CHEMISTRY LETTERS, pp. 939-940, 1987.

A Convenient Preparation of α-Oxo Ketene Dithioacetals

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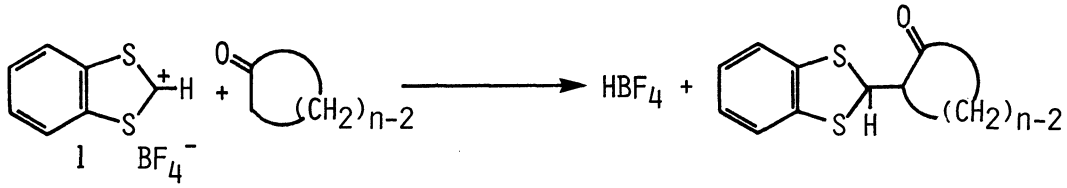
The reaction of a series of ketones with 2 equiv. of 1,3-benzodithiolylium tetrafluoroborate affords α-(1,3-benzodithiol-2-ylidene)ketones and 1,3-benzodithiole in good yields.

The synthetic utility of α-oxo ketene dithioacetals, especially as versatile three-carbon synthons, is a matter of a recent excellent review.[1] The only general method for preparation of these compounds involves the reaction of ketones with carbon disulfide in the presence of base followed by alkylation of the resulting β-oxo dithioic acids.[1] Herein we report a convenient preparation of α-(1,3-benzodithiol-2-ylidene)ketones by reaction of ketones with 1,3-benzodithiolylium tetrafluoroborate (1).[2,3]

A suspension of 1 (5 mmol) in 5 ml of cyclopentanone was stirred at room temperature until suspended 1 disappears to give a homogeneous solution (ca. 15 min). The usual workup of the mixture afforded 2-(1,3-benzodithiol-2-yl)cyclopentanone (2a) in 84% yield. In a similar way, cyclohexanone and cycloheptanone were allowed to react with 1 to give 2b and 2c in 93% and 65% yields, respectively. The reaction probably involves alkylation of the enolate of ketones by 1. Hydrofluoroboric acid formed by the reaction apparently assists the enolization since induction period is observed. Although the present reaction provides a novel method for introduction of a masked formyl group into α-position of ketones, the use of a large excess of ketones and their acid-catalyzed aldol condensation as a side reaction under the conditions are the weak points of the present procedure.



2a: n=5, 84%
b: n=6, 93%
c: n=7, 65%

Accordingly a stoichiometric amount of cyclopentanone was allowed to react with 1 in anhydrous methylene chloride at room temperature. This unexpectedly resulted in the formation of 2-(1,3-benzodithiol-2-ylidene)cyclopentanone [3; R^1,R^2=-$(CH_2)_3$-] in good yield along with 1,3-benzodithiole (4). This indicates that the hydride abstraction by 1 from the initial product 2a occurred to produce 2-(2-oxocyclopentyl)-1,3-benzodithiolylium salt [5; R^1,R^2=-$(CH_2)_3$-] and 4.[4] Deprotonation of the newly formed dithiolylium salt during workup gives the above dithioacetal.

This finding prompted us to apply the reaction to a variety of ketones since

it leads to a novel method for introduction of a masked ester group into α-position of ketones and also for preparation of α-oxo ketene dithioacetals. The results summarized in Table 1 show that the reaction is generally applicable to enolizable ketones, thereby affording the dithioacetals 3 in good yields.[5] In every case 4 was also isolated in good yield. 1,3-Benzodithiole 4 is converted to 1 by treatment with trityl tetrafluoroborate[2b] and can be recycled, if necessary.

The following is a general procedure. To a stirred solution of a ketone (10-12 mmol) in methylene chloride (30 ml) was added 1 (20 mmol). The mixture was stirred at room temperature. Suspended 1 gradually disappears and instead the precipitation of newly formed dithiolylium salt usually appears. After the completion of the reaction, 10% aqueous sodium carbonate solution was added and the resulting mixture was stirred and then worked up in appropriate ways.

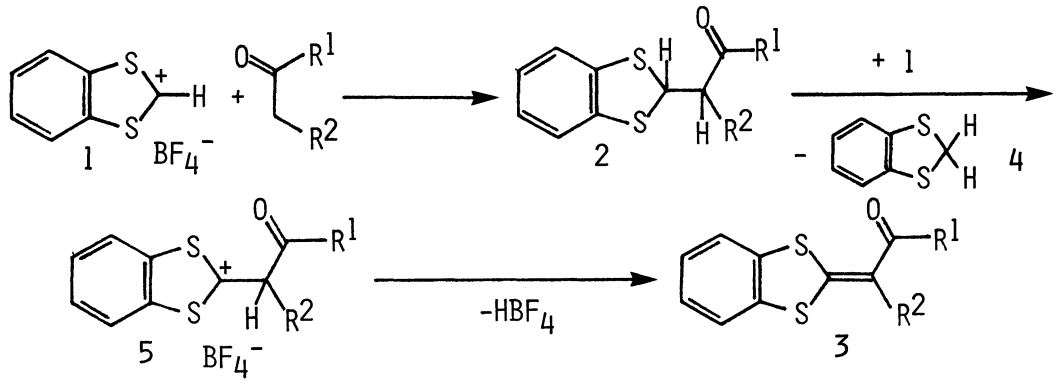
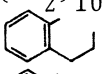
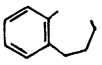


Table 1. Preparation of α-Oxo Ketene Dithioacetals 3

Run	R^1	R^2	Time/h	Yield/%[a]	Mp θm/°C
1	$-(CH_2)_3-$		3.5	74	181-181.5
2	$-(CH_2)_4-$		1.5	99	155.5-156.5
3	$-(CH_2)_5-$		3	86	163-163.5
4	$-(CH_2)_{10}-$		24	84	146.5
5			24	79	193.5-195
6			10	61	224.5-255.5
7	C_6H_5	H	24	72	117-118
8	2-thienyl	H	24	48	205-207
9	2-naphthyl	H	24	57	219.5-220.5

a) Yields based on ketones.

References
1) R. K. Dieter, Tetrahedron, 42, 3029 (1986).
2) a) J. Nakayama, K. Fujiwara, and M. Hoshino, Chem. Lett., 1975, 1099; b) J. Nakayama, K. Fujiwara, and M. Hoshino, Bull. Chem. Soc. Jpn., 49, 3567 (1976).
3) For synthesis with this reagent, see J. Nakayama, Sulfur Rep., 4, 159 (1985).
4) For hydride abstraction by 1 from 2-substituted 1,3-benzodithioles, see J. Nakayama, K. Yamashita, M. Hoshino, and T. Takemasa, Chem. Lett., 1977, 789; J. Nakayama, M. Imura, and M. Hoshino, Bull. Chem. Soc. Jpn., 53, 1661 (1980).
5) For reaction of 1 with acetone and 2-pentanone, even when ketones were used in large excess, hydride abstraction was observed. Thus, the reaction of 1 with acetone gave 1-(1,3-benzodithiol-2-yl)-2-propanone (13%) and 1-(1,3-benzodithiol-2-ylidene)-2-propanone (40%) and the reaction with 2-pentanone gave 3-(1,3-benzodithiol-2-yl)-2-pentanone (50%) and 3-(1,3-benzodithiol-2-ylidene)-2-pentanone (24%).

(Received March 2, 1987)