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Tri(hetero)substituted Carbonium Ions. XI. A Novel Synthetic Route to 2-Dialkylamino-4-alkyl-1,3-dithiolium Salts

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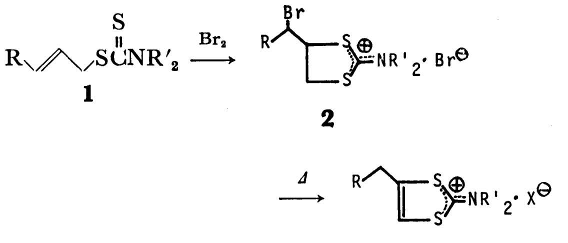
Synopsis. Pyrolysis of 2-dialkylamino-4-(α-bromoalkyl)-1,3-dithiolanylium bromides (**2**) readily prepared by bromination of the β,γ-unsaturated dithiocarbamates (**1**) affords 2-dialkylamino-4-alkyl-1,3-dithiolium salts (**3**) in good yields, providing a useful way to prepare dithiolium salts.

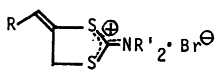
We have shown that bromination of β,γ-unsaturated dithiocarbamates (**1**) results in the quantitative formation of the corresponding 2-dialkylamino-4-(α-bromoalkyl)-1,3-dithiolanylium bromides (**2**) *via* regiospecific (S-5) participation by the dithiocarbamate function.[2] In this Note we wish to report an intriguing thermal transformation of **2** into 2-dialkylamino-4-alkyl-1,3-dithiolium salts (**3**) in good yields. The simple ring transformation is of interest since the dithiolium salt **3** has been an important class of synthetic intermediates[3] for the synthesis of tetrathiofulvalene derivatives which attracted attention in view of the interesting electroconductivity[4] of their charge transfer complexes. The new synthetic route to 4-alkyl-1,3-dithiolium salts is more advantageous than the recently developed methods[3c,5] in view of the operational simplicity and accessibility[6] of the starting materials.



a, R=H, R'=CH_3
b, R=H, R'=C_2H_5
c, R=CH_3, R'=CH_3

When 1,3-dithiolanylium salt (**2**) was heated in bulk at melting point (160—190 °C) in nitrogen under reduced pressure (*ca.* 5—10 mmHg), decomposition took place with the evolution of hydrogen bromide gas which was trapped in an ethanolic solution of triethylamine. The gas evolution ceased after 10—20 min. The resulting bromides, **3b** and **3c**, were converted, on treatment with an aqueous solution of sodium tetraphenylborate, into the tetraphenylborates which were then purified and characterized. The dithiolium salts thus obtained were identified by spectroscopic methods (NMR and UV) and elemental analyses, and/or by spectral comparison with authentic samples. Yields and physical properties of **3** are summarized in Table 1.

From the results it appears that the novel ring transformation involves an initial 1,2-dehydrobromination of **2** giving 4-alkylidene-1,3-dithiolanylium bromides (**4**) which further undergo 1,3-hydrogen shift, ultimately yielding the dithiolium salt **3**.



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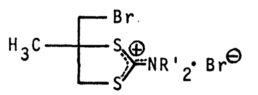

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(1) A similar pyrolysis of 4-bromomethyl-4-methyl-1,3-dithiolanylium bromide (**5**) which does not undergo 1,2-dehydrobromination gave no dithiolium salt, a ring expansion taking place.[7] This indicates that the transformation is initiated by the thermal 1,2-dehydrobromination.

(2) 4-Vinylidene-1,3-dithiolanylium bromide (**4a**; R=H, R'=CH_3) was isolated by the reaction of **2a** with triethylamine (Table 1). When **4a** thus obtained was

TABLE 1. 1,3-DITHIOLIUM SALTS (**3**) AND THE RELATED SALT

Salt (Anion)	Yield %	Mp °C	N, % Found/Calcd	NMR (DMSO-d_6)[a] (δ ppm from TMS)	UV (EtOH)[b] (λ_{max}, nm)
3a (X=Br)	91	178—180[c]		2.54(s, 3H), 3.57(s, 6H) 7.58(s, 1H)	247.5 303.5
3b (X=BPh_4)	~100	147—150	2.73/2.76	1.23(t, 6H), 2.32(s, 3H) 3.63(q, 4H), 6.5—7.5(m, 21H)	249 308.5
3c (X=BPh_4)	~100	183—187	2.88/2.84	1.40(t, 3H), 2.92(q, 2H) 3.65(s, 6H), 7.08(s, 1H)[a]	248 304.5
4a (X=Br)	83	189—190.5	5.97/5.83	3.62(s, 6H), 4.95(spl.s, 2H) 5.80—6.10(m, 2H)	253.5

a) All NMR spectra are those of the bromides except for **3b** (X=BPh_4). b) The molar extinction coefficients were not determined. Absorbances of the longer wavelength bands were greater than those of the shorter ones for all the dithiolium salts. c) Lit,[5b] mp 178—180 °C.

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heated under the same conditions as in the pyrolysis of **2a**, the dithiolium salt **3a** was obtained quantitatively, thus providing convincing evidence for occurrence of the 1,3-hydrogen shift of the intermediate **4**. A similar thermal 1,3-hydrogen shift was observed elsewhere.[8]

Experimental

All the melting points are uncorrected. NMR and UV spectra were recorded on Japan Electron Optics spectrometers (PS-100 or MH-60) and a Hitachi EPS-2 spectrometer, respectively.

4-Bromoalkyl-1,3-dithiolanylium Bromides (**2**) were prepared from the corresponding β,γ-unsaturated dithiocarbamates (**1**) following the procedure described previously[2]; **2a**, mp 193—195 °C (lit,[2] 193—195 °C); **2b**, mp 115—116 °C (Found: N, 4.10%. Calcd for $C_8H_{15}NS_2Br_2$: N, 4.01%); **2c**, mp 162—164 °C (lit,[2] 162—164 °C).

Pyrolysis of 2. Bromide **2a** (0.65 g, 2.0 mmol) was placed in a 30-ml distilling flask equipped with a nitrogen balloon. The flask was then connected with a vacuum pump through a trapping tube containing an ethanolic solution of triethylamine placed in a Dry Ice–acetone bath. When the flask was gradually heated up to 190 °C under reduced pressure (5—10 mmHg), the bromide gradually melted, evolution of hydrogen bromide being observed. After heating at 180—190 °C for 10 min, the gas evolution ceased. The flask was then cooled and the solid residue was recrystallized from a mixture of acetone and acetonitrile giving 0.44 g (91%) of the dithiolium bromide (**3a**). The physical data of **3a** (Table 1) are in agreement with the reported values.[5b]

Pyrolysis of **2b** at *ca.* 160 °C for 20 min gave the crude bromide which was further converted, on treatment with a saturated aqueous solution of sodium tetraphenylborate, into the dithiolium salt (**3b**, X=BPh_4); the salt was recrystallized from an aqueous acetone. Similarly, pyrolysis of **2c** at *ca.* 170 °C for 20 min followed by the anion exchange gave **3c** (X=BPh_4) which was then recrystallized from a mixture of acetone and acetonitrile.

Reaction of 2a with Triethylamine. Triethylamine (0.13 g, 1.3 mmol) was added to a solution of **2a** (0.40 g, 1.2 mmol) in dimethylformamide (6 ml) at 0 °C, and the mixture was stirred at room temperature for 1 hr. The solvent was then distilled off under reduced pressure below room temperature giving a white solid. The solid was washed five times with cooled acetone and recrystallized from a mixture of acetone and ethanol to give 0.25 g (83%) of **4a**. The physical properties and the nitrogen analysis of **4a** are given in Table 1. Found: C, 30.32; H, 4.27%. Calcd for $C_6H_{10}NS_2Br$: C, 30.0; H, 4.17%.

Dithiolium bromide **3a** was obtained quantitatively when **4a** was heated in bulk at *ca.* 180 °C for 10 min.

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6) It should be noted that the starting γ-alkyl-substituted β,γ-unsaturated dithiocarbamates (**1**) are easily derived from the S-allyl derivative (**1a**) and alkyl halides (RX) *via* α-alkylation of the lithium salt of **1a** with RX followed by thermal [3,3]-sigmatropic rearrangement: T. Hayashi, *Tetrahedron Lett.*, **1974**, 339; T. Nakai, H. Shiono, and M. Okawara, *ibid.*, **1974**, 3625.

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