MECHANISM OF THE REACTION OF EPITHIOCHLOROHYDRIN WITH NUCLEOPHILES

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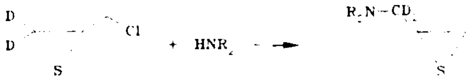
A variety of hypotheses have been proposed in the literature to account for the mechanism of reaction of epithiochlorohydrin with nucleophiles. The possibility of both direct halogen atom substitution [1] as well as substitution via sequential ring opening and reformation of the thiirane ring [2] has been discussed. The possibility of the reaction process proceeding via a 1-thioniumbicyclobutyl cation also cannot be excluded [2].

We have found that halogen atom substitution in (chloromethyl)thiirane in the presence of secondary amines, which occurs with formal retention of the thiirane ring, actually takes place completely via a ring cleavage-recyclization scheme. We synthesized 2-(chloromethyl)-thiirane-3,3-D_2 (I) via reduction of 2,3-dichloropropionyl chloride with lithium aluminum deuteride, followed by subsequent cyclization of 2,3-dichloropropanol-1,1-D_2 to 2-(chloromethyl)oxirane-3,3-D_2; the latter compound was then converted to episulfide I via isothiuronium salt [3]. The position of the label in compound I was verified by ^{1}H- and ^{13}C-NMR spectroscopy.

Reaction of compound I with secondary amines was carried out using the procedure published for the undeuterated analog [4].



I NR₂ = morpholino II

In the ^{13}C-NMR spectrum (in $CDCl_3$) of an independently synthesized sample of 4-(2,3-epithiopropyl)morpholine which did not contain deuterium the $C_{(1')}$-$C_{(3')}$ carbon atom signals for the epithiopropyl fragment were observed at 64.9, 31.1, and 24.4 ppm, respectively, while the $C_{(2)}$ and $C_{(3)}$ nuclei gave rise to signals at 66.9 and 53.8 ppm, respectively. In the spectrum of the deuterated product of reaction II the positions of all of these signals, with the exception of $C_{(1')}$, remained practically unchanged. The latter carbon atom signal appeared as a quintet at 64.1 ppm with $^1J_{^{13}C\text{-}D} = 20.66$ Hz, which corresponds to a $^1J_{^{13}C\text{-}H}$ value of ca. 134 HZ (for a thiirane carbon atom $^1J_{^{13}C\text{-}H} = 170$ Hz [2]). In the ^{1}H-NMR spectrum of compound II the 3'-H proton signals were observed at 2.05 and 2.42 ppm in the form of a doublet with $^3J_{2'3'} = 5.4$ Hz for both protons, and with a small geminal $^2J_{3'3'}$ SSCC value of 1.0 Hz, which is characteristic of thiiranes [2]. The spectra did not contain any signals which might be assigned to an episulfide with a different distribution of deuterium labels.

These data reveal that in the reaction product II all of the deuterium is found in the 1'-position, which in turn indicates that chlorine atom substitution in I occurs exclusively with rearrangement. This result was observed regardless of whether the reaction was carried out in the benzene or methanol, i.e., the solvent apparently does not affect the nature of the reaction process. We also examined the reaction of epithiobromohydrin with nucleophiles and found that it occurs via an analogous scheme. The results obtained herein also suggest a profound analogy between the reactions of epihalohydrins (cf. [5], for instance) and epithiohalohydrins with nucleophiles.

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INTRAMOLECULAR HYDROGEN BONDS IN 1-VINYL-5-PYRAZOLE CARBOXYLATE ESTERS

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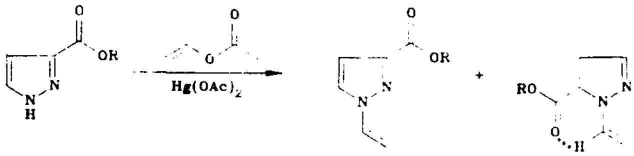
The presence of an intramolecular CH—N hydrogen bond has recently [1] been demonstrated in 2-vinylhydroxy(vinylthio)pyridine and -quinoline. We have discovered a similar interaction in 1-vinyl-5-pyrazole carboxylate esters II.

N-Vinylation of 3(5)-pyrazole carboxylate esters with vinyl acetate using mercuric acetate catalyst led to a mixture of the isomeric 1-vinyl-3- and -5-pyrazole carvoxylates I and II in 88-92% yield which were separated by straight distillation.



R = a CH_3; b C_2H_5; c i-C_3H_7; d C_4H_9 Ia-d IIa-d

According to PMR spectroscopy (CCl_4, internal standard HMDS) II have intermolecular hydrogen bonds between the vinyl α-proton and the carbonyl oxygen p-electrons (CH—O=C) resulting in a low field shift of the α-proton to 7.98, 8.03, 7.97, and 8.03 ppm (corresponding to the above named R substituents). Because deshielding of the α-proton by the carbonyl is impossible for steric reasons in the isomers I the chemical shift value is at higher field in a narrow range 7.10-7.20 ppm.

The boiling points (1 mm) of the synthesized compounds were: Ia 85; Ib 108; Ic 85; Id 124; IIa 54; IIb 75; IIc 69; IId 85°C. Elemental analysis for nitrogen agreed with that calculated.

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