3,77/*s* ($COOCH_3$); 4,15–4,7/*m* (2H, H–C(2) und H–C(3)); 6,7–7,7/*m* (7H, aromatische H); ~8,6/*m*, br. (2H, H–C(α) des Pyridyls und O–H). – MS.: 341 (5, M^+), 309 (38), 250 (39), 204 (80), 180 (92), 173 (100), 146 (50), 113 (40), 106 (33), 105 (78), 79 (37), 59 (22). – IR. (KBr): 3244 (O–H), 1744 und 1706 (C=O, Ester), 1612, 1590, 1576, 1569 und 1488 (Aromat, Heteroaromat), 1282 und 1225 (C–O–C), 767 (*o*-disubst. Aromat).

$C_{19}H_{19}NO_5$ (341,36) Ber. C 66.85 H 5.61 N 4.10% Gef. C 66.77 H 5.69 N 3.98%

*Dimethyl-2-(*o*-hydroxyphenyl)-3-(pyrid-4-yl)-1,1-cyclobutandicarboxylat* (**13**). **13** erhält man auf die gleiche Weise wie **12**: 30 g **7** ergeben 26 g weisse Kristalle vom Smp. 142–144°. – NMR. ($CDCl_3$, 60 MHz): 2,25–2,6/*m* und 3,1–3,35/*m* (2H, 2H–C(4)); 3,33/*s* (3H, in *m* eingeschlossen, $COOCH_3$); 3,83/*s* (3H, $COOCH_3$); 4,08–4,58/*m* (2H, H–C(2) und H–C(3)); 6,75–7,4/*m* (aromatische H und H–C(β) des Pyridyls); ~8,5/*m*, br. (3H, H–C(α) des Pyridyls und O–H). – MS.: 341 (0,2, M^+), 310 (0,5), 250 (20), 204 (95), 197 (37), 196 (25), 173 (70), 146 (48), 113 (100), 59 (41).

$C_{19}H_{19}NO_5$ (341,36) Ber. C 66.85 H 5.61 N 4.10% Gef. C 66.78 H 5.65 N 3.90%

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85. A Convenient Alkyl, Cycloalkyl and Aralkyl Disulfides Synthesis from Aliphatic and Aromatic Aldehydes, Aliphatic Ketones and Cycloketones

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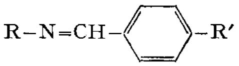
(31. VII. 75)

Summary. The reaction of aliphatic and aromatic aldehydes, aliphatic ketones, and cycloketones with hydrogen sulfide in anhydrous pyridine triethylamine medium, provides a satisfactory method for preparation of alkyl, cycloalkyl, and aralkyl disulfides.

As a part of our current research, we proceeded to synthesize and study thioamide derivatives of *Schiff* bases I through the thiolysis of corresponding nitriles II in anhydrous medium [1]. However in this case the reaction took an unusual path. The addition of hydrogen sulfide to II in the presence of triethylamine and pyridine, an excess of which may serve as solvent, and after 2 days at room temperature, in all cases afforded the same compound, m.p. 222°. It crystallized from *n*-butanol. Its mass spectrum showed a molecular ion peak at 364 *m/e* and were about 2% of the base peak. The base peak was observed at 116 *m/e* that we attribute to p-NC–$C_6H_4CH_2$–.

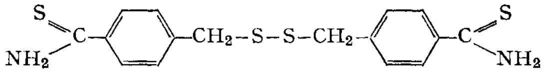
Other important fragments *m/e* were observed at 182 (26, *p*-$H_2NSC-C_6H_4-CH_2-S$); 150 (37, *p*-$H_2NSC-C_6H_4-CH_2$); 148 (13, $NC-C_6H_4-CH_2-S$); 122 (26, $C_6H_4CH_2-S$); 102 (10, $NC-C_6H_4$); 90 (47, $C_6H_4-CH_2$); 60 (16, H_2NSC).

Elemental analysis of this compound is in accordance with $C_{16}H_{16}N_2S_4$. The above mentioned data can correspond only to structure III which represents 4,4′-bis-(thiocarbamoyl)-dibenzyl disulfide.



R = C_6H_5, *p*-$CH_3-C_6H_4$, *p*-$CH_3O-C_6H_4$, *p*-$C_2H_5O-C_6H_4$, *m*-$Br-C_6H_4$

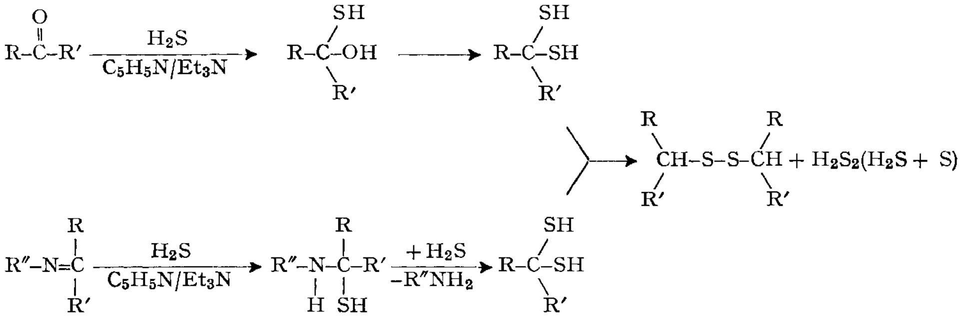
I: R′ = $CSNH_2$ II: R′ = CN



III

Under the same conditions we have obtained disulfides with aliphatic and aromatic aldehydes, aliphatic ketones, and cycloketones.

Consequently, the reaction of aliphatic and aromatic aldehydes, aliphatic ketones and cycloketones and corresponding *Schiff* bases with hydrogen sulfide in pyridine triethylamine medium, provides a satisfactory method for preparation of alkyl, cycloalkyl, and aralkyl disulfides for which we propose the following scheme:



$\overset{O}{\overset{\|}{R-C-R'}}$ = aliphatic and aromatic aldehydes, aliphatic ketones, cycloketones

R = alkyl, aryl R′ = H, alkyl R″ = aryl

The reaction is not applicable to alkyl aryl and diaryl ketones, perhaps because of steric hindrance.

The closest known similar reaction is reductive thiolation of highly fluorinated acids, acyl chlorides, aldehydes, and ketones that provide the synthesis of α-hydrofluoroalkanethiols and in a few cases between 2 to 21% disulfide formation as by-products [2]. The IR. spectra of the disulfides (Table 2) showed C–S absorption band at 585–555 cm^{-1} and S–S absorption band at 525–505 cm^{-1}.

The following methods are those usually used in the preparation of disulfides:

(1) $R{-}S{-}H \xrightarrow{\text{oxydized}} R{-}S{-}S{-}R$ [3–11]

(2) $R{-}X + Na_2S_2 \longrightarrow R{-}S{-}S{-}R$ [12] [13]

(3) $p\text{-}CH_3C_6H_4SO_3R + (Na_2S + S) \longrightarrow R{-}S{-}S{-}R$ [14]

(4) $Cl_3C{-}S{-}Cl + RSNa \longrightarrow [(RS)_3C{-}S]_2 + R{-}S{-}S{-}R$ [15]

(5) $CH_3SOCl + R{-}S{-}H \xrightarrow{\text{NaOH}} R{-}S{-}S{-}R$ [16]

(6) $RMgBr \xrightarrow{S} R{-}S{-}H + R{-}S{-}S{-}R$ [11] [17]

(7) $R{-}Br + Na_2S_2O_3 \longrightarrow R{-}S{-}S{-}R$ [18]

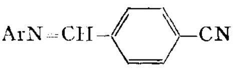
Experimental Part

General. – Melting points were measured on a *Kofler* hotbench apparatus. A *Beckman* IR-20A spectrophotometer was used for IR. spectra, which were run in KBr. The mass spectra were run on a *Varian* CH5 mass spectrometer. Microanalyses were performed by *C.N.R.S.* (Service Central de Microanalyse; 2, rue Henry-Dunant, 94-Thiais France).

All of the amines, benzaldehyde and vanillin were purchased from commercial sources. *p*-cyanobenzaldehyde, *p*-chlorobenzaldehyde, *p*-N, N-dimethylaminobenzaldehyde, *p*-methoxybenzaldehyde, and 2-hydroxynaphtaldehyde were prepared respectively by established procedures [19–22].

Schiff bases. – *(4-cyanobenzylidene) amino-benzene* (**1**, see Table 1). In a typical example, a mixture of 0.93 g (0,01 mol) aniline, 1.31 g (0.01 ml) *p*-cyanobenzaldehyde in 5 ml EtOH with a few drops of AcOH is heated under reflux for 5 min. The reaction mixture was filtered. Recrystallization from 2-propanol gave **1** (74%): m.p. 95°.

Table 1. Schiff *Bases*:

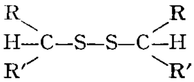


No.	Ar	m.p. °C	Crystalization solvent	yield %	Formula[a])
1	C_6H_5	95	2-propanol	74	$C_{14}H_{10}N_2$
2	p-$CH_3C_6H_4$	143	Toluene	80	$C_{15}H_{12}N_2$
3	p-$CH_3OC_6H_4$	116	Methanol	82	$C_{15}H_{12}N_2O$
4	p-$C_2H_5OC_6H_4$	112	Benzene	78	$C_{16}H_{14}N_2O$
5	m-BrC_6H_4	91	*n*-Butanol	60	$C_{14}H_9BrN_2$

[a]) Satisfactory analytical data (±0.40% for C, H, and N) were found for these compounds.

Alkyl, cycloalkyl, and aralkyl disulfides. – *4,4'-Bis-(thiocarbamoyl)-dibenzyl disulfide* (**6**, see Table 2). In a typical example, 0.1 mol *p*-cyanobenzaldehyde (or corresponding different *Schiff* bases) is dissolved in anhydrous pyridine and 10 ml triethylamine is added. Dry hydrogen sulfide is passed through the solution for 5–6 h. After 4 days (10 days for respective *Schiff* bases) at RT., the mixture is poured into cold water and the disulfide is collected by filtration and if necessary is washed twice with 10 ml cold methanol (in the case of *Schiff* bases to remove amine which is produced as a by-product). Recrystallisation from *n*-BuOH gave **6** (75–90%): m.p. 222°.

Table 2. *Disulfides*:



$\mathrm{R(R')HC{-}S{-}S{-}CH(R)R'}$

No.	$\mathrm{RR'CH}$	IR. bands [cm^{-1}] C–S	S–S	M.p. [°C]	B.p. [°C]	Crystallization solvent	Washing solvent	Yield [%]	Formula[a])
6	p-$H_2NCS{-}C_6H_4CH_2$*	575	500	222	–	n-BuOH	MeOH	90	$C_{16}H_{16}N_2S_4$
7	4-HO-3-$CH_3O{-}C_6H_4CH_2$*	565	525	133	–	EtOH	MeOH	80	$C_{16}H_{20}O_4S_2$
8	p-$(CH_3)_2N{-}C_6H_4CH_2$*	–	–	83	–	EtOH	MeOH	40	$C_{18}H_{24}N_2S_2$
9	2-$HO{-}C_{10}H_6CH_2$*	575	512	152	–	Ligroin (90–120°)	C_6H_6	40	$C_{22}H_{18}O_2S_2$
10	p-$CH_3O{-}C_6H_4CH_2$*	555	520	99	–	EtOH	MeOH	75	$C_{16}H_{18}O_2S_2$
11	p-$Cl{-}C_6H_4CH_2$	585	505	57	–	EtOH	–	95	$C_{14}H_{12}Cl_2S_2$
12	$C_6H_5CH_2$	568	505	71	–	EtOH	MeOH	90	$C_{14}H_{14}S_2$
13	Cyclopentyl	–	–	–	150^{14}	–	–	45	$C_{10}H_{18}S_2$
14	Cyclohexyl	–	–	–	117^{3}	–	–	61	$C_{12}H_{22}S_2$
15	C_2H_5	–	–	–	154	–	–	78	$C_4H_{10}S_2$
16	C_3H_7	–	–	–	193	–	–	43	$C_6H_{14}S_2$
17	C_4H_9	–	–	–	226	–	–	65	$C_8H_{18}S_2$
18	i-C_3H_7	–	–	–	177	–	–	13	$C_6H_{14}S_2$
19	s-C_4H_9	–	–	–	120^{12}	–	–	12	$C_8H_{18}S_2$

[a]) Satisfactory combustion analytical data for C, H, N and S (±0.4%) were found for these compounds.

*) New compound.

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86. Über das fluktuierende Verhalten von triphenylmethyl-substituierten Cyclopentadienyl-Metallverbindungen

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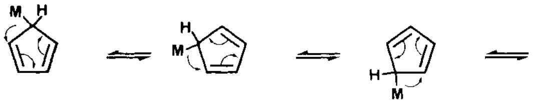
(6. XI. 75)

The fluxional behaviour of triphenylmethyl substituted cyclopentadienyl metal compounds. – *Summary.* ^{1}H-NMR. spectroscopy has been used to study the influence of the triphenylmethyl substituent on the metallotropic rearrangement in $C_5H_4(CPh_3)Si(CH_3)_3$ and $C_5H_4(CPh_3)Sn(CH_3)_3$. The most likely mechanism corresponds to a degenerate metal exchange between two neighbouring ring positions. The *AA'XX'* spectrum of the cyclopentadienyl ring protons in $C_5H_4(CPh_3)Sn(CH_3)_3$ has been analysed under rapid exchange conditions. The free energy of activation for the sigmatropic [1,5]-Sn shift has been measured by comparison with computer simulated spectra for slow exchange.

Einleitung. – Die Cyclopentadienylmetallverbindungen des Siliciums, Germaniums und Zinns gehören zu den ersten fluktuierenden metallorganischen Molekeln, die entdeckt und als solche erkannt worden sind [1]. In allen Fällen erfolgt die Umlagerung intramolekular als sigmatropische Metallverschiebung der Ordnung [1,5] entsprechend dem Schema:



Die freie Aktivierungsenthalpie der Umlagerung nimmt in der Reihe $M = Si(CH_3)_3 > Ge(CH_3)_3 > Sn(CH_3)_3$ mit steigender Ordnungszahl des Metalls ab [2]. Beim Ersatz von Methylgruppen durch Chlor, also z.B. in der Reihe $M = Si(CH_3)_3 < Si(CH_3)_2Cl < Si(CH_3)Cl_2 < SiCl_3$, nimmt $\Delta G^{\neq}$ zu [3]. Untersuchungen an Methylcyclopentadienyltrimethylsilan und -trimethylstannan sowie Pentamethylcyclopentadienyltrimethylstannan haben ausserdem gezeigt, dass die Methylsubstituenten den fluktuierenden Charakter dieser Verbindungen nur sehr wenig beeinflussen [4] [5]. Wie sich die Einführung einer Triphenylmethylgruppe in den Cyclopentadienylring auf die oben angegebene metallotrope Umlagerung für $M = Si(CH_3)_3$ und $Sn(CH_3)_3$ auswirkt, soll im folgenden gezeigt werden.

Ergebnisse. – 1. *(Triphenylmethyl-cyclopentadienyl)-trimethyl-silan.* Triphenylmethylcyclopentadien kann man durch Umsetzung von Dicyclopentadienylnickel $Ni(C_5H_5)_2$ mit Triphenylmethylchlorid gewinnen [6]. Man erhält unter Gleichgewichtsbedingungen bei Raumtemperatur ein Isomerengemisch von 21% 2- und 79% 3-substituiertem Cyclopentadien; das bei der Darstellung intermediär ent-