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THE ANCHIMERISM OF THE N,N-DISUBSTITUTED DITHIOCARBAMATE FUNCTION (1)

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

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During the course of study on the equimolar reaction of 1,2-dichloroethane (I) and sodium N,N-dimethyldithiocarbamate hydrate (II) we made the following observations:(i) unexpectedly the monosubstituted product, β-chloroethyl N,N-dimethyldithiocarbamate (III), could not be isolated;(ii) the disubstituted, ethylene bis(dithiocarbamate) (IV), and 2-dimethylamino-1,3-dithiolanylium ion (V) (2) were isolated in yields, varying largely with the solvent used as shown in Table 1.

The more favorable formation of (IV), especially in dioxane and THF, cannot be reasonably explained by two successive simple S_N2 reactions, (I)⟶(III)⟶(IV), which led us to an elaborate study on the reaction mechanism. In the present communication we wish to report the anchimerism of the dithiocarbamate function.

Winstein and co-workers (4) have proposed the anchimeric assistance by the neighboring acetoxy group through the presumed "acetoxonium ion"(VI) for the acetolysis of trans-2-acetoxycyclohexyl brosylate. Later the cation (VI) has been isolated as the tetrafluoroborate (5).

2-Dimethylamino-1,3-dithiolanylium ion (V) isolated in the present work can correspond to the anchimeric cation (VI). Then, the reaction of 2-dimethylamino-1,3-dithiolanylium perchlorate (Vc) (2) with (II) was attempted first.

TABLE 1

Products of the Equimolar Reaction of (I) with (II) (60°C, 6 hr.)

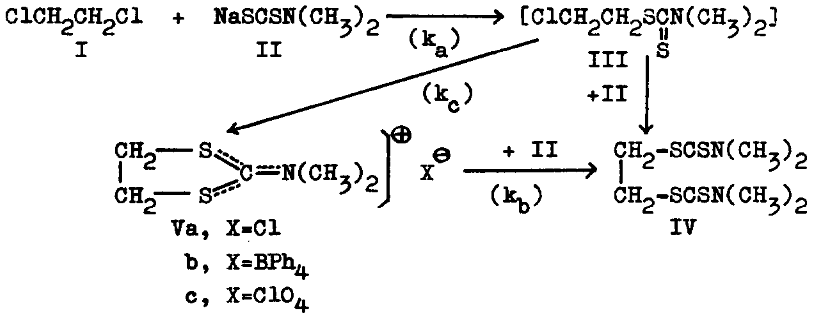
Solvent	Yield (%) based on (II)		
	IV	Vb[a]	Others
Ethanol(EtOH)	8.4	61.4	5.5[b], 3.9[c]
Ethylene glycol	trace	59.6	trace[c]
Dimethylformamide(DMF)	23.0±0.5	57.3±2.0	trace[c]
Dimethyl sulfoxide(DMSO)	13.4	51.5	trace[c]
Dioxane	56.9±0.1	29.0±1.0	trace[c]
Tetrahydrofuran(THF)	67.5±2.0	21.4±2.0	trace[c]

a, 2-Dimethylamino-1,3-dithiolanylium ion (V) formed could not be isolated quantitatively even by treating with potassium tetraphenylborate. (c.f. footnote (2)).

b, $C_2H_5OC(S)N(CH_3)_2$(VII), bp 53-3°(3mm.), n_D1.5161 (22°C) (6)

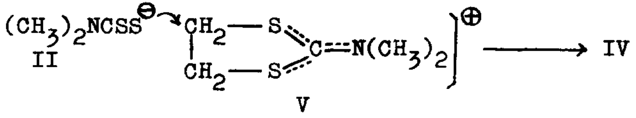
c, $HSCH_2CH_2SC(O)N(CH_3)_2$(VIII), bp 112-7°(4mm.), n_D1.584C(25°C) (6)

(Vc) easily reacted with (II) at 50° in DMF to result in the quantitative formation of (IV). Consequently, the formation of (IV) can be interpreted by the following scheme involving the intermediacy of the isolated anchimeric cation (V).



On the basis of the scheme proposed here, it may be reasonably expected that the rate of each process and the products ratio should be affected by the nature of the solvent used. Thus, kinetic experiments described below were carried out in ethanol, DMF and dioxane, which were selected from Table 1 as the representative dipolar protonic, dipolar aprotic and nonpolar aprotic solvent, respectively.

In order to obtain the unmeasurable rate (k_a) of the reaction (I)⟶(III), n-butyl chloride was employed instead of (I). Reactions of n-butyl chloride with (II) in various solvents followed a second-order rate equation. On the other hand, rate data for the reaction (Va)⟶(IV) were obtained by measuring the rate of the reaction (Vc)⟶(IV). This reaction also fits in a second-order rate equation, indicating that the dithiocarbamate anion attacks on the neutral (sp^3) carbon atom at the position 4 of (V) to give (IV) through the concerted S_N2-type mechanism as follows (7):



Rate data obtained for both reactions in various solvents are summarized in Table 2.

TABLE 2

Rate Constants for n-Butyl Chloride(k_a) and (Vc) (k_b) (60°)

Solvent	$k_a \times 10^3$ (1 mole^{-1}sec^{-1})	$k_b \times 10^3$ (1 mole^{-1}sec^{-1})	k_b/k_a	IV/V*
EtOH	0.4	7.34	18.4	0.092
DMF	70.8	40.9	0.58	0.30
Dioxane	0.3	34.0	113	1.32

* The more accurate products ratio (IV/V) could be calculated from IV/(100-IV)(Table 1) since the difficulty of the quantitative isolation of (V) formed was encountered.

Most important is the fact that in dioxane the second displacement reaction (V)⟶(IV) is about one hundred times faster than the first (I)⟶(III), which can reasonably explain the more favorable formation of (IV) for the equimolar reaction of (I) with (II). This fact also provides us with a direct evidence for the participation by the neighboring dithiocarbamate function of (III) in the second substitution process (III)⟶(IV), together with the solvent effect described above. The unusual rate enhancement in DMF for the reaction of n-butyl chloride with (II) can be attributed to the two major factors:(i) the enhanced nucleophilicity of the dithiocarbamate anion, being in agreement with many other observations for the nucleophilic substitution in dipolar aprotic media (8); (ii) the enhanced electrophilicity of the alkyl halide due to the complex formation (9) between the alkyl halide and DMF molecules.

REFERENCES AND NOTES

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

(2) 2-Dimethylamino-1,3-dithiolanylium ion (V) was isolated as the tetraphenylborate (Vb), mp 134-136°, and the perchlorate (Vc), mp 179-181°, of which the former was obtained in more yields than the latter, but not quantitatively. Analysis data of both salts were satisfactory. The structure of (V) was confirmed by its preparation according to another method (3) and its n.m.r. spectrum (Vc) in DMSO-d_6: δ 4.08 (singlet, CH_2-S) and 3.62 ppm (singlet, CH_3-N).

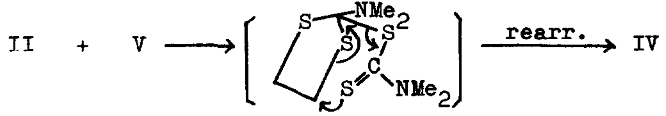
(3) K. C. Kennard and J. A. VanAllan, J. Org. Chem., **24**, 470 (1959).

(4) S. Winstein and R. E. Buckles, J. Amer. Chem. Soc., **64**, 2780 (1942); S. Winstein, E. Grundwald and R. E. Buckles, ibid., **70**, 816 (1948).

(5) C. B. Anderson, E. C. Friedrich and S. Winstein, Tetrahedron Letters, 2037 (1963).

(6) It has been clarified (see the subsequent paper) that (VII) and (VIII) are formed by the ethanolysis and hydrolysis of (V), respectively.

(7) Alternate possible mechanism, which fits in a second-order rate equation,



can be excluded by our result (the subsequent paper) that (Vc) also reacts with mercaptides incapable of rearrangement to give β-substituted ethyl dithiocarbamates.

(8) See, for example, A. J. Parker, Quart. Revs., **16**, 163 (1962).

(9) S. Yoneda, Z. Yoshida, I. Morishima, and K. Fukui, J. Chem. Soc. Japan (Ind. Sect.), **68**, 1074, 1077 (1965).