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REARRANGEMENT AND TRANS-ELIMINATION AGAINST THE CHUGAEV REACTION RULE (1)

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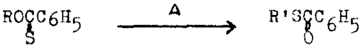
In the foregoing papers (2,3), it was reported that dialkylaminoalkyl S-alkyl xanthates thermally rearrange to dialkylaminoalkyl alkyl dithiolcarbonates with or without shift of the dialkylamino group. The general feature of the rearrangement is that it requires antiparallel coplanarity of the xanthate group with the dialkylamino group, where the latter group can anchimerically work on the carbon atom holding the former. The reaction mechanism was discussed and interpreted in a manner as proceeding through a transition state formulated as I_a (3). As far as the steric requirement is satisfactory, the rearrangement occurs regardless of in aliphatic, alicyclic (2,3) and heteroalicyclic (4) fields. As have been preliminarily reported (2), this aspect suggests that the rearrangement may be expanded into xanthates, thionocarboxylates, thionocarbamates and imidates which involve in neighbourhood of the ester function an anchimeric group such as the alkylthio group and the olefinic double bond. Thus, the present report concerns thermal treatments of esters which are well qualified for the requirement of the rearrangement. Tables 1~5 show compounds treated and products (5) formed.
Of dialkylaminoalkyl thionobenzoates (Table 1), dialkylaminoalkyl N,N-dimethylthionocarbamates (Table 2) and methylthioalkyl S-methyl xanthates (Table 3), all the compounds treated underwent transformation to thiol esters. Particularly, it should be noted that pairs of position isomers were converted to the same transformation product respectively and the rearrangement occured accompanying racemization

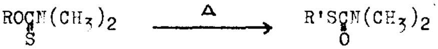
TABLE 1.



$$RO\underset{\overset{\|}{S}}{C}C_6H_5 \xrightarrow{\Delta} R'S\underset{\overset{\|}{O}}{C}C_6H_5$$

Material	Δ	Product	Yield
R	°C/mm	R'	%
$(C_2H_5)_2N(CH_2)_2$-	$138/2^a$	R	96
$(CH_3)_2N(CH_2)_3$-	280	R	-
 $N(CH_3)_2$ [DL-trans]	$175/4^a$	R	97
[(-)trans]	$163/3^a$	DL-R	82
$(CH_3)_2NCH_2CH(CH_3)$- [DL]	$142/1.5^a$	$(CH_3)_2NCH(CH_3)CH_2$- [DL]	91
$(CH_3)_2NCH(CH_3)CH_2$- [DL]	$132/2^a$	R	90
$(CH_3)_2NCH_2CH(C_6H_5)$- [DL]	200	R	91
$(CH_3)_2NCH(C_6H_5)CH_2$- [DL]	200	$(CH_3)_2NCH_2CH(C_6H_5)$- [DL]	87

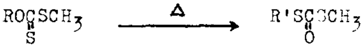
TABLE 2.



$$RO\underset{\overset{\|}{S}}{C}N(CH_3)_2 \xrightarrow{\Delta} R'S\underset{\overset{\|}{O}}{C}N(CH_3)_2$$

$(C_2H_5)_2N(CH_2)_2$-	180	R	85
 $N(CH_2)_2$-	200	R	76
 $N(CH_2)_2$-	200	R	78
 $N(CH_3)_2$ [DL-trans]	200	R	86
$(CH_3)_2NCH_2CH(CH_3)$- [DL]	200	$(CH_3)_2NCH(CH_3)CH_2$- [DL]	30
$(CH_3)_2NCH(CH_3)CH_2$- [DL]	200	R	76
 SCH_3	200	R	74

TABLE 3.



$$RO\underset{\overset{\|}{S}}{C}SCH_3 \xrightarrow{\Delta} R'S\underset{\overset{\|}{O}}{C}SCH_3$$

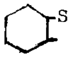
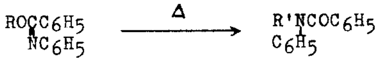
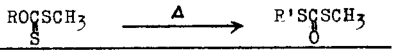
$CH_3SCH_2CH_2$-	$114/8^a$	R	48
 SCH_3 [DL-trans]	$140/4^a$	R	76
$CH_3SCH_2CH(CH_3)$- [DL]	$148/20^a$	$CH_3SCH(CH_3)CH_2$- [DL]	74
$CH_3SCH(CH_3)CH_2$- [DL]	$148/20^a$	R	71

TABLE 4. 

$$\mathrm{RO\underset{\overset{\|}{N}C_6H_5}{C}C_6H_5 \xrightarrow{\Delta} R'\underset{C_6H_5}{N}COC_6H_5}$$

Material R	°C/mm	Product R'	Yield %
$(C_2H_5)_2NCH_2CH_2$-		R	59
$(C_2H_5)_2NCH_2CH(CH_3)$- [DL] or $(C_2H_5)_2NCH(CH_3)CH_2$- [DL]	250~ 270	$(C_2H_5)_2NCH_2CH(CH_3)$- [DL] + $(C_2H_5)_2NCH(CH_3)CH_2$- [DL]	40~50[b]

TABLE 5. 

$$\mathrm{RO\underset{\overset{\|}{S}}{C}SCH_3 \xrightarrow{\Delta} R'S\underset{\overset{\|}{O}}{C}SCH_3}$$

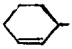
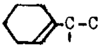
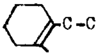
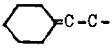
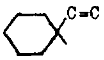
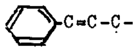
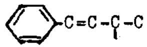
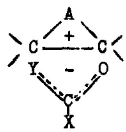
1	C=C-C-	57/3[a]	R	82
2	$\mathrm{C{=}C{-}\underset{\mid}{C}{-}C}$	86/7[a]	C-C=C-C-	63
3	C-C=C-C-	76/5.5[a]	$\mathrm{C{=}C{-}\underset{\mid}{C}{-}C}$	59
4	$\mathrm{C{-}C{=}C{-}\underset{\mid}{C}{-}C}$	79/2.5[a]	R	58
5	$\mathrm{C{-}C{=}C{-}\underset{\mid}{C}{-}C{-}C}$	92/3[a]	$\mathrm{C{-}C{-}C{=}C{-}\underset{\mid}{C}{-}C}$	69
6	$\mathrm{{}^{C}_{C}{>}C{=}C{-}C{-}}$	69/3[a]	$\mathrm{{}^{C}_{C}{>}\underset{\mid}{C}{-}C{=}C}$	73
7		95/3[a]	R	33
8		108/1.5[a]		60
9		118/2.5[a]		61
10		150	R	-
11		190	elimination[c]	-
12	$\mathrm{{}^{C}_{C}{>}C{=}C{-}\underset{\mid}{C}{-}C}$	170	elimination[d]	—

Table 1~5 a. vac. distilled at the temperature. b. Weight ratio =about 2:3. c. Product: 1-phenylbutadiene. d. Polymerization product with no sulphur atom, probably resulted from 1,1-dimethylbutadiene.

in the treatment of (-)trans-2-dimethylaminocyclohexyl thionobenzoate (Table 1). These observations tell us that the results parallel those reported earlier in the study of dialkylaminoalkyl S-methyl xanthates (2,3) and therefore, pathways might be closely related each other, thus indicating that an intermediate in each can be commonly represented by the general formula (I). Previously, Bordwell (6)



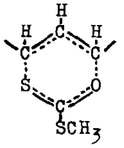
I

a. $A=R_2N$, $X=CH_3S$, $Y=S$

b. $A=R_2N$, $X=C_6H_5$, $Y=S$

c. $A=CH_3S$, $X=CH_3S$, $Y=S$

d. $A=R_2N$, $X=C_6H_5$, $Y=C_6H_5N$



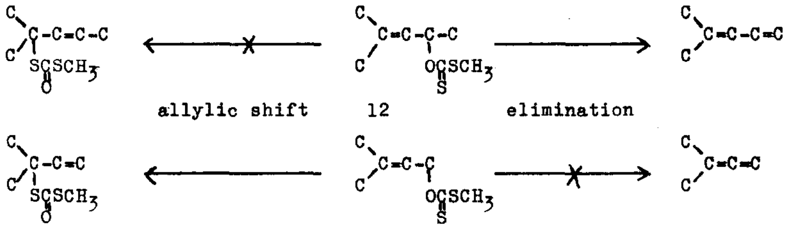
II

reported that DL-trans-2-p-tolylthiocyclohexyl S-methyl xanthate suffered cis-elimination by pyrolysis along the Chugaev reaction, behaving against the case of the methylthio analogue in the present study. This will be because the p-tolylthio group is not so anchimerically powerful to assist the rearrangement as the methylthio group is.

Thermal rearrangement of imidates to amides (the Chapman rearrangement (7)) has been widely studied. However, it is known that of alkyl imidates, the rearrangement occurs only when alkyl is methyl (8). To examine the neighbouring group effect for the rearrangement, alkyl imidates in which the alkyl group contains the dialkylamino function were submitted to pyrolysis. Thus, 2-diethylaminoethyl N-phenyl benzimidate was converted to the corresponding amide. And also pyrolysis of a pair of position isomers, the 2-diethylaminopropyl and the 2-diethylaminoisopropyl esters, equally gave a mixture of N-2-diethylaminopropyl and N-2-diethylaminoisopropyl N-phenylbenzamides, presumably suggesting that the reactions proceeded through Id in analogy with the cases of thionic acid esters. See Table 4.

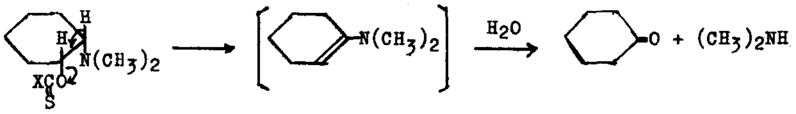
Rearrangements of allylic thiocyanates (9), thionobenzoates (10) and thionocarbonates (11) have been investigated from a viewpoint of allylic shift. These species also fall into the category which is discussed here. Hence, allylic xanthates which have been left for close examination were submitted to thermal treatment. As be shown in Table 5, compounds 1∼9 transformed to dithiolcarbonates accompanying allylic shift (12). Of those, a pair of position isomers, compounds 2 and 3, did not transform to a same product but to crosswise products with allylic shift respectively. This attitude in the formation of products suggests that the transformation occurs most likely through a type of cyclic intermediate (II) (S_Ni'), as P.A.S. Smith, et al (9) and S.G.Smith (10) pointed out in the kinetical studies of allylic thiocyanates and thionobenzoates. On the other hand, compound 10 suffered transformation of the xanthate group on the carbon atom to which it attaches and compound 11 did elimination to give 1-phenylbutadiene. These results may follow from a reason that stabilization of the olefinic double bond by conjugation with the benzene nucleus disturbed allylic shift in the two compounds.

Thus, the conjugation assisted the development of another conjugate double bond in compound 11 and the S_Ni-like transformation in compound 10 which is not reliable to elimination because an energically unfavourable allene derivative would be resulted. Compound 12 also suffered elimination of the xanthate group. This may be interpreted by a speculation that allylic shift to a branched carbon atom is less favourable than elimination which stabilizes the transition state by development of conjugation of double bonds.



6,9

However, as stated above, compounds 6 and 9 which are analogous with compound 12 in the structure relationship underwent allylic shift. The cases may be explained by considering that allylic shift preferred to elimination because the formation of allene derivatives from compounds 6 and 9 as results of elimination would be energically unfavourable. But it should be stated that the mechanistic discussion given for the behaviours of allylic xanthates is no more than a passing attempt at the present stage of the study. Unlike the examples where the dialkylamino group plays anchimerically as an inducer of the rearrangement as have been shown hitherto, there are cases where the group works as a basic catalyst for elimination when it situates unfavourably for the steric requirement of the rearrangement. The previous paper (2) reported that pyrolysis of DL-<u>cis</u>-2-dimethylaminocyclohexyl S-methyl xanthate (IIIa) caused <u>trans</u>-elimination to give cyclohexanone through 1-dimethylaminocyclohexene and the cause was explained in a sense that the reaction was catalyzed by the basic dimethylamino group. The present study also offered an associate of the example by revealing that DL-<u>cis</u>-2-dimethylaminocyclohexyl thionobenzoate (IIIb) suffered *trans*-elimination to give the same product



III a. X=CH$_3$S b. X=C$_6$H$_5$

as the case of IIIa. The finding must be a warning to the Chugaev reaction rule when it is applied to conformational analysis of a molecule involving a basic function.

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5. Analytical data obtained and also reaction sequences observed for the identifications of them were satisfactory.
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10. S. G. Smith, *J. Am. Chem. Soc.*, **83**, 4285 (1961).
11. D. L. Garmaise, A. Uchiyama and A. F. McKay, *Can. J. Chem.*, **27** 4509 (1962).
12. Actually, allylic shift was indistinguishable in 1 and 4, but it was presumed by the other example of 1~9.