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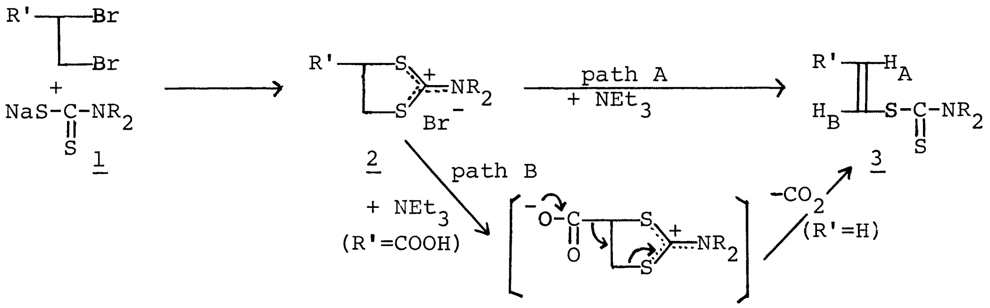
A NEW SYNTHETIC ROUTE TO 1,3-DITHIOLIUM SALTS INVOLVING NEIGHBORING GROUP PARTICIPATION OF DITHIOCARBAMATE GROUP

Kazuhisa HIRATANI, Hiroyuki SHIONO, and Makoto OKAWARA
Research Laboratory of Resources Utilization,
Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

A new and useful synthetic route to 1,3-dithiolium salts involving neighboring group participation of dithiocarbamate group as a key step is described. 4-Bromo-2-dialkylamino-1,3-dithiolan-2-ylium bromide was obtained in high yield by the addition of equimolar bromine to S-vinyl-N,N-dialkyldithiocarbamate, and then, pyrolysis of the salt under reduced pressure gave 1,3-dithiolium salt in excellent yield. 4-Substituted-1,3-dithiolium salts were also obtained in the same way.

Recently, 1,3-dithioles and 1,3-dithiolium salts[1)] have increasingly received attention from a viewpoint of their unique chemical and physical properties as hetero-aromatics, for example, their ion radical,[2)] the charge transfer complexes[3)] and their electrical conductivity.[4)] However, these cyclic sulfur compounds have been hitherto synthesized via multiple steps[5)] or in poor yield.[6)] Our previous studies[7)] have shown that neighboring group participation of dithiocarbamate group is useful as a synthetic tool for preparation of 1,3-dithio cyclic compounds. We wish to report here a new synthetic method of 1,3-dithiolium salts starting from S-vinyl-N,N-dialkyldithiocarbamate.

We reported previously that 2-dialkylamino-1,3-dithiolan-2-ylium perchlorate (2a) was obtained in high yield from the reaction of 1,2-dichloroethane with sodium N,N-dialkyldithiocarbamate (1) involving neighboring group participation of the dithiocarbamate group,[7)] and treatment of this cation with triethylamine gave S-vinyl-N,N-dialkyldithiocarbamate.[8)] In this work, some new S-vinyl derivatives (3b – 3d) with β-substituents were prepared in the similar way by use of corresponding dibromides (eq.1, path A). Further, the unsubstituted S-vinyl derivative (3a) was also obtained by treatment of 2 (R=Me, R'=COOH) with triethylamine in 25% yield presumably *via* the decarboxylation as shown in eq.1, path B. These products were identified by spectroscopic methods (NMR, IR and UV) and elemental analysis. The yield (2 → 3, path A), physical properties and spectral data of S-vinyl derivatives (3) are summarized in Table 1 . The *trans* geometry of 3b – 3d was determined by the NMR and IR data.



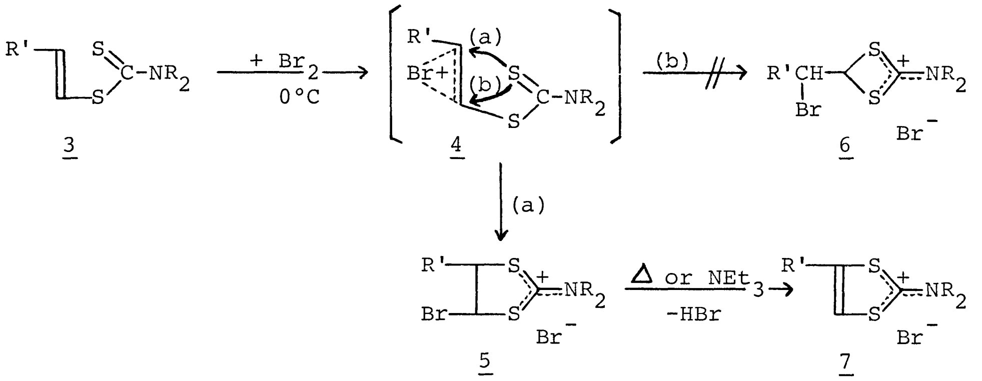
(1)

Table 1. The Yields and Properties of S-Vinyl Dithiocarbamates (3)

	R	R'	Yield** %	mp, °C (bp, °C/mmHg)	IR $\nu_{C=C}$, cm^{-1}	NMR, δ(ppm) from TMS H_A	H_B	J_{AB}, Hz
3a*	Me	H	65	(87–90/2)	1595	6.61	7.25	17
a'*	Et	H	63	(80–84/0.1)	1598	5.47	7.23	17
b	Me	Me	87	61–62	-	5.96	6.57	15
c	Me	Ph	80	62–63	1578	6.73	7.46	16
d	Me	AcO	60	54–56	1625	6.57	7.57	13

* These compounds (3a and 3a') were prepared in the same way as reported in our previous paper.[8] ** Based on 2, eq.1, path A.

The equimolar addition of bromine to the S-vinyl derivatives was carried out in carbon tetrachloride, chloroform or methylene chloride below 0°C. 4-Bromo-2-dialkylamino-1,3-dithiolan-2-ylium bromides (5) were obtained in good yield. The yield of the salts 5 increased in the order of solvent as follows: $CH_2Cl_2 > CHCl_3 > CCl_4$. The salts 5 were identified by the NMR,IR,and UV spectroscopic methods and elemental analysis. It should be noted that neither the corresponding α,β-dibromide nor the four-membered carbonium salt was obtained in this reaction. The formation of the five-membered 5 can be explained by neighboring group participation of the dithiocarbamate group *via* path (a) in formula 4. Although the four-membered 6 is possible to be formed *via* path (b), the formation of 6 is energetically less favorable due to the large distortion of the four-membered ring. The results thus obtained are summarized in Table 2.



(2)

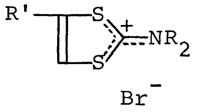
Table 2. Formation of 5 by the Treatment of 3 with Bromine

	Yield %	mp °C	UV (EtOH) λmax, nm	IR $\nu_{C=\overset{+}{N}}$, cm^{-1}	N, % Found	N, % Calcd
5a	88	132–135	254.5	1592	4.55	4.56
a'	85	103–104	258	1582	4.12	4.18
b	73	178–180	255.5	1584	4.30	4.36
c	94	181–182	225, 240, 316	1598	3.72	3.66
d	59	194(dec.)	253	1620	3.76	3.84

Finally, in order to eliminate hydrogen bromide from 5, the pyrolyses of 5 were undertaken in bulk at 140–180°C for 10 min under nitrogen atmosphere. It was found that the carbonium bromides (5a–5c) gave the corresponding 2-dialkylamino-1,3-dithiolium bromide (7) in excellent yields. Products thus obtained were identified by the spectroscopic methods (IR, NMR and UV), elemental analysis and comparisons of their physical properties with those of authentic samples. The yields and properties of 7 are summarized in Table 3. Treatment of 5a with triethylamine in acetonitrile also gave 7a. Pyrolytic method, however, is preferable to the triethylamine method since 7a is mixed up with triethylammonium bromide and is difficult to separate from triethylammonium bromide in the latter method.

Table 3. Pyrolysis of the Carbonium Salts (5)

	R	R'	Yield %	mp °C	UV (EtOH) λmax, nm
a	Me	H	99	196–198	296
a'	Et	H	84	136–137	300.5
b	Me	Me	98	203–204	303.5
c	Me	Ph	85	227–229	225, 315



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In summary, 1,3-dithiolium salt could be obtained readily and in high yield by the bromination of S-vinyl-N,N-dialkyldithiocarbamate followed by the elimination of hydrogen bromide through the pyrolytic method. This synthetic route to 1,3-dithiolium salt is superior to previously-reported methods.5),6) While the 4-aryl- or alkyl-1,3-dithiolium salts10),11) have been obtained by the cyclization of β-keto-dithioesters, the method fails in the absence of aryl or alkyl group. The preparation of other hetero aromatic systems by the present method involving neighboring group participation of groups other than N,N-dialkyldithiocarbamate is under investigation.

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