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SYNTHESIS OF 2-DIALKYLAMINO-1,3-DITHIETAN-2-YLIUM SALT. ACTION OF STRONG ACIDS ON BENZYLIDENEBIS(N,N-DIALKYLDITHIOCARBAMATES)

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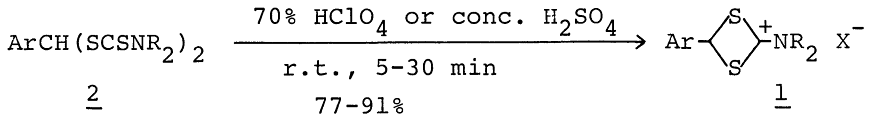
The protonation of benzylidenebis(N,N-dialkyldithiocarbamates) with 70% perchloric acid or conc. sulfuric acid produced new four-membered heteronium salts; 2-dialkylamino-4-aryl-1,3-dithietan-2-ylium salts in high yields. A possible mechanism for the formation and the structural elucidation of 1,3-dithietan-2-ylium salts were described.

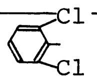
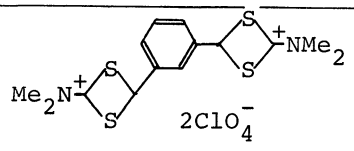
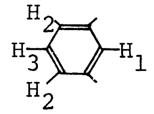
In this letter we wish to report a convenient method for the synthesis of the hitherto unknown four-membered heteronium salts; 2-dialkylamino-1,3-dithietan-2-ylium salts 1, which would be of great interest from the view point of their unexplored physical and chemical properties. Appropriate benzylidenebis(N,N-dialkyldithiocarbamates) 2 were easily obtained in 42-100% yields by the condensation of either two molar sodium N,N-dimethyl- or N,N-diethyl-dithiocarbamate with the required substituted benzylidene halides in DMF. Bis(dithiocarbamates) 2 were identified by elemental analyses and the characteristic IR absorption band about 1500 cm^{-1} due to the >N-CS-S- group. Upon treatment with strong acids such as 70% perchloric acid or conc. sulfuric acid, bis(dithiocarbamates) 2 were found to be converted readily under mild conditions (r.t., 5-30 min) into 2-dialkylamino-4-aryl-1,3-dithietan-2-ylium salts 1 (Table 1), which were not obtained by the direct condensation of sodium N,N-dialkyldithiocarbamates with benzylidene halides even under equimolar conditions.

$$ArCHCl_2 \text{ (or } ArCHBr_2) + 2\ NaSCSNR_2 \longrightarrow \underset{\underline{2}}{ArCH(SCSNR_2)_2}$$



The perchlorate salts were isolated by addition of water to the reaction mixture. In the case of conc. sulfuric acid, after the reaction mixture was poured into water followed by removal of the small amount of precipitates, perchlorate or iodide salt was isolated by either addition of aq. $NaClO_4$ or aq. NaI to the filtrate. The salts thus obtained were stable enough to be recrystallized from ethanol or acetonitrile.

Table 1. 2-Dialkylamino-4-aryl-1,3-dithietan-2-ylium salts 1

	R	Ar	X	Yield[a)] (%)	mp(°C)	$\nu_{C=N^+}$ (cm^{-1})	λ_{max}^{EtOH} (nm)	NMR(DMSO-d_6) (δ,ppm)
1a	Me	C_6H_5	ClO_4	90 77[b)]	178-179 (d.)	1650	238	3.33(NMe_2,s,6H) 5.93(>CH,s,1H) 7.53(Ph,m,3H) 7.90(Ph,m,2H)
1b	Et	C_6H_5	ClO_4	78 88[c)]	115-116 (d.)	1615	241	1.30($NCH_2\underline{CH_3}$,t,6H) 3.71($N\underline{CH_2}CH_3$,q,4H) 5.98(>CH, s,1H) 7.52(Ph,m,3H) 7.94(Ph,m,2H)
1c	Me		ClO_4	91	168-169 (d.)	1635	245	3.35(NMe_2,s,6H) 6.54(>CH,s,1H) 7.63(Ar,m,3H)
1d[d)]	Me	C_6H_5	I	89[b)]	169-170 (d.)	1630	225 236	3.37(NMe_2,s)[e)] 6.00(>CH,s,1H) 7.60(Ph,m,3H) 7.96(Ph,m,2H)
1e				86	184-185 (d.)	1650	242	3.30(NMe_2,s,12H) 5.92(>CH,s,2H) 7.60(H_3,t,1H) 7.96(H_2,d,2H) 8.18(H_1,s,1H) 

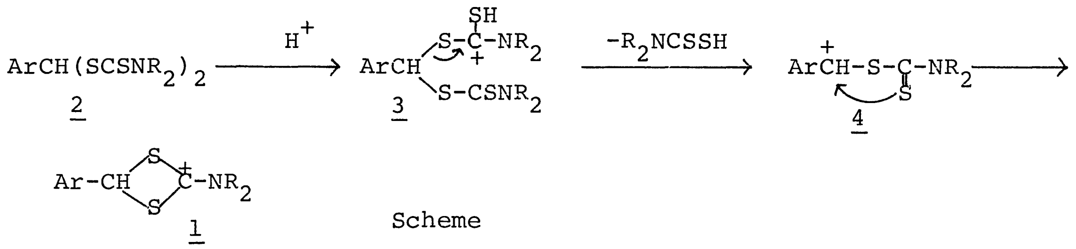
a) Unless otherwise indicated, yields refer to the 70% $HClO_4$ method

b) Conc. H_2SO_4 method c) Me_2SO_4 method (See below)

d) Found, C: 35.97, H: 3.51, N: 4.16%. Calcd., C: 35.63, H: 3.59, N: 4.16% Elemental analyses of 1a-c,e were not performed due to their explosions.

e) Exact proton numbers were not calculated due to overlapping with the H_2O peak in the solvent.

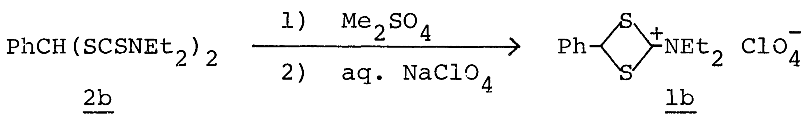
For the formation of 1,3-dithietan-2-ylium salt 1, we assumed that the prior protonation of thione-sulfur atom and the successive elimination of dithiocarbamic acid give α-(thiocarbamoylthio)benzyl cation, which is cyclized into 1,3-dithietan-2-ylium salt 1.



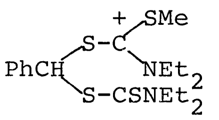
Scheme

On the other hand, both methylene- and ethylidenebis(N,N-dimethldithiocarbamate) were not affected by either 70% perchloric acid or conc. sulfuric acid and recovered unchanged. This fact indicates that the formation of relatively stable benzyl-type cation 4 is a motive force for the dithietan-2-ylium salt formation.

Furthermore, dimethyl sulfate in place of the acids was found to be effective for the above cyclization reaction. Thus the salt 1b was obtained in 88% yield in the reaction of 2b with equimolar amount of dimethyl sulfate at 80-90°C for 30 min followed by addition of aq. $NaClO_4$.



This reaction is assumed to proceed via the methylated intermediate 5 which corresponds to the intermediate 3 in the above scheme.



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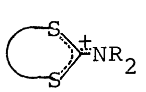
In general, hetero-substituted carbonium ions are strongly stabilized by accepting electrons from α-hetero atoms, and the positive charge is widely delocalized as expressed in formula 6.



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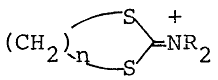

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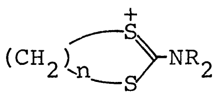

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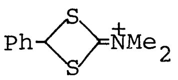

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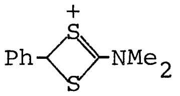

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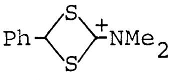
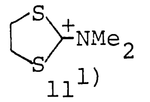
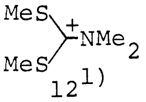
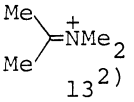
We have shown that the contribution of the sulfonium structure 8 to the overall structure increases with the decrease in their ring-size [n=2>3>4].[1)] An interesting problem concerning the structural aspects of the four-membered cation 1 (n=1) is whether the contribution of the sulfonium structure 10 increases or decreases due to the large strain energy, in comparison with the carbonium ions (n=2-4) or open chain analog 12. For this question, IR absorption band due to $\nu_{C=N^+}$ affords usefull suggestions, since this value reflects directly the double bond character between central carbon and nitrogen, in other words, the degree of the contribution of the iminium structure 9. The value of $\nu_{C=N^+}$ absorption of several carbonium perchlorates are summarized in Table 2.

Table 2. IR absorption of carbonium perchlorates

	 1a	 11 1)	 12 1)	 13 2)
$\nu_{C=N^+}$	1650 cm^{-1}	1584 cm^{-1}	1553 cm^{-1}	1687 cm^{-1}

From the Table 2 we can see the contribution of the iminium structure increases in the order; 12<11<1a<13, and that the value for 1a(1650 cm^{-1}) is close to the value for the pure iminium salt 13(1687 cm^{-1}). This indicates that the four-membered cation is stabilized mainly by the contribution of the iminium structure 9 and hence the contribution of the sulfonium structure 10 is fairly small. This is explained by the assumption that 1,3-overlap in this ring system, *i.e.*, $S\text{--}\overset{+}{C}\text{--}S$, is quite unfavorable due to the large strain energy of cyclobutene-type structure 10

Studies on the interesting chemical properties of 2-dialkylamino-1,3-dithietan-2-ylium salts newly obtained are now in progress.

References

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