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PREPARATION OF VINYL ALKANEDITHIOATES

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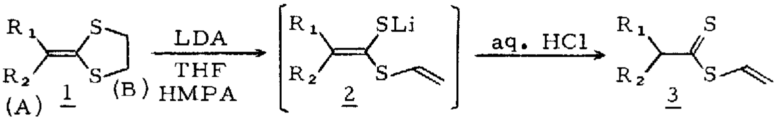
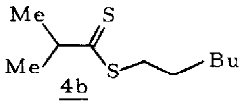
Summary : S-vinyl dithioesters are prepared by ring-opening of 2-alkylidene-1,3-dithiolanes in basic medium.

We have shown previously that dithioesters are useful synthetic intermediates ; in particular we developed various paths for the preparation of β -unsaturated ketones[1] and some applications of interest have been achieved recently[2]. The dithioesters containing a double bond α to the sulfur atom cannot be prepared by the usual methods [3]; a few 1-alkenyl alkanedithioates were synthesized by isomerization of the corresponding S-allylic dithioesters, using an efficient base-catalysis[4]. We describe here a direct method for the preparation of the S-vinyl dithioesters which are not substituted on the double bond.

We used 2-alkylidene-1,3 dithiolanes 1 as starting materials to prepare the novel S-vinyl dithioesters 3. Compounds 1 offer two reactive sites toward bases, i.e., the allylic carbon atom (A) and the ring-methylene carbon atom (B). We found that, with lithium diisopropylamide in THF in the presence of HMPA, the regioselective deprotonation at carbon (B) occur and concomitant opening of the ring afforded the lithium salt 2 ; subsequent hydrolysis gave the dithioester 3 in fairly good yield.





4b

a : R_1= H R_2= Me b : R_1= R_2= Me

A similar reaction has been achieved previously and S-vinyl dithiocarbamates were obtained from 2-dialkylamino-1,3 dithiolanylium perchlorates with triethylamine [5]. The facility encountered for this elimination process in dithiolanes may be explained by the acidity of the hydrogen atoms of the ring and the concomitant presence of an alkylthio group, which is a good leaving group, at the β -position. The six-membered ring analogs are known to react differently with organolithiums : with 2-alkylidene-1,3-dithianes metallation at the allylic group or addition of the organometallic on the double bond occured [6].

The utility of HMPA has been demonstrated : in THF alone with LDA, compound 1b remained unchanged at -50°C, and at higher temperature afforded a mixture of dithioester 3b and further reaction-products ; treated by n-butyllithium as nucleophilic base in THF, compound 1b underwent both nucleophilic substitution and proton-abstraction at the site (B) leading to dithioesters 4b and 3b respectively, and this competitive reaction has been mentionned already with sulfur nucleophiles[5]; dithioester 3b alone was obtained when the reaction was run in the presence of HMPA.

Experimental

Known 1a and 1b[7] were prepared by alkylation of the corresponding dithioacids according to the procedure developed in our laboratory[3a)], using 3 equivalents of NaOH and 1 equivalent of 1,2-dibromo ethane in in aqueous THF at reflux and at good enough dilution to decrease intermolecular alkylation.

Vinyl alkanedithioates 3 were obtained as follows : under N_2, a lithium diisopropyl-amide solution was prepared in 10 ml of THF below -10°C from diisopropylamine (13 mmol) and n-butyllithium (12.5 mmol, ~2M solution in n-hexane) ; 5 ml of HMPA were added at -40°C ; the mixture was cooled at -50°C and 10 mmol of 1 were added within 10 min. ; the reaction mixture was stirred over a 30-min. period at -50°C, then hydrolyzed with a 50 % H_2O-HCl solution and allowed to come to room temperature ; the mixture was extracted with pentane; the organic layer was washed with water, dried over Na_2SO_4 ; evaporation of the solvent gave crude dithioester 3 as an orange liquid then purified by distillation under vacuum. [3a : b.p. : 53°C/0.02 Torr ; yield : 50%; MS (obtained by direct introduction of the compound at the ion source as usually done for solid compounds) : 132 ($M^{+\cdot}$) ; analysis : $C_5H_8S_2$: calc. C 45.41 H 6.09 S 48,49, found C 45.61 H 5.98 48.59 ; NMR ^1H (CCl_4, $\delta_{TMS}=0$) : 1.35 (t, J= 7 Hz, 3H), 2.93 (qd, J= 7 Hz, 2H), ABX system : $\delta_A = 5.59$, $\delta_B = 5.55$, $\delta_X = 7.14$ ($J_{AX} = 9.8$ Hz, $J_{BX} = 17.3$ Hz, $J_{AB} \sim 0$ Hz); NMR ^{13}C ($CDCl_3$, $\delta_{TMS}=0$) : 236.0, 131.1, 119.0, 44.8, 15.0. 3b : b.p. : 70°C/12 Torr ; yield : 55 % ; MS (obtained as for 3a) : 146 ($M^{+\cdot}$) ; analysis : $C_6H_{10}S_2$: Calc. C 49.26 H 6.89 S 43.84, found C 49.29 H 7.08 S 43.98 ; NMR ^1H (CCl_4) : 1.31 (d, J= 7 Hz, 6H), 3.30 (sept., J= 7 Hz, 1H), ABX system : $\delta_A = 5.59$, $\delta_B = 5.56$, $\delta_X = 7.18$ ($J_{AX} = 9.9$ Hz, $J_{BX} = 17.5$ Hz, $J_{AB} \sim 0$ Hz) ; NMR ^{13}C ($CDCl_3$) : 241.8, 130.6, 119.1, 49.3, 23.9]. The same procedure with n-butyllithium as base in THF afforded a mixture of 3b and 4b, which were separated by VPC. [4b : analysis : $C_{10}H_{20}S_2$ (204) : Calc. C 58.75 H 9.86 S 31.37, found C 59.47 H 10.66 S 31.38 ; NMR ^1H (CCl_4) : 0.9 to 1.9 (m, 11H), 1.28 (d, J= 7 Hz, 6H), 3.25 (~t, J= 7 Hz, 2H), ~ 3.3 (m, 1H) ; 4'b (from deuterolysis) : NMR ^1H (CCl_4) : 0.6 to 1.9 (m, 11H), 1.28 (~s, 6H), 3.25 (~t, J= 7 Hz, 2H)].

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