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# REGIOSPECIFIC NEIGHBORING-GROUP PARTICIPATION BY DITHIOCARBAMATE FUNCTION DURING BROMINATION OF γ-SUBSTITUTED S-ALLYL N,N-DIMETHYLDITHIOCARBAMATES(1)

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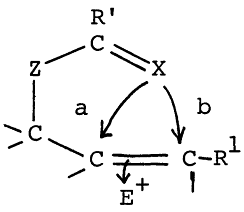
Bromination of the title compounds (1) resulted in the formation of the corresponding 2-dimethylamino-4-bromomethyl-1,3-dithiolan-2-ylium bromide (2) via regiospecific (S-5) participation by the dithiocarbamate function, irrespective of substitution on the γ-carbon atom. This is in contrast to the C-protonation of 1 in which the ratio of S-5 vs. S-6 depends on the γ-substitution.

Formation of heterocyclic carbonium ions via neighboring-group participation by various types of functions has received considerable attention.(2) Neighboring-group participation during electrophilic addition of allylic system I (X,Z = heteroatoms) is of particular interest in view of the possibility for two discrete pathways for participation, X-5 and X-6 closure, as shown below.

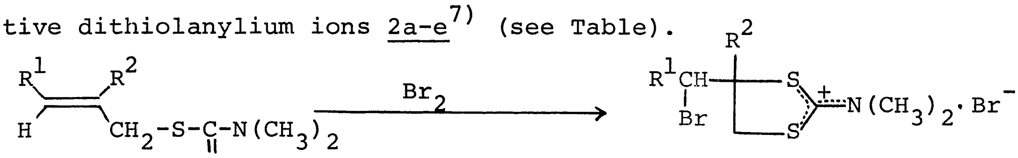


(I)

a, X-5 closure
b, X-6 closure

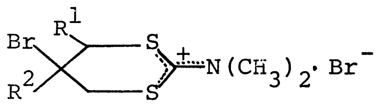
A few of the reports(3,4) have shown that the X-5 cyclization took place exclusively upon electrophilic olefin addition in some particular systems in which the β-carbon atom is more highly substituted than the γ-carbon. However, the question of X-5 vs. X-6 closure still remains unsolved,(2,4b) especially in γ-substituted allyl systems in which the unsaturated carbon atoms are equally substituted. Herein we wish to report that the cyclization during bromination of variously substituted S-allyl N,N-dimethyldithiocarbamates proceeded specifically at the β-carbon atom via S-5 participation by the dithiocarbamate function,(5) irrespective of substitution on the γ-carbon atom.

When bromine was added dropwise to a solution of S-crotyl dithiocarbamate (1a) in carbon tetrachloride at 0°C, 2-dimethylamino-4(α-bromoethyl)-1,3-dithiolan-2-ylium bromide (2a) precipitated out immediately. Ion 2a was identified by its NMR spectrum ($CF_3COOH$), which exhibited a doublet at δ 1.93 (3H, $>CBr-CH_3$), a doublet at 3.70 (6H, $N(CH_3)_2$), two doublets at 4.15 and 4.14 (2H, $S-CH_2$), and two multiplets at 4.44 - 4.76 (1H, >CBr-H) and 4.88 - 5.16 (1H, S-CH<). Dithiolanylium ion formation proved to be general and essentially quantitative as illustrated by the cyclization upon bromination of dithiocarbamates 1a-e$^{6)}$ to the respective dithiolanylium ions 2a-e$^{7)}$ (see Table).



1 2

a, $R^1=CH_3$, $R^2=H$; b, $R^1,R^2=H$
c, $R^1=C_6H_5$, $R^2=H$; d, $R^1,R^2=CH_3$
e, $R^1=H$, $R^2=CH_3$



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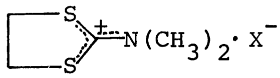
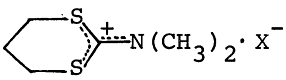
The assignment of ions 2 to the five-membered ring (S-5) structure, not to the six-membered 3 (S-6 structure), was based on the following facts:(1) the NMR spectra$^{7)}$ of ions 2 were more consistent with the S-5 structure;(2) comparisons of the frequencies of the ν(C=N) bands in the IR spectra of 2 with those of spectral reference ions 4 and 5$^{8)}$ (see Table) unequivocally established the S-5 structure for 2;(3) UV-spectral comparisons of 2 with 4 and 5$^{8)}$ also supported the X-5 structure for 2.

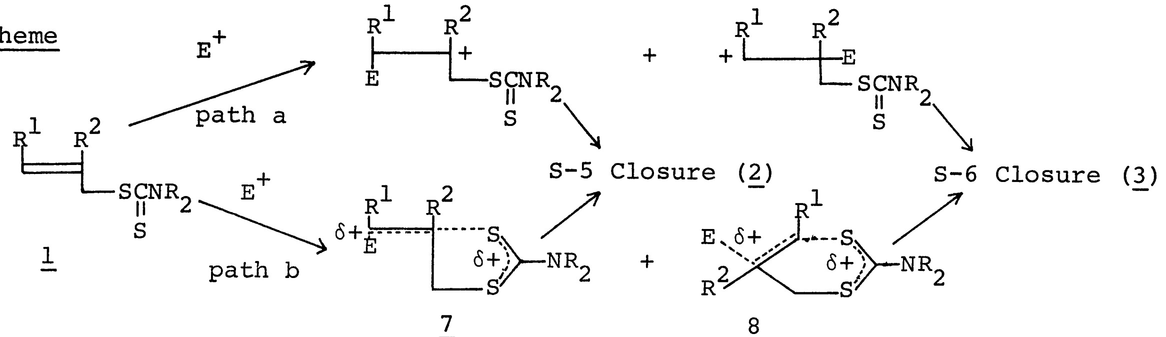
Table Yields and Physical Properties of 2

| Ion | Yield % | Mp °C | IR(KBr) ν(C=N), $cm^{-1}$ | UV(EtOH) λmax, nm |
|---|---|---|---|---|
| 2a | 98 | 162-164 | 1599 | 251.5 |
| b | 93 | 193-195 | 1590 | 250.5 |
| c | 95 | 150-152.5 | 1600 | 252 |
| d | 98 | 144-147 | 1590 | 253 |
| e | 97 | 202-204 | 1595 | 252 |
| 4 |  | | 1590-1600<br>(X=Br, $ClO_4$, etc) | 249-252<br>(X=Br, $ClO_4$) |
| 5 |  | | 1550-1575<br>(X=Br, $ClO_4$, etc) | 262<br>(X=$ClO_4$, TsO) |

It is interesting to note that no trace of the simple dibromide was formed in the bromination of 1; this is in contrast to bromination of N-allylcarbamates,[10) -benzamides,[3) and -ureas[11) in which the simple dibromides were formed. This is an indication of the superiority of $R_2NCSS$ over $R_2NCOO$, PhCONH, and $H_2NCONH$ for neighboring-group participation.

Of the greatest mechanistic interest is the fact that the cyclization during bromination of 1 proceeded exclusively at the β-carbon atom via S-5 participation by dithiocarbamate function, irrespective of substitution on the γ-carbon atom. This interesting result is in stark contrast to the cyclization during olefinic protonations of 1[12) and γ-substituted N-allylbenzthioamides[4b) (6; X=S, Z=NH, R'=Ph in I) in which the position of cyclization is altered by change of γ-substituent ($R^1$). For example, C-protonation of 1b ($R^1$=H) and 1a ($R^1$=$CH_3$) resulted in an exclusive S-5 closure and a mixture of S-5 and S-6, respectively, whereas that of 1c ($R^1$=Ph) resulted in an exclusive S-6 closure. In view of the possibility for two discrete pathways for cyclization of 1 during electrophilic addition (see Scheme), the results of cyclization during C-protonation of 1 and 6 are consistent with the concept of preferred cyclization to the more highly substituted carbon atom (path a).[4a,c) In contrast, the exclusive S-5 cyclization during bromination of 1 undoubtedly does not follow the Markovnikov rule. The origin of the regiospecificity of neighboring-group participation by dithiocarbamate function is interpreted on mechanistic grounds in terms of direct formation of 2 (path b) as follows.

Scheme



If neighboring-group participation is well developed in transition states 7 or 8, the stabilizing effect of the developing cyclic ions should swamp out the effect of the $R^1$ group. Thus the ratio of S-5 vs. S-6 turns out to be determined mainly by the relative stability of 2 and 3 rather than by the effect of the R$^1$ group. This permits us to predict an exclusive, at least preferable, formation of five-membered 2 since, in general, five-membered heterocyclic carbonium ions are thermodynamically more stable than the six-membered analogues2) which has been vigorously established for cyclic ions closely related to 2 and 3.9b)

## REFERENCES AND NOTES

* To whom correspondence may be addressed.

1) Tri(hetero)substituted Carbonium Ions. X. For paper IX in this series, see K.Hiratani, T.Nakai, and M.Okawara, Bull. Chem. Soc. Japan, 47, 904 (1974).

2) C.U.Pittman,Jr., S.P.McManus, and J.W.Larsen, Chem. Rev., 72, 357 (1972).

3) S.Winstein and L.Goodman, J. Amer. Chem. Soc., 79, 4788 (1950).

4) (a) S.P.McManus, J.T.Carroll, and C.U.Pittman,Jr., J. Org. Chem., 35, 3768 (1970) and references cited therein;(b) P.A.S.Smith and J.M.Sullivan, ibid., 26, 1132 (1961);(c) C.U.Pittman,Jr. and S.P.McManus, Tetrahedon Lett., 339 (1969).

5) For neighboring-group participation by dithiocarbamate function in systems otherthan allylic systems, see T.Nakai, Y.Ueno, and M.Okawara, Bull. Chem. Soc. Japan, 43, 156 (1970); T.Nakai, H.Kawaoka, and M.Okawara, ibid., 42, 508 (1969); K.Hiratani, H.Shiono, and M.Okawara, Chem. Lett., 867 (1973).

6) 1a-e were prepared by the reaction of the appropriate allyl bromides with NaSCSN(CH$_3$)$_2$ and fully characterized. 1d was a mixture of the E- and Z-isomers.

7) Ions 2a-e gave satisfactory elemental analyses. The NMR spectral data of 2b-e will be described in a full paper.

8) Effects of ring-size on $\nu$(C$\doteq$N)9a) and λmax9b) for 4 and its ring homologues have been fully discussed.

9) (a) T.Tanaka, K.Tanaka, and T.Yoshimitsu, Bull. Chem. Soc. Japan, 44, 112 (1971);(b) T.Nakai, Y.Ueno, and M.Okawara, ibid., 43, 3175 (1970).

10) M.Bergmann, F.Dreyer, and F.Radt, Ber., 54, 2139 (1921).

11) R.Andreasch, Monatsh., 5, 33 (1884).

12) H.Shiono, T.Nakai, K.Hiratani, and M.Okawara, unpublished results.

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