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A NEW GENERAL METHOD FOR SYNTHESIS OF KETENE DITHIOACETAL

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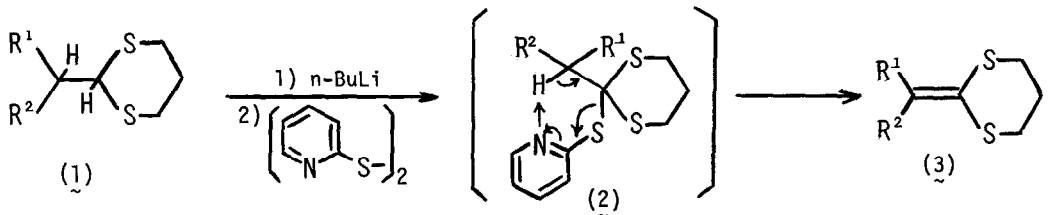
Summary: Dithioacetals (1) were treated with n-butyllithium and 2,2'-dipyridyl disulfide to give ketene dithioacetals (3) in high yields, which constituted a new efficient synthetic method for the latter compounds.

Ketene dithioacetal (3) has been reported to show the interesting reactivities.[1,2,3] It must develop as a very useful compound for exploitation of new reactions and syntheses. Thus, many synthetic methods for ketene dithioacetal have been exploited in recent years.[1,2,4,5] Most of them, however, seem to be not convenient, because of the specific precursors [*e. g.* compound (4) or (5)].[1,4,5]

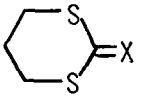
We have exploited a new convenient synthesis of ketene dithioacetals (3a~k) utilizing the bifunctionality of pyridine 2-thio group, which is reported here. (Scheme 1)



(1) (2) (3)

a R^1=C_3H_7, R^2=H(85%)[6]; b R^1=iso-Pr, R^2=H(87%); c R^1=C_4H_9, R^2=H(90%);
d R^1=C_5H_{11}, R^2=H(90%); e R^1=C_6H_{13}, R^2=H(87%); f R^1=C_7H_{15}, R^2=H(86%);
g R^1=C_8H_{17}, R^2=H(92%); h R^1=Ph, R^2=H(88%); i R^1=$EtSCH_2$, R^2=H(93%);
j R^1=$PhSCH_2$, R^2=H(85%); k R^1=R^2=-$(CH_2)_5$-(99%)

Scheme 1

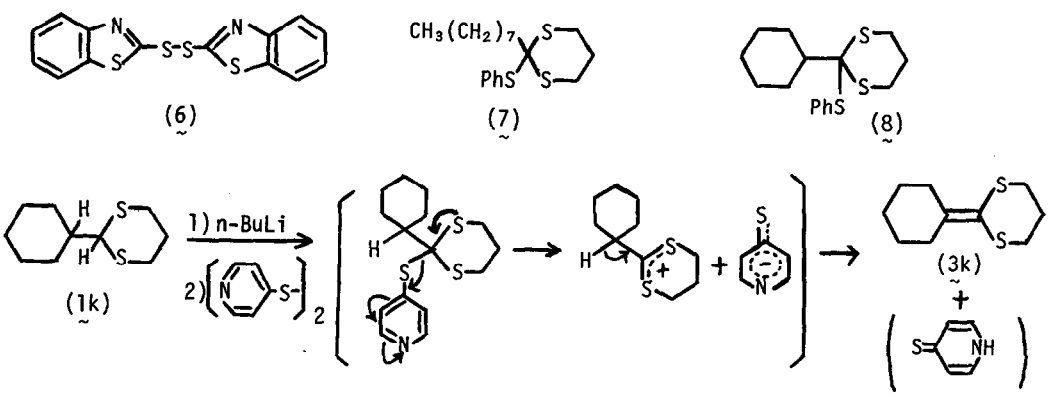


(4) X=H,$Si(CH_3)_3$
(5) X=$P(OCH_3)_3$ or $P(C_6H_5)_3$

Dithioacetals (1a~k) obtained readily from aldehydes by usual treatment with 1,3-propanedithiol and BF_3-Et_2O were dissolved in THF, respectively, to which a solution of n-BuLi (1.2 eq) in n-hexane was added dropwise at -40° with stirring under N_2. The mixture was slowly warmed up to -10° over 1h and stirred for further 1h at the same temperature to accomplish the formation of 2-lithio 1,3-dithiane derivative. Then the mixture was cooled to -70°, to which a solution of

2,2'-dipyridyl disulfide (1.2 eq) in THF was added dropwise. Finally, the mixture was slowly (over 2~3h) warmed up to room temperature to afford desirable ketene dithioacetals (3a~k) in high yields (85~99%).

The similar performance for preparation of ketene dithioacetals was achieved also by using 2,2'-dithio-bis(benzothiazole) (6). [(1f)→(3f) in 75% yield.] Treatment of (1k) with n-BuLi and 4,4'-dipyridyl disulfide also resulted in the formation of the ketene dithioacetal (3k) in 74% yield. In the use of diphenyl disulfide, however, orthothioester was yielded : compound (7) (91%) from (1f) and (8) (85%) from (1k). These facts suggest that the reaction may proceed not only *via* a potential transition state (2) (Ei like process) involving the bifunctionality of pyridine-2-thio group but also *via* E1 like process (see Scheme 2) involving the "Pull-Push" effect between pyridine-4-thio group and S atoms of 1,3-dithiane.



Scheme 2

Because dithioacetal (1) can be synthesized also from 2-lithio-1,3-dithiane and alkyl halide,[7] our new method may have a great generality and promise its utility.

Acknowledgement

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References and Notes

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