Tetrahedron Letters No.39, pp. 3835-3838, 1967. Pergamon Press Ltd. Printed in Great Britain.

A NEW AMBIDENT CATION. REACTIONS OF 2-DIALKYLAMINO-1,3-DITHIOLANYLIUM SALTS WITH VARIOUS NUCLEOPHILES (1)

Takeshi Nakai and Makoto Okawara
Research Laboratory of Resources Utilization
Tokyo Institute of Technology, Meguro, Tokyo, Japan

(Received in Japan 6 April 1967)

In the preceding paper (2) we have reported the isolation and the intermediacy of 2-dimethylamino-1,3-dithiolanylium ion in the reaction of 1,2-dichloroethane with sodium dimethyldithiocarbamate hydrate. Little information is available on the electrophilic reactivity of 2-dialkylamino-1,3-dithiolanylium ion, which may be regarded as one of the stable carbonium ions substituted by three hetero atoms (one nitrogen and two sulfur atoms).

In the present communication, a wide spectrum of reactivity is shown by 2-dimethylamino-1,3-dithiolanylium perchlorate and its ambident character is demonstrated first. There are some reports on the reactions of carbonium ions substituted by three sulfur (3) or three oxygen atoms (4), of which no ambident character has been recognized.

2-Dimethylamino-1,3-dithiolanylium perchlorate (I) was prepared in a yield of 65% by the reaction of 1,2-dichloroethane with sodium dimethyldithiocarbamate in ethanol followed by the treatment of the resulting mixture with an aqueous solution of sodium perchlorate. Thus, (I) was reacted with oxygen nucleophiles (hydroxide and ethoxide), sulfur nucleophiles (mercaptides and dithiocarbamates), cyanide ion, and amines.

The results thus obtained are summarized in Chart and some characterization data of products are shown in Table 1.

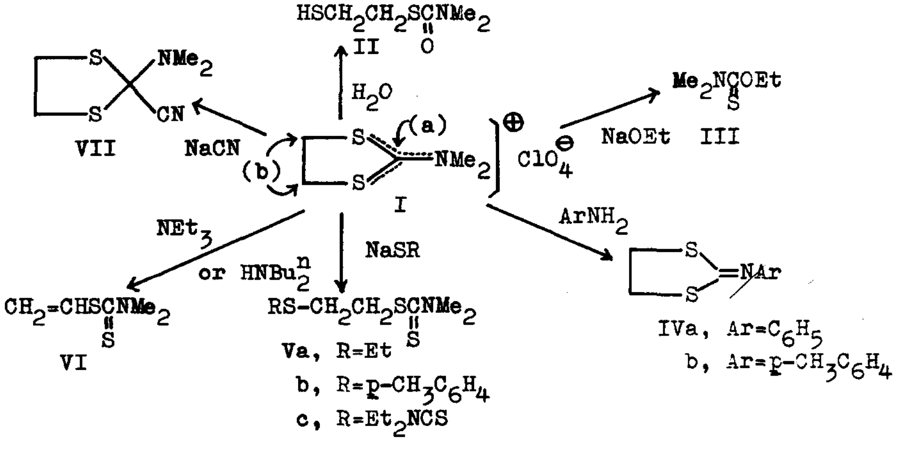


TABLE 1

Products from (I) and Nucleophiles

Compd	Yield(%)[a]	Phys. Properties Bp(mmHg), [Mp], °C	Some Spectral Data
II	40	84-7(2); n_D1.6038(25°)	IR:1650 cm^{-1}(C=C)
III	52	81-2(10); n_D1.5082(25°)	IR:identical with that of the authentic sample
IVa [b]	70	[47-8]	IR:1570 cm^{-1}(C=N) NMR(δ):3.32 ppm(CH_2-S)
IVb	77	Oil;HCl-salt [b] [190-2]	IR:1580 cm^{-1}(C=N)
Va [b]	36	67-8(0.14); n_D1.5819(22°)	UV: λ_{max}(EtOH) 250, 278 mμ [c]
Vb [b]	77	[48-9]	UV: λ_{max}(EtOH) 257, 278 mμ [c]
Vc [b]	90	[102-3]	UV: λ_{max}(EtOH) 253, 279 mμ [c]
VI	65	87-90(2); n_D1.5907(25°)	IR:identical with that of the authentic sample
VII[b]	64	114-6(3); n_D1.5633(27°)	IR:2250 cm^{-1}(CN) NMR(δ):3.37(CH_2S), 2.47 ppm(CH_3N)

a) No attempt to maximize conditions has been made.

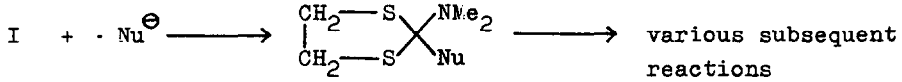
b) Analytical data obtained for this compound were satisfactory.

c) Characteristic bands for $RS\underset{\overset{\|}{S}}{C}NMe_2$. (*Cf.* M. J. Janssen, *Rec. trav. chim.*, **79**, 454 (1960)).

The above results indicate that 2-dimethylamino-1,3-dithiolanylium ion (I) is an ambident cation with two different reactive centers (see arrows (a) and (b) in formula (I)), and reacts with nucleophiles by the following three reaction modes, according to the nucleophilicity of the reagent used.

The reaction mode A involves initial attack of the nucleophile at (a) with retention of the ring structure to yield the adduct (VIII), which, in some cases, can undergo various subsequent reactions, i.e., the proton transfer ($^{\ominus}$OH) and loss of episulfide ($^{\ominus}$OR) with the ring cleavage, and deamination with the ring retention ($ArNH_2$).

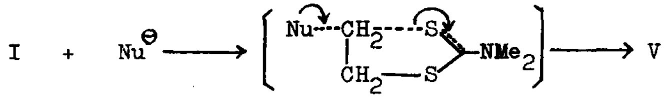
Mode A



VIII

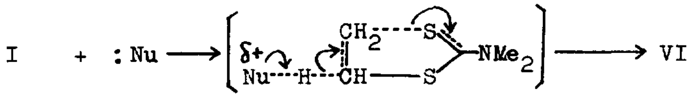
The mode B, which can explain the formation of the β-substituted ethyl dithiocarbamates (V) from (I) and sulfur nucleophiles, involves initial attack at (b) through the S_N2-type mechanism verified kinetically in the preceding paper (2).

Mode B



Finally, there are two possible mechanisms for the formation of S-vinyl dithiocarbamate (VI) from (I) and triethylamine. The first mechanism involves the Hofmann elimination of the tetraalkylammonium salt (replaced SR by $^{\oplus}NEt_3$ in formula (V)) formed by the mode B. The other consists in the reaction mode C, which involves initial abstraction of the proton on the carbon next to sulfur followed by the ring scission through the well-known concerted mechanism accepted for the general E2 reaction.

Mode C



It seems reasonable to assume that the mode C is operative since triethylamine is basic and so combines more preferentially with the proton than the neutral (sp^3) carbon atom bearing the proton.

In conclusion, although rough, it should be said that if the nucleophile is basic, e.g., $^{\ominus}$OH or $^{\ominus}$OR, the mode A is favored, but if the nucleophile has a large substituent, *e.g.*, NEt_3 or $HNBu^n_2$, the initial proton abstraction (mode C) is predominant. On the other hand, if the nucleophile is polarizable, *e.g.*, $^{\ominus}SR$ or $^{\ominus}SCSNR_2$, the mode B is favored. These facts are in agreement with the observations for other ambident cations (5).

In our full paper, we will report the similar reactivity of 2-diethylamino-1,3-dithiolanylium ion, and discuss in more details the major factors operating in deciding the position of attack.

REFERENCES

(1) Part II in a series on "Heterosubstituted Carbonium Ions".

(2) T. Nakai, Y. Ueno, and M. Okawara, *Tetrahedron Letters*, the preceding paper.

(3) For 2-methylthio-1,3-dithiolanylium ions see R. Gompper and E. Kutter, *Chem. Ber.*, **98**, 1365 (1965) and for 2-methylthio-1,3-dithiolium ions see E. Campaign and R. D. Hamilton, *J. Org. Chem.*, **29**, 1711, 2877 (1964); A. Lüttringhaus, H. Berger, and H. Prinzbach, *Tetrahedron Letters*, 2121 (1965).

(4) For trialkoxycarbonium ions see H. Meerwein, *Houben-Weyl Vol.VI/3*, p.346 (1965); H. Meerwein, K. Bodenbenner, P. Borner, F. Kunert, and K. Wunderlich, *Ann.*, **632**, 38 (1960).

(5) S. Hünig, *Angew. Chem. internat. Edit.*, **3**, 548 (1964); R. Gompper, *ibid.*, 560 (1964).