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A New Insertion Reaction of Diazoalkanes with Dialkylaminomethyl Esters of Dialkyldithiocarbamic Acid and of Ethylxanthic Acid

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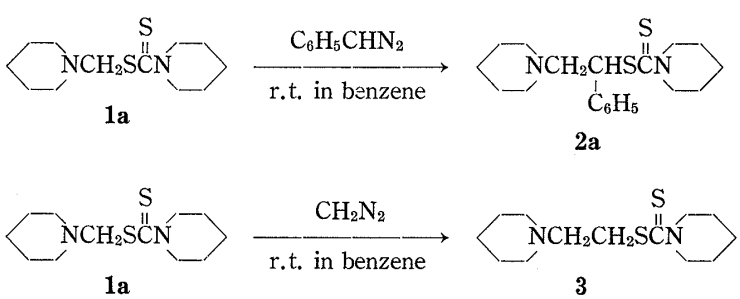
We have found a new insertion reaction of diazoalkanes, especially phenyldiazomethane, with dialkylaminomethyl esters of dialkyldithiocarbamic acid and of ethylxanthic acid. The scope and limitations of this reaction are described.

Keywords——insertion reaction; diazoalkane; phenyldiazomethane; dithiocarbamic acid ester; ethylxanthic acid ester; dialkylaminomethyl ester; N,S-linking methylene compound; NMR

The reaction of N,N-dialkylmethyleniminium halides with diazomethane and ethyl diazoacetate to give N,N-dialkyl-N-(2-chloroethyl)amines has been well documented.[2] A recent report from this laboratory described the reaction of N,N-dialkylaminomethyl arenesulfonates (hydrate) with diazoalkanes to give 2-(dialkylamino)ethanol arenesulfonates.[3] If it is supposed that there is some methyleniminium contribution to the substrate structure, these two reactions are similar in nature. There are few reports on diazoalkane insertion reactions with methylene compounds possessing two covalent bonds with hetero atoms in the literature. In fact, there is only a report[4] of the formation of 9-acyloxy-9-(dialkylaminomethyl)fluorenes in the reaction of N,N′-methylenebisdialkylamines with diazofluorene in acid anhydride, where dialkylaminomethyl acylate is assumed to be the reacting intermediate.

We have now found that methylene compounds of the type $R^1R^2NCH_2SC(S)X$ (X= NR^3R^4, OEt) undergo a new insertion reaction of diazoalkanes. Initial experiments centered on the reactions of 1-piperidinecarbodithioic acid piperidinomethyl ester (**1a**) with phenyldiazomethane and diazomethane. These reactions proceeded in benzene at room temperature with evolution of nitrogen to give the corresponding insertion products, **2a**, mp 87—88° and **3**, mp 65—66°, respectively. In these reactions, insertion of benzylidene and methylene into the methylene carbon–sulfur bond was considered to occur, based on assignment of the structures **2a** and **3** to the products from their nuclear magnetic resonance (NMR) spectral data. The ethylene moiety of compound **3** was confirmed by the presence of two sets of



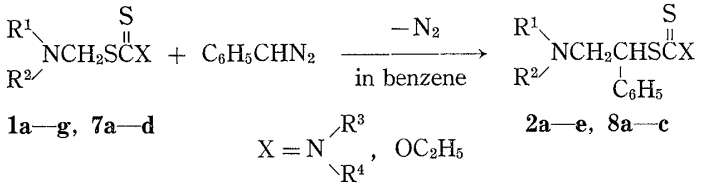
1a **2a** **1a** **3**

1) Location: *2-2-1, Oshika, Shizuoka, 422, Japan.*
2) H. Böhme, E. Mundlos, W. Lehners, and O.-E. Herboth, *Chem. Ber.*, **90**, 2008 (1957).
3) Y. Akasaka, T. Morimoto, and M. Sekiya, *Chem. Pharm. Bull.* (Tokyo), **27**, 803 (1979).
4) A. Schönberg, E. Singer, and W. Knöfel, *Chem. Ber.*, **99**, 3813 (1966).

triplets of methylene protons at 2.62 ppm (2H, J=7.5 Hz) and 3.46 ppm (2H, J=7.5 Hz). The NMR spectrum of **2a** exhibited a higher order ABX spin system owing to non-equivalence of its methylene protons, *i.e.*, a doublet of doublets at 5.40 ppm (1H, J=8 Hz, 7.5 Hz) and two sets of deformed doublets of doublets at 2.78—3.07 ppm (2H). Based on these data, the benzylidene proton and the methylene protons of **2a** can be assigned as those of carbons linked to S and N, respectively, on the basis of published data; $>NCH_2\dot{C}S-$ 2.52—2.97 ppm[5a] and $-\dot{C}CH_2SC(S)-$ 3.17—3.36 ppm.[5b] Phenyldiazomethane was much reactive than diazomethane in the insertion reaction. The former gave the insertion product **2a** in 56% yield but the latter gave **3** in only 6% yield. Diazoethane and 2-phenyldiazoethane did not give insertion products, though nitrogen evolution was observed.

We next thought to determine the scope and limitations of the insertion reaction of phenyldiazomethane with various dithiocarbamate derivatives, $XCH_2SC(S)NR^3R^4$ [X=R^1R^2N (**1b**—**g**), CH_3O (**4**), CH_3S (**5**), $C_6H_4(CO)_2N$ (**6**)] and with ethylxanthate derivatives, $R^1R^2NCH_2SC(S)OC_2H_5$ (**7a**—**d**). The dithiocarbamate derivatives **1a**—**g**, where X=R^1R^2N=R^3R^4N, were prepared by the reaction of N,N′-methylenebisdialkylamines with carbon disulfide and, where $R^1R^2N \neq R^3R^4N$ (involving not only aliphatic but also aromatic moieties), by the condensation of amine hydrochlorides, formalin and sodium dialkyldithiocarbamates.[6,7] The 1-piperidinecarbodithioic acid esters **4**—**6** (NR^3R^4=$N(CH_2)_5$; X=CH_3O, CH_3S, $C_6H_4(CO)_2N$) were prepared by allowing 1-piperidinecarbodithioic acid potassium salt to react with chloro-

Table I. Reactions[a] of Phenyldiazomethane with Dialkylaminomethyl Esters of Dialkyldithiocarbamic Acid and of Ethylxanthic Acid



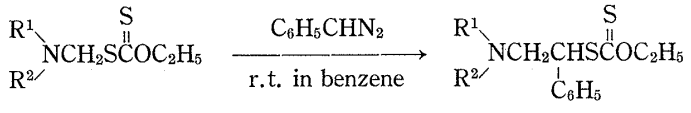
Starting material	R^1 R^2N	X	Reaction temp. (°C)	Reaction time (hr)	Product	Yield (%)
1a			r.t.	Overnight	**2a**	56
1b	$(CH_3)_2N$	$N(CH_3)_2$	r.t.	Overnight	**2b**	43
1c			r.t.	Overnight	**2c**	28
1d			r.t.	Overnight	**2d**	43
1e			r.t.	Overnight	**2e**	23
1f			60	9		0
1g			60	—		0[b]
7a		OC_2H_5	r.t.	Overnight	**8a**	34
7b	$(CH_3)_2N$	OC_2H_5	r.t.	Overnight	**8b**	36
7c		OC_2H_5	r.t.	Overnight	**8c**	36
7d		OC_2H_5	55	10		0[b]

r. t. : room temperature.
a) Molar ratio; starting material: phenyldiazomethane=1:1.
b) Starting material was recovered.

5) *a*) N.F. Chamberlain, "The Practice of NMR Spectroscopy," Plenum Press, New York, 1974, p. 137; *b*) *Idem*, *ibid.*, p. 133.
6) H. Ulrich and A.A.R. Sayigh, *Angew. Chem.*, **78**, 827 (1966).
7) N. Kreutzkamp and H.Y. Oei, *Arch. Pharm. Ber. Dtsch. Pharm. Ges.*, **299**, 906 (1966).

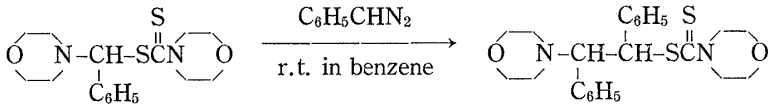
methyl methyl ether, chloromethyl methyl thioether and N-bromomethylphthalimide, respectively, in acetone at room temperature. The ethylxanthate derivatives **7a—d** were prepared by reacting amine hydrochlorides, formalin and potassium ethylxanthate in water under ice-cooling.

Control experiments were conducted with a series of dithiocarbamate derivatives, $XCH_2SC(S)N(CH_2)_5$, where $X=(CH_2)_5N$ (**1a**), $C_6H_5(CH_3)N$ (**1f**), CH_3O (**4**), CH_3S (**5**) and $C_6H_4(CO)_2N$ (**6**), carrying out the reaction with phenyldiazomethane in benzene at room temperature. However, compounds other than **1a** were inert. The ethylxanthate derivatives **7a—c** reacted with phenyldiazomethane to give the corresponding insertion products **8a—c**.



7a—c **8a—c**

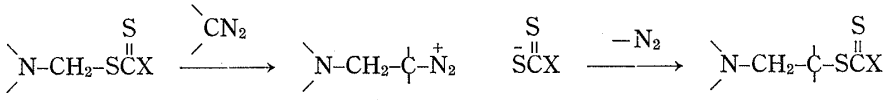
The results obtained with dialkylaminomethyl esters of dialkyldithiocarbamic acid and of ethylxanthic acid are summarized in Table I. In addition to these methylene insertion compounds, an insertion reaction with the benzylidene compound **9** occurred as shown below.



9 **10**

Based on the experimental data shown in Table I, it can be concluded that the reactivities of the compounds, $R^1R^2NCH_2SC(S)NR^3R^4$ (**1a—g**) are in the order of basicity of R^1R^2N: $(CH_2)_5N>(CH_3)_2N>O(CH_2CH_2)_2N\gg C_6H_5(CH_3)N$, and substrates in which NR^3R^4 is replaced by OC_2H_5 are also reactive.

Although such a reaction with methyleniminium salts has been reported,[2] the present paper describes the diazoalkane insertion reaction newly with such covalent methylene compounds represented by $R^1R^2NCH_2SC(S)X$ ($X=NR^3R^4$, OC_2H_5). In view of the susceptibility of these reactive substrates to nucleophiles,[8] which may be enhanced by an increase in the basicity of R^1R^2N, the mechanism of the insertion reaction may be as follows, with diazoalkane acting as a nucleophile.



Experimental[9]

Dialkyldithiocarbamic Acid Dialkylaminomethyl Esters (1a—g, 9)——A series of these compounds **1a—g**, **9**, for which analytical and spectral data are listed in Table II, were prepared by the following procedures with reference to previous papers;[6,7] Method (A) was used for **1a—c**, **9** and Method (B) for **1d—g**.

Method (A): A solution of N,N′-alkylidenebisamine (0.03 mol) in 30 ml of carbon disulfide was heated under reflux for 1 hr. After removal of excess carbon disulfide, the crystalline residue was purified by recrystallization from an appropriate solvent.

Method (B): A solution of secondary amine hydrochloride (0.05 mol) in 50 ml of water was added dropwise to a stirred mixture of 35% formalin (0.05 mol) and a solution of sodium dialkyldithiocarbamate (0.05 mol) in 50 ml of water under ice-cooling, and the reaction mixture was stirred for 1 hr. During this time the product separated out as crystals. The precipitated crystals were collected by filtration and purified by recrystallization from an appropriate solvent.

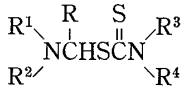
8) N. Kreutzkamp and H.-Y. Oei, *Chem. Ber.*, **101**, 2459 (1968).
9) All melting and boiling points are uncorrected. NMR spectra were measured with a Hitachi R-24 spectrometer, and all chemical shifts are given in ppm downfield from tetramethylsilane (TMS).

Methoxymethyl, Methylthiomethyl and Phthalimidomethyl Esters of 1-Piperidinecarbodithioic Acid (4, 5, 6)——A solution of the appropriate halogenomethyl compound (chloromethyl methyl ether, chloromethyl methyl thioether or N-bromomethylphthalimide) (0.03 mol) in acetone was added dropwise to a stirred solution of 1-piperidinecarbodithioic acid potassium salt (0.03 mol) in 60 ml of acetone at room temperature. After stirring for 1 hr, the precipitated potassium halide was filtered off. The filtrate was evaporated to dryness. For **4** and **5**, benzene was added to the residue, and the benzene solution was washed with water and then dried over anhyd. $MgSO_4$. After removal of benzene, the oily residue was distilled under reduced pressure to give a liquid. For **6**, the solid residue was recrystallized from acetone to give pure crystals. The yields and analytical and spectral data of the products are given below.

1-Piperidinecarbodithioic Acid Methoxymethyl Ester (**4**): Yield, 57%. Liquid, bp 126—127° (0.25 mmHg). *Anal.* Calcd. for $C_8H_{15}NOS_2$: C, 46.79; H, 7.36; N, 6.82. Found: C, 47.04; H, 7.33; N, 6.76. NMR ($CDCl_3$) δ: 1.50—1.90 (6H, m, $(CH_2)_3$), 3.40 (3H, s, CH_3), 3.75—4.50 (4H, m, $N(CH_2)_2$), 5.55 (2H, s, OCH_2S).

1-Piperidinecarbodithioic Acid Methylthiomethyl Ester (**5**): Yield, 81%. Liquid, bp 116° (0.2 mmHg). *Anal.* Calcd. for $C_8H_{15}NS_3$: C, 43.40; H, 6.83; N, 6.33. Found: C, 43.44; H, 6.83; N, 6.36. NMR ($CDCl_3$) δ: 1.50—1.95 (6H, m, $(CH_2)_3$), 2.25 (3H, s, CH_3), 3.75—4.35 (4H, m, $N(CH_2)_2$), 4.45 (2H, s, SCH_2S).

Table II. Dialkyldithiocarbamic Acid Dialkylaminomethyl Esters



Compd.	R^1R^2N	NR^3R^4	R	Preparation method	Yield (%)	mp (°C)	Recryst. solvent	Formula
1a			H	A	85	58— 60 (Lit.,[7] 59)	EtOH	—
1b	$(CH_3)_2N$	$N(CH_3)_2$	H	A	73	39—40	Petr. ether	$C_6H_{14}N_2S_2$
1c			H	A	78	114—115 (Lit.,[10] 112—114)	Ligroin	—
1d		$N(C_6H_5)CH_3$	H	B	57	86—87	Ligroin	$C_{14}H_{20}N_2S_2$
1e		$N(C_6H_5)CH_3$	H	B	55	84—85	Ligroin	$C_{13}H_{18}N_2OS_2$
1f	$(C_6H_5)(CH_3)N$		H	B	64	40—41	iso-Pr_2O	$C_{14}H_{20}N_2S_2$
1g	$(C_6H_5)(CH_3)N$	$N(C_6H_5)CH_3$	H	B	28	83—84	Ligroin	$C_{16}H_{18}N_2S_2$
9			C_6H_5	A	57	98—99 (Lit.,[7] 98)	iso-Pr_2O	—

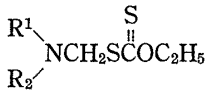
Compd.	Analysis (%) Calcd. (Found) C	H	N	NMR ($CDCl_3$) δ ppm: R >NCHS–	S –SCN<CH_n– CH_n–	R –CH_n– –CH_n>NCH–	Other $(CH_2)_n$	$(C_6H_5)_n$
1a	—	—	—	5.18 2H, s	4.00—4.40 2H, m	2.45—2.85 4H, m	1.35—2.00 12H, m	—
1b	40.42 (40.16	7.91 7.92	15.71 15.61)	5.15 2H, s	3.52 6H, s	2.34 6H, s	—	—
1c	—	—	—	5.21 2H, s	4.00—4.40 4H, m	2.45—2.80 4H, m	3.50—3.90 8H, m	—
1d	59.96 (59.75	7.19 7.28	9.99 9.91)	5.00 2H, s	3.71 3H, s	2.25—2.70 4H, m	1.15—1.75 6H, m	7.00—7.50 5H, m
1e	55.29 (55.36	6.42 6.46	9.92 9.98)	4.98 2H, s	3.72 3H, s	2.35—2.70 4H, m	3.40—3.75 4H, m	7.02—7.50 5H, m
1f	59.96 (60.15	7.19 7.27	9.99 10.16)	5.55 2H, s	3.50—4.50 4H, m	3.00 3H, s	1.38—1.80 6H, m	6.58—7.38 5H, m
1g	63.54 (64.48	6.00 5.95	9.26 9.26)	5.45 2H, s	3.73 3H, s	2.98 3H, s	—	6.55—7.55 10H, m
9	—	—	—	6.98 1H, s	4.04—4.45 4H, m	2.54—2.93 4H, m	3.52—3.97 8H, m	7.10—7.72 5H, m

10) H. Böhme and H.-H. Otto, *Arch. Pharm. Ber. Dtsch. Pharm. Ges.*, **300**, 647 (1967).

1-Piperidinecarbodithioic Acid Phthalimidomethyl Ester (**6**): Yield, 61%. Prisms (acetone), mp 144—145°. *Anal.* Calcd. for $C_{15}H_{16}N_2O_2S_2$: C, 56.23; H, 5.03; N, 8.74. Found: C, 56.38; H, 5.08; N, 8.79. NMR ($CDCl_3$) δ: 1.50—1.90 (6H, m, $(CH_2)_3$), 3.70—4.40 (4H, br, $N(CH_2)_2$), 5.65 (2H, s, NCH_2S), 7.60—8.05 (4H, m, C_6H_4).

Ethylxanthic Acid Dialkylaminomethyl Esters (7a—d)——A series of these compounds, **7a—d**, for which analytical and spectral data are listed in Table III, were prepared by the following procedure. A solution of secondary amine hydrochloride (0.05 mol) in 50 ml of water was added dropwise to a stirred mixture of 35% formalin (8.6 g, 0.1 mol) and a solution of potassium ethylxanthate (17.6 g, 0.11 mol) in 100 ml of water under ice-cooling, and stirring was continued for 1 hr. For **7a—c**, the liberated oily material was extracted with benzene and the extract was dried over anhyd. $MgSO_4$. After removal of benzene, the product was obtained by distillation of the oily residue under reduced pressure. For **7d**, the product, which precipitated in the reaction solution, was purified by recrystallization from petr. ether.

Table III. Ethylxanthic Acid Dialkylaminomethyl Esters



Compd.	$R^1 \atop R^2 > N$	Yield (%)	bp (°C) (mmHg)	Formula	Analysis (%) Calcd. (Found) C	H	N
7a		88	113—115(0.09) [Lit.,[10] 109(0.02)]	—	—	—	—
7b	$(CH_3)_2N$	52	117—118(14)	$C_6H_{13}NOS_3$	40.19 (40.39	7.31 7.47	7.81 7.90)
7c		80	136(0.2) [Lit.,[10] 120—121(0.01)]	—	—	—	—
7d	$C_6H_5 \atop CH_3 > N$	83	160—163(0.13)[a]	$C_{11}H_{15}NOS_2$	54.74 (54.85	6.26 6.31	5.80 5.81)

Compd.	NMR ($CDCl_3$) δ ppm $>NCH_2S-$ 2H, s	$-OCH_2CH_3$ 2H, q, J=7 Hz	$-OCH_2CH_3$ 3H, t, J=7 Hz	$-CH_n$ $-CH_n > NCH_2-$	Other $(CH_2)_n$	C_6H_5 5H, m
7a	4.90	4.67	1.49	2.35—2.75 4H, m	1.12—1.82 6H, m	—
7b	4.90	4.67	1.45	2.35 6H, s	—	—
7c	4.90	4.67	1.41	2.40—2.70 4H, m	3.50—3.80 4H, m	—
7d	5.33	4.65	1.38	3.00 3H, s	—	6.65—7.45

a) Prisms (petr. ether), mp 35— 36°.

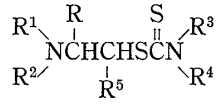
Reaction of Dialkyldithiocarbamic Acid Dialkylaminomethyl Esters (1a—g) with Phenyldiazomethane——General Procedure: Phenyldiazomethane was prepared from N-[(N-nitrosobenzylamino)methyl]benzamide as a petr. ether solution by the method[11] reported from this laboratory. Petr. ether was replaced by benzene through careful evaporation. A benzene solution of phenyldiazomethane (0.02 mol, 10 ml) was added dropwise to a stirred solution of **1a—g** (0.02 mol) in 40 ml of benzene. The progress of the reaction was indicated by the evolution of N_2. The reaction mixture was stirred overnight at room temperature. The concentrated solution was chromatographed on a silica gel column, eluting with benzene–AcOEt to give dialkyldithiocarbamic acid 2-dialkylamino-1-phenylethyl ester (**2a—e**). The yields and analytical and spectral data of the products are listed in Tables I and IV, respectively.

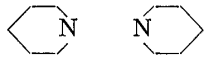
11) M. Sekiya, Y. Ohashi, Y. Terao, and K. Ito, *Chem. Pharm. Bull.* (Tokyo), **24**, 369 (1976).

Reaction of 1-Piperidinecarbodithioic Acid Piperidinomethyl Ester (1a) with Diazomethane——An ethereal solution of diazomethane (0.02 mol, 140 ml), which was prepared from N-[(N-nitrosomethylamino)methyl]-benzamide by the method[11] reported from this laboratory, was added dropwise to a stirred solution of **1a** (5.2 g, 0.02 mol) in 50 ml of ether, and evolution of N_2 was observed. Stirring was continued overnight at room temperature. After removal of ether, the residue was subjected to silica gel chromatography using benzene–AcOEt to give 1-piperidinecarbodithioic acid 2-piperidinoethyl ester (**3**). Yield, 0.3 g (6%). The analytical and spectral data are listed in Table IV.

Reaction of 4-Morpholinecarbodithioic Acid α-Morpholinobenzyl Ester (9) with Phenyldiazomethane——A benzene solution of phenyldiazomethane (0.02 mol, 10 ml) was added dropwise to a stirred solution of **9** (0.02 mol) in 50 ml of benzene, and evolution of N_2 was observed. The reaction mixture was stirred overnight at room temperature. After removal of benzene, the residue was triturated with isopropyl ether and the resulting solid was collected by filtration. Recrystallization from acetone gave pure crystals of 4-morpholine-carbodithioic acid 2-morpholino-1,2-diphenylethyl ester (**10**). Yield, 4.0 g (47%). The analytical and spectral data are listed in Table IV.

Table IV. Dialkyldithiocarbamic Acid 2-(Dialkylamino)ethyl Esters



Compd.	R^1R^2N	NR^3R^4	R	R^5	mp (°C)	Appearance (Recryst. solvent)	Formula
2a			H	C_6H_5	87—88	Prisms (Acetone)	$C_{19}H_{28}N_2S_2$
2b	$(CH_3)_2N$	$N(CH_3)_2$	H	C_6H_5	72—73	Prisms (Petr. ether)	$C_{15}H_{20}N_2S_2$
2c			H	C_6H_5	107—108	Prisms (iso-Pr_2O)	$C_{17}H_{24}N_2O_2S_2$
2d		$N<^{C_6H_5}_{CH_3}$	H	C_6H_5	—	Oil[a]	$C_{21}H_{26}N_2S_2$
2e		$N<^{C_6H_5}_{CH_3}$	H	C_6H_5	—	Oil[b]	$C_{29}H_{24}N_2OS_2$
3			H	H	65—66	Plates (Acetone)	$C_{13}H_{24}N_2S_2$
10			C_6H_5	C_6H_5	195—196	Prisms (Acetone)	$C_{23}H_{28}N_2O_2S_2$

Compd.	Analysis (%) Calcd. (Found) C	H	N	NMR ($CDCl_3$) δ ppm (J=Hz) >NCHCH–	>NCHCH–	–CH$_n$–CH$_n$>NCH–	–SCN<CH$_n$–CH$_n$–	Other $(CH_2)_n$	$(C_6H_5)_n$
2a	65.47 (65.63)	8.10 (8.11)	8.04 (8.06)	2.78—3.07 2H, m	5.40, 1H, dd(8, 7.5)	2.30—2.60 4H, m	3.80—4.30 4H, m	1.20—1.91 12H, m	7.09—7.51 5H, m
2b	58.17 (58.27)	7.51 (7.49)	10.43 (10.45)	2.70—2.99 2H, m	5.35, 1H, dd(8, 7.5)	2.30 6H, s	3.19—3.64 6H, br	—	7.09—7.54 5H, m
2c	57.92 (57.87)	6.86 (6.86)	7.95 (8.00)	2.80—3.10 2H, m	5.42, 1H, dd(8, 7.5)	2.37—2.67 4H, m	3.90—4.37 4H, m	3.50—3.90 8H, m	7.10—7.53 5H, m
2d	54.08 (54.02)	4.87 (4.85)	11.68 (11.63)	2.70—2.95 2H, m	5.30, 1H, dd(8, 7.5)	2.28—2.56 4H, m	3.70 3H, s	1.15—1.70 6H, m	7.00—7.50 10H, m
2e	58.73 (58.73)	6.16 (6.26)	6.85 (6.84)	2.75—3.00 2H, m	5.34, 1H, dd(8, 7.5)	2.30—2.65 4H, m	3.70 3H, s	3.45—3.80 4H, m	7.00—7.55 10H, m
3	57.31 (57.16)	8.88 (8.82)	10.28 (10.26)	2.62, 2H, t (7.5)	3.46, 2H, t (7.5)	2.20—2.80 4H, m	3.68—4.38 4H, m	1.18—1.98 12H, m	—
10	64.45 (64.42)	6.58 (6.61)	6.54 (6.57)	4.06, 1H, d (12)	6.09, 1H, d (12)	2.20—2.80 4H, m	3.94—4.38 4H, m	3.42—3.88 8H, m	6.90—7.39 10H, m

a) Picrate: prisms (acetone), mp 174—175°
b) Hydrochloride: prisms (EtOH), mp 215—216°

Reaction of Ethylxanthic Acid Dialkylaminomethyl Esters (7a—d) with Phenyldiazomethane——A benzene solution of phenyldiazomethane (0.02 mol, 10 ml) was added dropwise to a stirred solution of **7a—d** (0.02 mol) in 40 ml of benzene, and N_2 evolution was observed. The reaction mixture was stirred overnight at room temperature. The concentrated solution was chromatographed on a silica gel column, eluting with benzene–AcOEt to give ethylxanthic acid 2-dialkylamino-1-phenylethyl ester (**8a—c**). Yields of the products are listed in Table I and analytical and spectral data are given below.

Ethylxanthic Acid 1-Phenyl-2-piperidinoethyl Ester (**8a**): Prisms (petr. ether), mp 78—79°. *Anal.* Calcd. for $C_{16}H_{23}NOS_2$: C, 62.10; H, 7.46; N, 4.53. Found: C, 61.99; H, 7.46; N, 4.57. NMR ($CDCl_3$) δ: 1.10—1.70 (6H, m, $(CH_2)_3$), 1.30 (3H, t, $J=7$ Hz, CH_3), 2.29—2.58 (4H, m, CH_2NCH_2), 2.76 (2H, d, $J=7$ Hz, $NC\underline{H}_2CHS$), 4.55 (2H, q, $J=7$ Hz, OCH_2), 4.95 (1H, t, $J=7$ Hz, $NCH_2C\underline{H}S$), 7.12—7.45 (5H, m, C_6H_5).

Ethylxanthic Acid 2-Dimethylamino-1-phenylethyl Ester (**8b**): Oil [picrate: prisms (acetone), mp 152—153°]. *Anal.* Calcd. for $C_{13}H_{19}NOS_2$: C, 45.78; H, 4.45; N, 11.24. Found: C, 45.83; H, 4.42; N, 11.21. NMR ($CDCl_3$) δ: 1.32 (3H, t, $J=7$ Hz, $CH_2C\underline{H}_3$), 2.27 (6H, s, $N(CH_3)_2$), 2.80 (2H, d, $J=7$ Hz, $NC\underline{H}_2CHS$), 4.56 (2H, q, $J=7$ Hz, OCH_2), 4.95 (1H, t, $J=7$ Hz, $NCH_2C\underline{H}S$), 7.15—7.48 (5H, m, C_6H_5).

Ethylxanthic Acid 2-Morpholino-1-phenylethyl Ester (**8c**): Prisms (petr. ether), mp 80—81°. *Anal.* Calcd. for $C_{15}H_{21}NO_2S_2$: C, 57.85; H, 6.80; N, 4.50. Found: C, 57.98; H, 6.78; N, 4.56. NMR ($CDCl_3$) δ: 1.31 (3H, t, $J=7$ Hz, CH_3), 2.38—2.66 (4H, m, CH_2NCH_2), 2.84 (2H, d, $J=7$ Hz, $NC\underline{H}_2CHS$), 3.50—3.80 (4H, m, CH_2OCH_2), 4.55 (2H, q, $J=7$ Hz, $C\underline{H}_2CH_3$), 4.97 (1H, t, $J=7$ Hz, $NCH_2C\underline{H}S$), 7.21—7.50 (5H, m, C_6H_5).

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