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New Compounds

Synthesis of New Urethans. p-Cyclohexylsulfamoyl and p-Piperidinosulfonylcarbanilic Acid Esters

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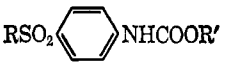
In continuation of our search for new anticancer compounds,[1] new urethans listed in Table I were prepared by Curtius degradation of appropriate benzoyl azides.

Table I



R	R'	Mp, °C	Yield, %	Formula[a]
Cy[b]	Et	187	68	$C_{15}H_{22}N_2O_4S$
Cy	*i*-Pr	188	77	$C_{16}H_{24}N_2O_4S$
Cy	*tert*-Bu	182	61	$C_{17}H_{26}N_2O_4S$
Cy	*n*-Am	142	76	$C_{18}H_{28}N_2O_4S$
Cy	*n*-Hex	130	72	$C_{19}H_{30}N_2O_4S$
Cy	*n*-Oct	135	73	$C_{21}H_{34}N_2O_4S$
Cy	Allyl	172	64	$C_{16}H_{22}N_2O_4S$
Cy	Benzyl	180	71	$C_{20}H_{24}N_2O_4S$
Cy	Cholesteryl	225	40	$C_{40}H_{61}N_2O_4S$
Cy	Cyclopentyl	200	87	$C_{18}H_{26}N_2O_4S$
Cy	Cyclohexyl	176	82	$C_{19}H_{28}N_2O_4S$
Cy	Cycloheptyl	194	62	$C_{20}H_{30}N_2O_4S$
Cy	Cyclooctyl	178	86	$C_{21}H_{32}N_2O_4S$
Cy	*o*-Methoxyphenyl	160	54	$C_{20}H_{24}N_2O_5S$
Cy	*p*-Nitrophenyl	187	40	$C_{19}H_{21}N_3O_6S$
Cy	Ethylfurfuryl	154	97	$C_{20}H_{26}N_2O_5S$
Cy	α-Cyclohexyl-α-methylbenzyl	198	30	$C_{27}H_{36}N_2O_4S$
Cy	Ph_2CH	209	63	$C_{26}H_{28}N_2O_4S$
Pip[c]	Thymyl	178	85	$C_{22}H_{28}N_2O_4S$
Pip	*o*-Carboxyphenyl	141.5	92	$C_{19}H_{20}N_2O_6S$
Pip	Trityl	110	82	$C_{31}H_{30}N_2O_4S$

[a] All compounds were analyzed for C, H, and the results were satisfactory. Similarly ir and nmr spectra were as expected. [b] Cyclohexylamino. [c] Piperidino.

The compounds proved to be inactive[2] (T/C = 89–103% at 400 mg/kg) against the L 1210 lymphoid leukemia in BDF_1 mice, and the Walker carcinosarcoma 256 in random-bred albino rats.

Experimental Section[3]

p-Cyclohexylsulfamoylbenzoyl Azide.—*p*-Cyclohexylsulfamoylbenzoic acid ethyl ester (mp 100) was prepd by known methods from *p*-cyclohexylsulfamoylbenzoic acid[4] and transformed to *p*-cyclohexylsulfamoylbenzhydrazide (mp 174°). The hydrazide (2.97 g, 0.01 mole) in 20 ml of 50% AcOH was stirred at ice bath temp with 20 ml of a 5% aq $NaNO_2$ to give 2.56 g of azide (80%), mp 110° dec. *Anal.* ($C_{13}H_{16}N_4O_3S$) C, H.

p-Piperidinosulfonylbenzoyl azide was prepd similarly. *p*-Piperidinosulfonylbenzoic acid[5] was transformed to the corresponding ester (mp 100°) then to hydrazide (mp 205°). This treated as above gave 1.8 g of azide (90%), mp 115° dec. *Anal.* ($C_{12}H_{14}N_4O_3S$) C, H.

General Preparation of Urethans.—The benzoyl azides (0.01 mole) and 0.02 mole of appropriate alcohol or phenol were refluxed for 1 hr in 20 ml of dry PhMe. The solvent was evapd and the residue was recrystd from dil EtOH. Et esters were also prepd by 5-hr refluxing of the azide in 10 times its wt of abs EtOH.

(1) N. Sharghi, I. Lalezari, Gh. Niloufari, and F. Ghabgharan, *J. Med. Chem.*, **13**, 1248 (1970).

(2) Screening results were supplied by CCNCS of the National Institutes of Health, Bethesda, Md.

(3) Melting points were taken on a Leitz hot stage microscope and were uncorrected. The ir spectra were determined with a Leitz Model III spectrograph. Nmr spectra were obtained on a Varian A60A instrument.

(4) C. S. Miller, U. S. Patent 2,608,512 (1953); *Chem. Abstr.*, **47**, 5440*d* (1953).

(5) Fujio Nagasawa, Japanese Patent 278 (1954); *Chem. Abstr.*, **49**, 11024*e* (1955).

Aldehyde Disubstituted Aminoacethydrazones as Potential Hypertensive Agents

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In the course of our research on new nitrofuran derivatives, the usual pharmacological screening showed a hypertensive activity for 5-nitrofuran-2-aldehyde diethylaminoacethydrazone, 5-nitrofuran-2-aldehyde *N*-pyrrolidinoacethydrazone, and 5-nitrofuran-2-aldehyde *N*-piperidinoacethydrazone.[1]

This observation prompted us to synthesize a series of disubstituted acethydrazones. No activity on arterial pressure was found except for compds **1**, **8**, **15**, **16**, **33**, and **44** which exhibited a light hypotensive activity. Some derivatives of naphthaldehydes, of 2,3,5,6-tetramethylbenzaldehyde, of 2-methylbenzofuran-3-aldehyde and of *p*-chlorobenzaldehyde (**10**, **11**, **13**, **21**, **30**, **32**, **37**, **48**, **50**, and **56**) were found active ip in mice at 30–50 mg/kg (corresponding to about 0.2 LD_{50}) as anticonvulsants in electroshock.[2]

Experimental Section[3]

2-Formylbenzofuran.[4]—A mixt of 48.6 g (0.03 mole) of benzofuran-2-carboxylic acid and 178.47 g (1.5 moles) of $SOCl_2$ was refluxed for 2 hr. The $SOCl_2$ was distd at reduced pressure. The residue, dissolved in 450 ml of PhMe, was reduced by the procedure of Rosenmund. The catalyst was filtered, and the solvent was evapd *in vacuo* at 40° under N_2. The crude oil distd at 98° (0.5 mm), yield 31 g (72%). *Anal.* ($C_9H_6O_2$) C, H.

Aminoacethydrazones. Method A.—A mixt of 0.01 mole of aldehyde, 0.01 mole of aminoacethydrazide, and 3 ml of EtOH was refluxed for 2 hr. When the products crystd, they were collected

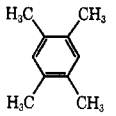
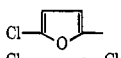
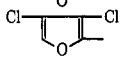
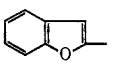
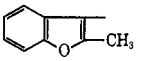
(1) E. Massarani, D. Nardi, A. Tajana, and L. Degen, *J. Med. Chem.*, **14**, 633 (1971).

(2) E. Massarani, D. Nardi, and M. J. Magistretti, *ibid.*, **9**, 617 (1966).

(3) Melting points are uncorrected and were determined in a capillary tube. Analyses are indicated only by the symbols of the elements. The anal. results were within ±0.4% of theor values.

(4) Other authors synthesized this compound with other methods [T. Reichstein and I. Reichstein, *Helv. Chim. Acta*, **13**, 1275 (1930); H. Normont, *C. R. Acad. Sci.*, **218**, 683 (1944); M. Bisagni, *J. Chem. Soc.*, 3688 (1955)].

TABLE I: DIETHYLAMINOACETHYDRAZONES
$(C_2H_5)_2NCH_2CONHN{=}CHR$

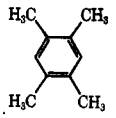
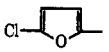
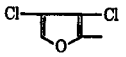
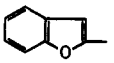
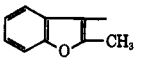
No.	R	Method	Recrystn solvent	Mp, °C	Yield, %	Formula[a]
1	2-ClC_6H_4	AB	Hexane	76	70	$C_{13}H_{18}ClN_3O$
			EtOH	208		$C_{13}H_{18}ClN_3O \cdot HCl$
2	4-ClC_6H_4	AB	*i*-PrOH	161–162	70	$C_{13}H_{18}ClN_3O \cdot HCl$
3	2-HOC_6H_4	AA	EtOH	202–203	61	$C_{13}H_{19}N_3O_2 \cdot HCl$
4	4-HOC_6H_4	AD	MeOH–Et_2O	252	88	$C_{13}H_{19}N_3O_2 \cdot HCl$
5	3,4-HOC_6H_3	AA[b]	*i*-PrOH	183	80	$C_{13}H_{19}N_3O_3$
			EtOH	175		$C_{13}H_{19}N_3O_3 \cdot HCl$
6	2-$O_2NC_6H_4$	AC	C_6H_6–petr ether	68–69	63	$C_{13}H_{18}N_4O_3$
			i-PrOH	168		$C_{13}H_{18}N_4O_3 \cdot HCl \cdot H_2O$
7	4-$O_2NC_6H_4$	AA	EtOH–H_2O	141	60	$C_{13}H_{18}N_4O_3$
			EtOH	147		$C_{13}H_{18}N_4O_3 \cdot HCl \cdot H_2O$
8	3,4,5-$(CH_3O)_3C_6H_2$	B	Ligroin	110–111	50	$C_{16}H_{25}N_3O_4$
			i-PrOH	177–179		$C_{16}H_{25}N_3O_4 \cdot HCl$
9		B	Petr ether	73–74	47	$C_{13}H_{25}N_3O$
10	1-Naphthyl	B	Ligroin	92–93	51	$C_{17}H_{21}N_3O$
			EtOH–Et_2O	208–210		$C_{17}H_{21}N_3O \cdot HCl$
11	4-Cl-1-naphthyl	B	Ligroin	126–127	74	$C_{17}H_{20}ClN_3O$
			EtOH–Et_2O	203–205		$C_{17}H_{20}ClN_3O \cdot HCl$
12	2-Naphthyl	B	EtOH–Et_2O	230–232	25	$C_{17}H_{21}N_3O \cdot HCl$
13		B	Ligroin	141–143	50	$C_{17}H_{27}N_3O$
			EtOH–Et_2O	187–188		$C_{17}H_{27}N_3O \cdot HCl$
14	2-Furyl	AD	*i*-PrOH	177–178	75	$C_{11}H_{17}N_3O_2 \cdot HCl$
15		B[c]	Ligroin	89–91	63	$C_{11}H_{16}ClN_3O_2$
			EtOH	196–198		$C_{11}H_{16}ClN_3O_2 \cdot HCl$
16		B	Ligroin	97–99	64	$C_{11}H_{15}Cl_2N_3O_2$
			EtOH–Et_2O	181–182		$C_{11}H_{15}Cl_2N_3O_2 \cdot HCl$
17		AD[d]	EtOH	228	83	$C_{15}H_{19}N_3O_2 \cdot HCl$
18		AB[d]	EtOH–H_2O	109	52	$C_{16}H_{21}N_3O_2$
			i-PrOH	207		$C_{16}H_{21}N_3O_2 \cdot HCl$

[a] All compds gave analyses for C, H, N, and Cl within 0.4% of theory. [b] Reaction in *i*-PrOH. [c] The reaction was carried out in stoppered flask, because of the ready sublimation of 5-chlorofuran-2-aldehyde. [d] Reaction in *i*-PrOH for 4 hr.

TABLE II: *N*-PYRROLIDINOACETHYDRAZONES

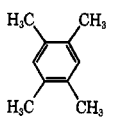
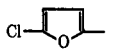
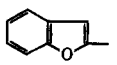
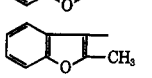
No.	R	Method	Recrystn Solvent	Mp, °C	Yield, %	Formula[a]
19	C_6H_5	AC	EtOH–H_2O	130–131	91	$C_{13}H_{17}N_3O$
20	2-Cl-C_6H_4	AA	EtOH	150	67	$C_{13}H_{16}ClN_3O$
			EtOH	232		$C_{13}H_{16}ClN_3O \cdot HCl$
21	4-Cl-C_6H_4	AA	C_6H_6	135	60	$C_{13}H_{16}ClN_3O \cdot H_2O$
			EtOH	175		$C_{13}H_{16}ClN_3O \cdot HCl \cdot H_2O$
22	2-HOC_6H_4	AA	EtOH	154–155	81	$C_{13}H_{17}N_3O_2$
23	4-HOC_6H_4	A[b]	EtOH–Et_2O	224	45	$C_{13}H_{17}N_3O_2 \cdot HCl$
24	3,4-HOC_6H_3	AA	EtOH	218–220	75	$C_{13}H_{17}N_3O_3 \cdot HCl$
25	2-$O_2NC_6H_4$	AA	EtOH	133	73	$C_{13}H_{16}N_4O_3$
			EtOH	224–225		$C_{13}H_{16}N_4O_3 \cdot HCl$
26	4-$O_2NC_6H_4$	AA	MeOH	168	74	$C_{13}H_{16}N_4O_3 \cdot H_2O$
			EtOH	241		$C_{13}H_{16}N_4O_3 \cdot HCl$
27	3,4,5-$(CH_3O)C_6H_2$	B	C_6H_6–ligroin	142–143	62	$C_{16}H_{23}N_3O_4$
			EtOH–Et_2O	230–231		$C_{16}H_{23}N_3O_4 \cdot HCl$
28		AC[c]	Ligroin–petr ether	95	72	$C_{13}H_{23}N_3O$
29	1-Naphthyl	B	EtOH–H_2O	116–117	57	$C_{17}H_{19}N_3O$
			EtOH–Et_2O	210–211		$C_{17}H_{19}N_3O \cdot HCl$
30	4-Cl-1-Naphthyl	B	EtOH–H_2O	183–184	71	$C_{17}H_{18}ClN_3O$
			EtOH–Et_2O	234–236		$C_{17}H_{18}ClN_3O \cdot HCl$
31	2-Naphthyl	B	EtOH–Et_2O	240–242	32	$C_{17}H_{19}N_3O \cdot HCl$

TABLE II (*Continued*)

No.	R	Method	Recrystn Solvent	Mp, °C	Yield, %	Formula[a]
32		B	C_6H_6–ligroin	167–169	63	$C_{17}H_{25}N_3O$
			EtOH–Et_2O	233–235		$C_{17}H_{25}N_3O \cdot HCl$
33	2-Furyl	AC	C_6H_6	112–113	90	$C_{11}H_{15}N_3O_2$
			EtOH	225 dec		$C_{11}H_{15}N_3O_2 \cdot HCl$
34		B[d]	EtOH–H_2O	138–140	48	$C_{11}H_{14}ClN_3O_2$
			EtOH–Et_2O	220–221		$C_{11}H_{14}ClN_3O_2 \cdot HCl$
35		B	EtOH	144–145	55	$C_{11}H_{13}Cl_2N_3O_2$
			EtOH–Et_2O	222–223		$C_{11}H_{13}Cl_2N_3O_2 \cdot HCl$
36		AC[e]	EtOH–H_2O	149	59	$C_{15}H_{17}N_3O_2$
			EtOH	238		$C_{15}H_{17}N_3O_2 \cdot HCl \cdot H_2O$
37		AA[e]	EtOH–H_2O	140–141	56	$C_{16}H_{19}N_3O_2$
			MeOH	260 dec		$C_{16}H_{19}N_3O_2 \cdot HCl$

[a] All compds gave analyses for C, H, N, and Cl within 0.4% of theory. [b] The base was pptd by adding H_2O. [c] Reaction for 4 hr. [d] See footnote *c*, Table I. [e] Reaction in *i*-PrOH for 4 hr.

TABLE III: *N*-PIPERIDINOACETHYDRAZONES

No.	R	Method	Recrystn solvent	Mp, °C	Yield, %	Formula[a]
38	C_6H_5	AC[b]	EtOH–H_2O	153–154	96	$C_{14}H_{19}N_3O$
			EtOH	231–232		$C_{14}H_{19}N_3O \cdot HCl$
39	2-ClC_6H_4	AA	EtOH	153–154	75	$C_{14}H_{18}ClN_3O$
			EtOH	242		$C_{14}H_{18}ClN_3O \cdot HCl$
40	4-ClC_6H_4	AB	EtOH–H_2O	140–141	35	$C_{14}H_{18}ClN_3O \cdot H_2O$
			EtOH	236–237		$C_{14}H_{18}ClN_3O \cdot HCl$
41	2-HOC_6H_4	AA	EtOH	109–110	85	$C_{14}H_{19}N_3O_2 \cdot H_2O$
			MeOH–Et_2O	243–245		$C_{14}H_{19}N_3O_2 \cdot HCl$
42	4-HOC_6H_4	AA	MeOH	243–245	69	$C_{14}H_{19}N_3O_2 \cdot HCl$
43	3,4-$(HO)_2C_6H_3$	AA	EtOH	213–214	65	$C_{14}H_{19}N_3O_3 \cdot HCl$
44	3,4,5-$(CH_3O)_3C_6H_2$	B	C_6H_6–ligroin	147–148	79	$C_{17}H_{25}N_3O_4$
			EtOH–Et_2O	211–213		$C_{17}H_{25}N_3O_4 \cdot HCl$
45	2-$O_2NC_6H_4$	AA	EtOH	135	70	$C_{14}H_{18}N_4O_3$
			EtOH	209–210		$C_{14}H_{18}N_4O_3 \cdot HCl \cdot H_2O$
46	4-$O_2NC_6H_4$	AA	EtOH–H_2O	187	62	$C_{14}H_{18}N_4O_3$
			MeOH	259–261		$C_{14}H_{18}N_4O_3 \cdot HCl$
47	H	AC[c]	Ligroin	93–94	90	$C_{14}H_{25}N_3O$
48	1-Naphthyl	B	Ligroin	134–136	49	$C_{18}H_{21}N_3O$
			EtOH–Et_2O	208–209		$C_{18}H_{21}N_3O \cdot HCl$
49	4-Cl-Naphthyl	B	C_6H_6	168–169	59	$C_{18}H_{20}ClN_3O$
			EtOH–Et_2O	244–246		$C_{18}H_{20}ClN_3O \cdot HCl$
50	2-Naphthyl	B	EtOH–Et_2O	239–241	27	$C_{18}H_{21}N_3O \cdot HCl$
51			EtOH	160–162	60	$C_{18}H_{27}N_3O$
			EtOH–Et_2O	199–201		$C_{18}H_{27}N_3O \cdot HCl$
52	2-Furyl	AC	EtOH–H_2O	124	76	$C_{12}H_{17}N_3O_2$
			EtOH	248–250		$C_{12}H_{17}N_3O_2 \cdot HCl$
53		B[d]	C_6H_6–ligroin	150–151	75	$C_{12}H_{16}ClN_3O_2$
			EtOH–Et_2O	235–237		$C_{12}H_{16}ClN_3O_2 \cdot HCl$
54		B	EtOH–H_2O	173–174	62	$C_{12}H_{15}Cl_2N_3O_2$
			MeOH–Et_2O	265 dec		$C_{12}H_{15}Cl_2N_3O_2 \cdot HCl$
55		AB[e]	EtOH	176	63	$C_{16}H_{19}N_3O_2$
			EtOH	250 dec		$C_{16}H_{19}N_3O_2 \cdot HCl$
56		AA[f]	EtOH	150	54	$C_{17}H_{21}N_3O_2$
			EtOH	253 dec		$C_{17}H_{21}N_3O_2 \cdot HCl$

[a] All compds gave analyses for C, H, N, and Cl within 0.4% of theory. [b] Reaction in 10 ml of EtOH. [c] Reaction time 4 hr. [d] See footnote *c*, Table I. [e] The reaction was carried out in 6 ml for 4 hr. [f] The reaction was carried out in 6 ml for 4 hr.

and recrystd (AA). Sometimes the crystn took place by addn of H_2O (AB). In other cases the EtOH was evapd, and the residue was washed with H_2O and crystd (AC). When we were not able to isolate the bases, we obtd the hydrochlorides by acidification of the reaction mixt (AD) (see Tables I, II, and III).

Method B.—A soln of 0.01 mole of aldehyde and 0.011 mole of

aminoacethydrazide in 10 ml of AcOH was stirred for 2 hr at 21–25°. Then 20% aq Na_2CO_3 was added to alkalinity. Some products pptd as solids, others sepd as thick oils which solidified on standing. The sepd solids were collected and crystd. The hydrochlorides were prepd by conventional procedures (see Tables I, II, and III).

1-Substituted-3,3-dimethylspiro[indoline-2,3′-thietane] 1′,1′-Dioxides Derived from 2-Methyleneindolines

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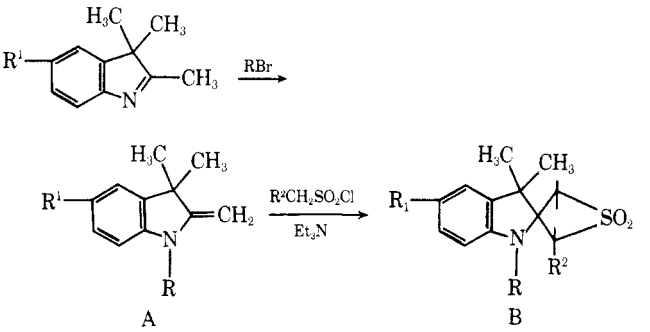
The enamine character of 2-methylene-1,3,3-trimethylindoline (A, R = Me; R¹ = H) was the subject of a review in 1949 by Coenen.[2] Stork and Borowitz[3] more recently reported a new class of amino-substituted, four-membered cyclic sulfones (thietane 1,1-dioxides) synthesized by reaction of enamines with $CH_2{=}{=}SO_2$, the intermediate sulfene generated *in situ* from MsCl upon treatment with Et_3N.[4] Cycloaddition of $CH_2{=}{=}SO_2$ and $PhCH{=}{=}SO_2$ to 1-substituted-2-methylene-3,3-dimethylindolines (A) under the Stork-Borowitz conditions has resulted in the new spiroindolinethietane ring system B as shown in the following reaction sequence.



No significant activity was observed under conditions of the test models in antiviral, antibacterial, antifungal, anthelmintic, hypotensive, and antiinflammatory, or reproductive physiology screening procedures.

Experimental Section

The following examples serve as general procedures for the preparation of compds A and B listed in Table I.

3,3-Dimethyl-1-hexyl-2-methyleneindoline (A-5).—A mixt of 68 ml (0.4 mole) of 2,3,3-trimethylindolenine (Fairmount Chemical Co.) and 65 g (0.4 mole) of *n*-$C_6H_{13}Br$ in 250 ml of PhMe was refluxed 24 hr with stirring.[5] The semisolid reaction mixt was treated with 100 ml of 30% KOH and stirred vigorously for 0.5 hr.[6] The PhMe layer was sepd and fractionally distd. After a forerun of unchanged *n*-$C_6H_{13}Br$, 30 ml of starting indolenine was recovered at 75–78° (0.25 mm). The desired product distd at 115–117° (0.82 mm) and amounted to 42 g of yellow oil that turned purple on exposure to air.

1-Hexyl-3,3-dimethylspiro[indoline-2,3′-thietane] 1′,1′-Dioxide (B-5).—To a stirred mixt of 32 g (0.2 mole) of the indoline A-5 and 40 ml of Et_3N in 200 ml of pure PhMe maintained at 5° was added dropwise 16.5 ml (0.2 mole) of MsCl in 30 ml of PhMe in 1 hr.[3] The mixt was stirred overnight at room temp then filtered, and the ppt was washed with 100 ml of PhMe. The product obtained by rotary evapn of the filtrate was recrystd from MeOH and washed with Et_2O to remove pink coloration.

TABLE I
1-SUBSTITUTED-3,3-DIMETHYLSPIRO[INDOLINE-2,3′-THIETANE] 1′,1′-DIOXIDES (B) AND THEIR INTERMEDIATE 2-METHYLENEINDOLINES (A)

	A					B			
	R	R¹	Bp (mm), °C	% yield	Formula (Analysis)[a]	R²	Mp (corr) °C (dec)	% yield	Formula (Analysis)[a]
1	CH_3	H	*b*			H	138–140	62	$C_{13}H_{17}NO_2S$
2	CH_3	H	*b*			Ph	130[c]	45	$C_{19}H_{21}NO_2S$
3	CH_3	H	*b*			CH_2CH_2Cl	129–30	25	$C_{15}H_{20}ClNO_2S$[d]
4	CH_3	Cl	*e*			H	200[c]	50	$C_{13}H_{16}ClNO_2S$
5	*n*-Hexyl	H	115–117 (0.28)	43	$C_{17}H_{25}N$	H	90–91	62	$C_{18}H_{27}NO_2S$
6	CH_2CO_2Et	H	111–113 (0.10)	29	$C_{15}H_{19}NO_2$[f]	H	143–144	57	$C_{16}H_{21}NO_4S$
7	Benzyl	H	130–132 (0.20)	48	$C_{18}H_{19}N$[g]	H	201[c]	41	$C_{19}H_{21}NO_2S$
8	2-Phenethyl	H	134–136 (0.25)	50	$C_{19}H_{21}N$	H	143–144	53	$C_{20}H_{23}NO_2S$
9	1-Naphthylmethyl	H	188–193 (0.20)	49	$C_{20}H_{21}N$[h]	H	190–192	20	$C_{23}H_{23}NO_2S$

[a] C, H, N (type A) and C, H, S (type B) analyses were within ±0.4% of calcd values unless indicated in this column. [b] Obtd from Aldrich Chemical Co., Inc. [c] Decomposes without melting. [d] S anal. not obtained; Cl and N values in good agreement with calcd. [e] Obtained from Gallard-Schlesinger Chemical Mfg. Corp. [f] Not analyzed as it decompd rapidly and required immediate use. [g] N anal. inadvertently omitted. [h] Used crude without anal.

The ir, uv, and nmr spectra, as well as elementary anal., were compatible with the structure proposed for B. For example, the nmr spectrum of B-1 (R = Me; R¹ = R² = H) showed chemical shifts as follows: δ 1.36 (singlet, 6 H, 3,3-Me_2); 2.95 (singlet, 3 H, NMe); 4.20, 4.25, 4.28, and 4.30 (singlets, each 1 H, 4 thietane ring H's); 6.3–7.3 (multiplet, 4 H, arom). Unexpectedly, these compds (B) were not sufficiently basic to form HCl salts.

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(2) M. Coenen, *Angew. Chem.*, **61**, 11 (1949).

(3) G. Stork and I. Borowitz, *J. Amer. Chem. Soc.*, **84**, 313 (1962); similar results were published almost simultaneously by G. Opitz and H. Adolph, *Angew. Chem., Int. Ed. Engl.*, **1**, 113 (1962).

(4) The existence of $CH_2{=}{=}SO_2$ and related sulfenes as intermediates generated *in situ* has been well documented since 1962; *cf.* the reviews by T. J. Wallace, *Quart. Rev.*, **20**, 67 (1966), and G. Opitz, *Angew. Chem., Int. Ed. Engl.*, **6**, 107 (1967). Opitz also reviews the cycloaddition of sulfenes to enamines.

(5) P. Lochon and O. O. Jamboo-Geoffroy, *Bull. Soc. Chim. Fr.*, 393 (1965), quarternarized with $Cl_2C{=}{=}CHCl$ as solvent.

(6) B. Robinson, *J. Chem. Soc.*, 586 (1963), reported this procedure.