BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (8), 2339—2340 (1976)

Tri(hetero)substituted Carbonium Ions. XII. A Novel Ring Expansion of 1,3-Dithiolanylium Salts into 1,3-Dithia-4-cyclohexene (1,3-Dithiine) System

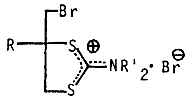
Kazuhisa HIRATANI,[1] Takeshi NAKAI,* and Makoto OKAWARA

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

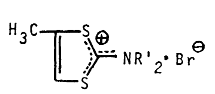
(Received March 12, 1976)

Synopsis. Pyrolysis of 2-dialkylamino-4-bromomethyl-4-methyl-1,3-dithiolanylium bromides (**2**) readily prepared by bromination of the *S*-(2-methylallyl) dithiocarbamates afforded the six-membered 2-alkylimino-5-methyl-1,3-dithiines (**4**) in good yields. A reasonable mechanism for the novel ring expansion is presented.

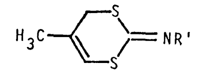
There has been considerable interest in the ring transformations of heterocyclic systems and their synthetic applications.[2] In the preceding paper,[3] we described the pyrolysis of 2-dialkylamino-4-bromomethyl-1,3-dithiolanylium bromides (**1**) readily prepared by bromination[4] of the *S*-allyl dithiocarbamates; this affords the 2-dialkylamino-4-methyl-1,3-dithiolylium salts (**3**) with retention of the five-membered structures.



1, R=H, R′=CH_3, C_2H_5
2, R=CH_3, R′=CH_3, C_2H_5

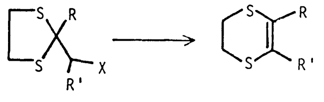


3



4a, R′=CH_3
b, R′=C_2H_5

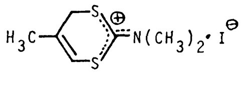
In this note we wish to report that pyrolysis of 2-dialkylamino-4-bromomethyl-4-methyl-1,3-dithiolanylium bromides (**2**) obtained by bromination of the *S*-(2-methylallyl) dithiocarbamates takes an entirely different course to give the six-membered 2-alkylimino-5-methyl-1,3-dithia-4-cyclohexenes (2-alkylimino-5-methyl-1,3-dithiines) (**4**). This novel ring transformation is, to our knowledge, the first example of a ring expansion of 1,3-dithiolane derivatives into 1,3-dithiine systems, although ring expansions of 1,3-dithiolane derivatives such as **5** into 2,3-dihydro-1,4-dithiine systems (**6**) are well precedented.[5]



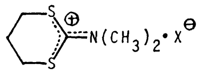
5, X=Cl, Br, OAc **6**

When the 1,3-dithiolanylium bromide **2a** (R=CH_3) was heated in bulk at the melting point (*ca.* 200 °C) for 10 min in nitrogen, **2a** was completely pyrolyzed, with the evolution of gases including methyl bromide, to afford 2-methylimino-1,3-dithiine (**4a**) and its hydrobromide salt (**4a′**) in 16% and 48% yields, respectively, along with an intractable tar. A similar pyrolysis of **2a** at 190 °C for 10 min followed by base treatment and column chromatography gave **4a** in 52%. Both **4a** and **4a′** were identified on the basis of their elemental analyses and spectroscopic properties: **4a**, IR (neat), 1592 cm^{-1} (C=N); NMR ($CDCl_3$), δ 2.05 (3H, d), 3.25 (3H, s), 3.0—3.5 (2H, m), and 6.1—6.3 (1H, m); **4a′** IR (KBr), 1580 cm^{-1} ($C=N^+$); NMR (DMSO-d_6), δ 2.16 (3H, s), 3.33 (3H, s), 3.97 (2H, s), 6.75 (1H, s), and 7.9—9.0 (1H, br. s).

The methylimino-1,3-dithiine **4a** was allowed to react with methyl iodide to give the 2-dimethylamino-1,3-dithiinylium iodide (**7**). The UV spectrum of **7** was very similar to that of the 1,3-dithianylium salt (**8**),[6] supporting the six-membered structure for **4a**.



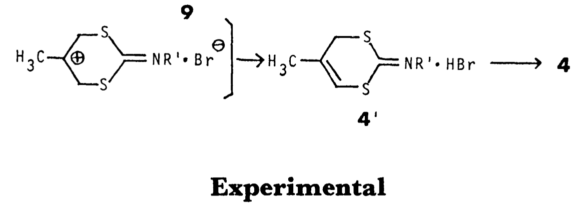
7



8, X=Br, ClO_4

A similar pyrolysis of **2b** (R′=C_2H_5) at 180—190 °C for 45 min followed by base treatment afforded the ethylimino-1,3-dithiine (**4b**) in 51% yield; **4b**, NMR (neat), δ 1.21 (3H, t), 2.04 (3H, s), 3.33 (2H, q), 3.4—3.6 (2H, m), and 6.1—6.3 (1H, m).

The tetrafluoroborate salt obtained by anion exchange of bromide **2a** with sodium tetrafluoroborate failed to undergo the ring expansion under the same conditions as in the pyrolysis of **2a** and was recovered quantitatively. This finding indicates that the thermal ring expansion is initiated by the elimination of alkyl bromide *via* the attack of the bromide anion on the *N*-alkyl carbon atoms. Therefore, the novel ring transformation is best rationalized by the following mechanism, which involves the ring expansion of the imino-1,3-dithiolane **9** formed *via* the elimination of alkyl bromide from **2**. The mechanism for the ring expansion process is analogous to the one accepted for the ring expansions[5] of **5** into **6** described above.



Experimental

All melting points are uncorrected. NMR and IR spectra were recorded on Japan Electron Optics spectrometers

---

* To whom inquires should be addressed: Department of Chemical Engineering, Tokyo Institute of Technology, Meguro, Tokyo 152.

(PS-100 or MH-60) and a Hitachi EPI-S2 spectrometer, respectively.

1,3-Dithiolanylium Bromides (2) were prepared by bromination of the corresponding *S*-(2-methallyl) dithiocarbamate, following the procedures described in the previous paper[4]; **2a** (R′=CH_3), mp 202—204 °C; **2b** (R′=C_2H_5), mp 116—120 °C. Treatment of **2a** with sodium tetrafluoroborate gave the tetrafluoroborate of **2a**, mp 151—153 °C (from ethanol).

Pyrolysis of Salts 2. (*a*): When the bromide **2a** (1.36 g, 4.0 mmol) was heated at 210 °C under nitrogen, the bromide gradually melted and the evolution of gases was observed. After heating at that temperature for 10 min, the gas evolution ceased. A white solid and a yellowish oil were formed at the top side of the flask, and a dark-brown tar was left at the bottom of the flask. The white solid was collected, washed with ether, and recrystallized from acetone-ethanol to give 0.45 g (48%) of the hydrobromide of **4a** (**4a′**); mp 175—177 °C. The spectral data are described above.

Found: C, 29.72; H, 4.19; N, 5.68%. Calcd for $C_6H_{10}BrNS_2$: C, 30.00; H, 4.17; N, 5.83%.

The ethereal washings were freed from solvent to give 0.01 g (16%) of **4a** as an oily residue. The spectral data are described above.

Treatment of the hydrobromide **4a′** thus obtained with triethylamine in benzene afforded the free imine **4a** in 96% yield. Furthermore, **4a** thus obtained was allowed to react with methyl iodide in acetone to give the 1,3-dithiinylium iodide (**7**); UV (EtOH), λ_{max} 244 (sh.) and 269 nm; IR (KBr), 1570 cm^{-1} ($C=N^+$).

Found: C, 27.32; H, 4.02; N, 4.73%. Calcd for $C_7H_{12}INS_2$: C, 27.90; H, 3.99; N, 4.65%.

(*b*): The bromide **2a** (5.00 g, 14.9 mmol) was pyrolyzed at 190 °C for 10 min in a similar manner. After cooling, an aqueous solution of sodium carbonate was added to the residue with stirring and the resulting mixture was extracted twice with ether. The combined extracts were dried over anhydrous sodium sulfate and freed from solvent to give an oily residue. Purification of the oil by chromatography on silica gel, using chloroform as eluent, followed by distillation, gave 1.23 g (52%) of **4a**: bp 77—79 °C/0.07 mmHg.

(*c*): The bromide **2b** (3.15 g, 8.7 mmol) was pyrolyzed at 180—190 °C for 45 min. After cooling, the residue was subjected to the same work-ups as in the case of (*b*) yielding 0.76 g (51%) of **4b** as an oil. The spectral data are described above.

(*d*): The tetrafluoroborate of **2a** (0.51 g) was heated at 210 °C for 10 min. After cooling, 0.506 g (99%) of the starting salt was recovered.

References

1) Present address: Industrial Product Research Institute, Ohta-ku, Tokyo 144.

2) H. C. Van Der Plas, "Ring Transformations of Heterocyclics," Vol. 1 and 2, Academic Press, London and New York (1973).

3) T. Nakai, K. Hiratani, and M. Okawara, *Bull. Chem. Soc. Jpn.*, **49**, 827 (1976).

4) K. Hiratani, T. Nakai, and M. Okawara, *Chem. Lett.*, **1974**, 1041.

5) L. F. Fieser, C. Yuan, and T. Goto, *J. Am. Chem. Soc.*, **82**, 1996 (1960); G. Karmas, *J. Org. Chem.*, **32**, 3147 (1967); M. Tomoeda, M. Ishizaki, H. Kobayashi, S. Kanamoto, T. Koga, M. Inuzaka, and T. Furuta, *Chem. Pharm. Bull.*, **12**, 383 (1964) and *Tetrahedron*, **21**, 733 (1965); J. L. Massingill, M. G. Reinecke, and J. E. Hodgkins, *J. Org. Chem.*, **35**, 823 (1970).

6) The definite effect of the ring-size on λ_{max} for the cyclic dithiocarbamidium salts such as **8** has been fully discussed in our previous paper [T. Nakai, Y. Ueno, and M. Okawara, *Bull. Chem. Soc. Jpn.*, **43**, 3175 (1970)].