were decolorized with Pittsburgh Type RB activated carbon and dried over magnesium sulfate. The volatiles were then removed *in vacuo*, and the residue was distilled, giving 80–85% of γ-3-chloropropylpyridine:

$$b_{0.8}\ 57\text{–}8°;\ n_D^{25}\ 1.5230$$

Anal. Calcd. for $C_8H_{10}ClN$: N, 9.0 Found: N, 9.2.

This compound was stored at −20° to prevent polymerization which occurs slowly at room temperature. Although a larger quantity may be prepared in one experiment, attempts to distill more than about 125 g. at one time resulted in a lower yield and occasionally led to a violent, exothermic polymerization in the distillation flask.

3-(γ-Pyridyl)propyl dimethyldithiocarbamate (I). To 10.1 g. of sodium dissolved in 500 ml. of dry methanol was added 73 g. of dimethylammonium dimethyldithiocarbamate (Eastman Kodak Co. No. 812), with stirring. The yellow-to-green solution was treated with 45 g. of γ-3-chloropropylpyridine, and the reaction mixture was heated, with stirring, for 6.5 hr. The volatiles were removed on the steam bath until the volume of solution was about 250 ml. This boiling residue was treated with Pittsburgh Type RB activated carbon and filtered. The filtrate was cooled, and 250 ml. of water was added, with cooling and scratching of the flask with a glass rod. After standing in the refrigerator overnight, the light-brown crystals were filtered and recrystallized from hexane chloroform solution, yielding 41.5 g. (60%) of 3-(γ-pyridyl)propyl dimethyldithiocarbamate which melted at 60.5–63°. Further recrystallization from the same solvent afforded an analytical sample, m.p. 62–64°.

γ-[3-(Dimethyldithiocarbamato)propyl]-N-methylpyridinium p-toluenesulfonate (I-S). To 3.8 g. of 3-(γ-pyridyl)propyl dimethyldithiocarbamate in 50 ml. of dry ether was added 3.5 g. of freshly distilled methyl *p*-toluenesulfonate, and the solution was heated under reflux for 3–6 hr. The precipitate was filtered and recrystallized twice from acetone: m.p. 109.5–111°; yield, 4.8 g. (71%).

Benzyl methyl(2-γ-pyridylethyl)dithiocarbamate (XII). To a solution of 27.2 g. of 4-(2-methylaminoethyl)pyridine[5] and 8 g. of sodium hydroxide in 75 ml. of water was added 15.2 g. of carbon disulfide. The solution was cooled and 100 ml. of methanol added, followed by 25.2 g. of benzyl chloride. After 15 min. at 25°, the mixture was filtered and recrystallized from methanol (see Table I).

Diethylthiocarbamoyl diphenylphosphinothioyl sulfide (XXIV). A mixture of 25 g. of diphenyldithiophosphinic acid[6] and 5.4 g. of sodium methoxide in 600 ml. of benzene was heated under reflux for 15 min., then 200 ml. of benzene methanol azeotrope was distilled off. An additional 400 ml. of benzene was added, followed by a solution of diethylthiocarbamoyl chloride in benzene. The solution cleared, and sodium chloride gradually separated. The mixture was filtered, concentrated, and ligroin was added to the residual oil. The resulting crystalline solid was recrystallized from benzene-ligroin: yield, 28 g.; m.p. 130–132.5°.

Anal. Calcd. for $C_{17}H_{20}NPS_3$: C, 56.0; H, 5.5; N, 3.8; S, 26.3. Found: C, 56.2; H, 5.8; N, 3.6; S, 26.1.

Acknowledgment. The authors are grateful to the following colleagues: Dr. C. F. H. Allen for many helpful suggestions; Mr. D. Ketchum for microanalyses; Miss T. Davis for infrared spectra; and Mr. E. E. Richardson for ultraviolet spectra.

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[4] Melting and boiling points are uncorrected.

[5] A. P. Phillips, *J. Am. Chem. Soc.*, **78**, 4441 (1956).

[6] Courtesy of The Lubrizol Corp., Cleveland, Ohio.