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A Clean, Facile and Practical Synthesis of α-Oxoketene *S,S*-Acetals in Water

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Abstract: A clean, facile and practical synthesis of α-oxoketene *S,S*-acetals in water has been developed. Catalyzed by tetrabutylammonium bromide (TBAB) at room temperature in water, a range of β-dicarbonyl compounds have been converted to the corresponding α-oxoketene *S,S*-acetals in very high yields. The catalyst in the aqueous phase can be recycled after the separation of organic products.

Keywords: carbon disulfide; β-dicarbonyl compounds; α-oxoketene *S,S*-acetals; tetrabutylammonium bromide; water

Introduction

Over the past decades, the utility of α-oxoketene *S,S*-acetals as versatile intermediates in organic synthesis has been recognized.[1] As three-carbon 1,3-bielectrophilic synthons, α-oxoketene *S,S*-acetals have been extensively investigated and widely applied in the synthesis of substituted and fused aromatic and heterocyclic structural frameworks by reacting them with nucleophiles such as Grignard reagents,[2] Reformatsky reagents,[3] organolithium reagents[4] and organocuprate reagents.[5] Indeed, the first synthesis of an α-oxoketene *S,S*-acetal was reported in 1910 by Kelber and co-workers.[6] This compound was prepared by alkylation of β-oxodithioic acid which was obtained in poor yield by reaction of an aryl ketone with CS_2 and KOH at 100 °C followed by neutralization with sulfuric acid. In the early 1960s, Thuillier and Vialle successfully prepared α-oxoketene *S,S*-acetals directly from ketones in good yields by using sodium *tert*-amylate as the base and two equivalents of an alkyl halide.[7] Subsequent workers devoted their efforts towards improving the synthetic methodology and achieved mild reaction conditions, high yields and wide generality to wide substrates for the synthesis of α-oxoketene *S,S*-acetals.[8] However, there are only a few reports so far on the synthesis of α-oxoketene *S,S*-acetals in aqueous media,[9] and none in water.

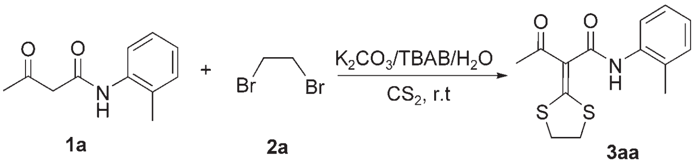
The use of water as a solvent in organic chemistry was rediscovered in the 1980s in Breslow's work, which showed that a hydrophobic effect can strongly enhance the rates of some organic reactions.[10] Organic reactions in water without the use of any organic solvent can also benefit from the fact that water is an easily available, cheap, safe and environmentally benign solvent.[11] Later on, extensive work has revealed that a variety of organic reactions including the Mukaiyama aldol reaction, allylation reactions, Diels–Alder reaction, Michael reactions, Mannich-type reactions and even dehydration reactions can be realized in the presence of various catalysts such as inverse phase-transfer catalysts and surfactant-type Lewis or Brønsted acids in water.[12,13]

Our laboratory has been engaging in the synthesis and application of α-oxoketene *S,S*-acetals for a decade.[14] Recently, we developed a novel thioacetalization reaction in water using an α-oxoketene *S,S*-acetal, 3-(1,3-dithian-2-ylidene)pentane-2,4-dione, as a 1,3-propanedithiol equivalent and *p*-dodecylbenzenesulfonic acid (DBSA, a surfactant-type Brønsted acid) as the catalyst.[15] As part of our continuing interest in organic reactions in water, the present work aims at the synthesis of α-oxoketene *S,S*-acetals in water.

Results and Discussion

Acyl(alkoxycarbonyl)ketene *S,S*-acetals are known to be prepared in poor yields from ketones using a strong base such as sodium *tert*-amylate, sodium hydride and lithium 4-methyl-2,3-di-*tert*-butylphenoxide in the presence of carbon disulfide and subsequent *S*-alkylation with the appropriate alkyl halide.[1a] Choi and co-workers improved the method by choosing K_2CO_3 as the base and *N,N*-dimethylformamide as the reaction medium and obtained acyl(alkoxycarbonyl)ketene *S,S*-acetals from β-oxo esters in very high yields, and applied

Table 1. Preparation of **3aa** from acetyl acetone **1a** in water.



Entry	Cat.	Amount[a] [mmol]	H_2O [mL]	K_2CO_3 [mmol]	**1a** [mmol]	Time[b] [h]	Yield[c] [%]
1	SDBS	5.0	15	25	10	24	0
2	TBAB	5.0	15	25	10	6.0	97
3	TBAB	2.5	15	25	10	6.0	96
4	TBAB	1.0	15	25	10	6.0	96
5	TBAB	0.5	15	25	10	7.0	82
6	TBAB	0.0	15	25	10	24	0
7	TBAB[d]	2nd use	0	25	10	6.0	96
8	TBAB[e]	3rd use	0	25	10	6.0	95
9	TBAB[f]	4th use	0	25	10	7.0	91

[a] Amount of catalyst
[b] The reaction time was recorded after the addition of bromoethane
[c] Isolated yields of **3aa** obtained by filtration.
[d] Aqueous filtrate from entry 4.
[e] Aqueous filtrate from entry 7.
[f] Aqueous filtrate from entry 8.

this protocol in the synthesis of acyl(arylcarbamoyl)ketene *S,S*-acetals from β-oxo amides.[16]

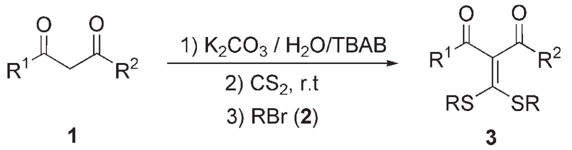
In the present work, the reaction of 3-oxo-*N*-*o*-tolylbutanamide **1a** (1.0 equiv.) with carbon disulfide (1.2 equivs.) in the presence of K_2CO_3 (2.5 equivs.) and sodium *p*-dodecylbenzenesulfonate (SDBS, 0.5 equivs.) in water and subsequent *S*-alkylation with 1,2-dibromoethane **2a** (1 equiv.) was first attempted (Table 1, entry 1). Unfortunately, no desired α-oxoketene *S,S*-acetal product was even detected in the reaction mixture. Then the reaction was performed on **1a** (1.0 equiv.) with carbon disulfide (1.2 equivs.) in the presence of K_2CO_3 (2.5 equivs.) and tetrabutylammonium bromide (TBAB, 0.5 equivs.) in water and subsequent *S*-alkylation with **2a** (1 equiv.). To our delight, the reaction proceeded smoothly at room temperature to afford 2-(1,3-dithiolan-2-ylidene)-3-oxo-*N*-*o*-tolylbutanamide **3aa** in 97% yield (entry 2). To optimize the reaction conditions, several reactions were carried out in which the feed molar ratio of TBAB to **1a** was changed from 1/2 to 1/100, and the molar ratio among other reactants was kept constant. Some of the results are summarized in Table 1. It is noted that there is nearly no change in the yields and rates of the reactions when decreasing the addition of DBAB from a stoichiometric amount to a catalytic amount of TBAB/**1a** (entries 2–4). Too low a feed molar ratio of TBAB/**1a**, 5 mol % for example, makes the reaction a little sluggish and with accompanying small amounts of unreacted starting materials (entry 5). In the cases of entries 2–4, the product is solid and can deposit from the reaction system once formed. The pure product is obtained in excellent yield after the solid has been filtered and washed with water, which provides a very simple separation process. In contrast to the above results, the reaction without TBAB cannot yield the desired α-oxoketene *S,S*-acetal product (entry 6). The results indicate that the catalyst TBAB plays a key role in the reactions in water.

Obviously, the resulting aqueous filtrate after the separation of organic products still contains the catalyst TBAB, which prompted us to investigate recycling of the catalyst. Thus, the reaction of **1a** with carbon disulfide (1.2 equivs.) and K_2CO_3 (2.0 equivs.) was carried out using the aqueous filtrate containing TBAB as reaction medium following in a similar fashion as described above. After the reaction was completed as indicated by TLC, separation of the resulting mixture by filtration furnished **3aa** in 96% yield (entry 7). Further studies reveal that TBAB can attain very high catalytic activity even when it was used for the four times (entry 9). The results demonstrate that the catalyst can be recycled, at least for several times, by reuse of the aqueous phase after the separation of organic products. Therefore, we present a clean, facile and practical protocol for the synthesis of α-oxo ketene *S,S*-acetals in water.

To test the general applicability of this protocol, a series of β-dicarbonyl compounds **1b**–**f** were selected for the investigation. Subjected to the optimized reaction conditions as described in Table 1 entry 4, compounds **1b**–**f** were converted into the corresponding α-oxoketene *S,S*-acetals **3** in excellent yields. Some of the results are summarized in Table 2.

On the basis of these results, an interfacial mechanism for the reaction **1** with carbon disulfide and alkyl halide **2**

Table 2. Preparation of α-oxoketene *S,S*-acetals **3** from β-dicarbonyl compounds **1** in water.



Entry	Substrate			Substrate			Time[a] [h]	Product 3	Yield[c] [%]	Ref.
	1	R^1	R^2	**2**	R	R				
1	**1a**	CH_3	$2\text{-}CH_3C_6H_4NH$	**2a**	$-(CH_2)_2-$		6.0	**3aa**	98	
2	**1a**	CH_3	$2\text{-}CH_3C_6H_4NH$	**2b**	$-(CH_2)_3-$		6.0	**3ab**	96	
3	**1a**	CH_3	$2\text{-}CH_3C_6H_4NH$	**2c**	$PhCH_2$	$PhCH_2$	6.0	**3ac**	97	
4	**1b**	CH_3	$2\text{-}CH_3OC_6H_4NH$	**2a**	$-(CH_2)_2-$		6.0	**3ba**	97	
5	**1b**	CH_3	$2\text{-}CH_3OC_6H_4NH$	**2b**	$-(CH_2)_3-$		6.0	**3bb**	98	
6	**1b**	CH_3	$2\text{-}CH_3OC_6H_4NH$	**2c**	$PhCH_2$	$PhCH_2$	6.0	**3bc**	99	
7	**1c**	CH_3	$4\text{-}ClC_6H_4NH$	**2a**	$-(CH_2)_2-$		6.0	**3ca**	93	
8	**1c**	CH_3	$4\text{-}ClC_6H_4NH$	**2b**	$-(CH_2)_3-$		6.0	**3cb**	95	
9	**1c**	CH_3	$4\text{-}ClC_6H_4NH$	**2c**	$PhCH_2$	$PhCH_2$	6.0	**3cc**	96	
10	**1d**	CH_3	CH_3	**2a**	$-(CH_2)_2-$		8.0	**3da**	97	[14b, g]
11	**1d**	CH_3	CH_3	**2b**	$-(CH_2)_3-$		8.0	**3db**	92	[14b, g]
12	**1d**	CH_3	CH_3	**2c**	$PhCH_2$	$PhCH_2$	8.0	**3dc**	95	[14e]
13	**1e**	CH_3	OC_2H_5	**2a**	$-(CH_2)_2-$		8.0	**3ea**	94	[16a]
14	**1e**	CH_3	OC_2H_5	**2b**	$-(CH_2)_3-$		8.0	**3eb**	95	[16a]
15	**1e**	CH_3	OC_2H_5	**2c**	$PhCH_2$	$PhCH_2$	8.0	**3ec**	98	[14e]
16	**1f**	OC_2H_5	OC_2H_5	**2a**	$-(CH_2)_2-$		8.0	**3fa**[b]	91	[14f]
17	**1f**	OC_2H_5	OC_2H_5	**2b**	$-(CH_2)_3-$		8.0	**3fb**	90	[14g]
18	**1f**	OC_2H_5	OC_2H_5	**2c**	$PhCH_2$	$PhCH_2$	8.0	**3fc**	92	[14e]

[a] The reaction time was recorded after the addition of alkyl halide.

[b] Liquid product, separation was carried out by extraction with diethyl ether followed by washing with water.

[c] Isolated yields for solid products **3**, separation was carried out by filtration and washing with water.

is assumed as shown in Scheme 1. The reaction starts from the deprotonation of β-dicarbonyl compound **1** to afford the enolates **4** and **5** in the presence of K_2CO_3 and TBAB. In the aqueous phase near the interface, the nucleophilic attack of the enolates **4** and **5** on carbon disulfide occurs to form thiolate **6**. As a tautomer of **6**, unsaturated monothiolate anion **7** undergoes the *S*-alkylation with alkyl bromide, finally yielding the corresponding α-oxoketene *S,S*-acetal **3**.

Conclusion

In summary, a clean, facile and practical synthesis of α-oxoketene *S,S*-acetals has been developed based on the reaction of β-dicarbonyl compounds with carbon disulfide and alkyl bromide catalyzed by tetrabutylammonium bromide in the presence of potassium carbonate in water. The simple procedure, mild conditions, easy separation, high yields, and especially the relation to the current environmental concerns, make this protocol most attractive for academic research and practical applications.

Experimental Section

Typical Procedure for the Preparation of α-Oxoketene *S,S*-Acetals 3 (3aa as Example)

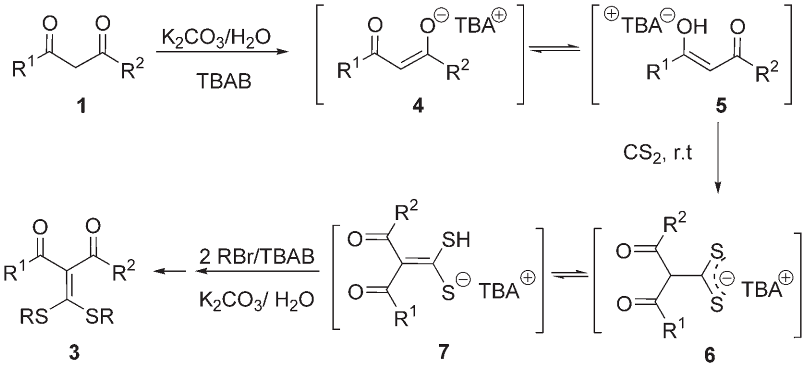
To a solution of 3-oxo-*N*-*o*-tolylbutanamide **1a** (10 mmol), K_2CO_3 (25 mmol) and TBAB (1.0 mmol) in water (15 mL) at room temperature was added CS_2 (12 mmol) under stirring. After the reaction mixture was stirred at room temperature for 1.0 h, 1,2-dibromoethane (10 mmol) was added dropwise within 15 min. Then the resulting mixture was stirred for 6 h at room temperature. The precipitated solid was collected by filtration, washed with water (3 × 25 mL), and dried under vacuum to afford the product **3aa** as a yellowish solid; yield: 98%.

All the compounds **3** listed in Table 2 were prepared following the same procedure. As an exception, the separation of **3fa** was carried out by extraction with diethyl ether followed by washing with water.

Physical Data of Compounds Isolated

Products **3da**–**3fc** are known compounds.

3aa: yellowish solid, mp 140–142 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.34$ (s, 3H), 2.46 (s, 3H), 3.38 (m, 2H), 3.44 (m,



Scheme 1. A proposed mechanism for the reaction of **1** with CS_2 and alkyl bromide in the presence of TBAB and K_2CO_3 in water.

2H), 7.11 (m, 1H), 7.22 (m, 2H), 7.93 (m, 1H), 8.10 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.1, 28.8, 36.7, 38.4, 122.8, 123.8, 125.4, 126.8, 129.3, 130.6, 135.1, 165.1, 170.1, 193.3; IR (KBr, neat): ν = 3442, 3284, 1647, 1625, 1456, 1306, 1219, 753 cm^{-1}; anal. calcd. for $C_{14}H_{15}NO_2S_2$: C 57.31, H 5.15, N 4.77; found: C 57.40, H 5.11, N 4.75; MS: *m/e* = 293 (M$^+$, 187).

3ab: yellowish solid, mp 122–124 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (t, *J* = 6.0 Hz, 2H), 2.32 (s, 3H), 2.43 (s, 3H), 2.99 (t, *J* = 6.0 Hz, 4H), 7.11 (m, 1H), 7.20–7.25 (m, 2H), 7.90 (s, 1H), 7.97 (d, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.0, 24.0, 28.2, 29.0, 29.7, 122.9, 125.4, 126.7, 129.3, 130.6, 132.3, 135.5, 164.2, 164.4, 194.3; IR (KBr, neat): ν = 3457, 3348, 1646, 1516, 1454, 1285, 834 cm^{-1}; anal. calcd. for $C_{15}H_{17}NO_2S_2$: C 58.60, H 5.57, N 4.56; found: C 58.51, H 5.61, N, 4.55; MS: *m/e* = 307 (M$^+$, 214).

3ac: yellowish solid, mp 70–72 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.18 (s, 3H), 2.41 (s, 3H), 4.15 (m, 4H), 6.92–7.45 (m, 14H), 7.76 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.8, 30.1, 39.4, 41.5, 123.0, 125.5, 126,6 127.7, 128.8, 129.0, 129.3, 129.6, 130.4, 131.4, 132.8, 134.9, 135.1, 136.7, 143.8, 146.0, 162.1, 198.7; IR (KBr, neat): ν = 3370, 3026, 1668, 1515, 1453, 1203, 866 cm^{-1}; anal. calcd. for $C_{26}H_{25}NO_2S_2$: C 69.77, H 5.63, N 3.13, Found: C 69.69; H 5.61, N 3.15.

3ba: yellowish solid, mp 112–114 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.32 (s, 3H), 3.35 (m, 2H), 3.45 (m, 2H), 3.88 (s, 3H), 6.91 (d, *J* = 7.8 Hz, 1H), 7.03 (m, 1H), 7.09 (m, 1H), 8.25 (s, 1H), 8.47 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.3, 36.5, 38.5, 55.8, 110.1, 120.0, 121.2, 124.3, 127.3, 148.3, 165.2, 169.6, 191.8, 192.1; IR (KBr, neat): ν = 3410, 1652, 1521, 1461, 1434, 1285, 1251, 753 cm^{-1}; anal. calcd. for $C_{14}H_{15}NO_2S_2$: C 54.35, H 4.89, N 4.53; found: C 54.24, H 4.93, N 4.54.

3bb: yellowish solid, mp 162–164 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.23 (m, 2H), 2.34 (s, 3H), 2.96 (m, 4H), 3.88 (s, 3H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.99 (m, 1H), 7.04 (m, 1H), 8.20 (s, 1H), 8.47 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.9, 28.8, 28.9, 29.3, 55.1, 110.1, 119.9, 121.1, 124.3, 127.4, 132.7, 148.2, 164.3, 164.7, 197.8; IR (KBr, neat): ν = 3282, 1665, 1637, 1600, 1528, 1462, 1258, 1230, 756 cm^{-1}; anal. calcd. for $C_{15}H_{17}NO_2S_2$: C 55.70, H 5.30, N 4.33, found: C 55.62, H 5.34, N, 4.31.

3bc: yellowish solid, mp 163–165 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.20 (s, 3H), 3.85 (s, 3H), 4.12 (m, 4H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.87–7.15 (m, 2H), 7.16–7.27 (m, 10H), 8.30 (s, 1H), 8.36 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.7, 33.3, 41.5, 55.7, 110.1, 120.1, 120.8, 121.0, 124.3, 124.6, 127.2, 128.7, 129.1, 136.4, 142.6, 147.7, 148.4, 162.2, 197.9, 204.6; IR(KBr, neat): ν = 3409, 1651, 152, 1433, 1251, 752 cm^{-1}; anal. calcd. for $C_{26}H_{25}NO_2S_2$: C 67.36, H 5.44, N 3.02; found: C 67.26, H 5.45, N, 3.04.

3ca: yellowish solid, mp 184–186 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 3H), 3.33–3.45(m, 4H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 2H), 8.64 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.7, 36.7, 38.5, 121.3, 123.5, 129.1, 129.6, 136.5, 162.2, 171.1, 193.3; IR (KBr, neat): ν = 3281, 1625, 1453, 1247, 831 cm^{-1}; anal. calcd. for $C_{13}H_{12}ClNO_2S_2$: C 49.75, H 3.85, N 4.46; found: C 49.64, H 3.81, N 4.42.

3cb: yellowish solid, mp 194–196 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.19 (m, 2H), 2.38 (s, 3H), 2.90–3.01 (m, 4H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.67 (d, *J* = 7.8 Hz, 2H), 8.50 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.0, 29.0, 29.2, 29.8, 121.1, 129.0, 129.5, 132.2, 136.6, 164.2, 165.6, 194.1; IR (KBr, neat): ν = 3430, 1644, 1397, 1249, 829 cm^{-1}; anal. calcd. for $C_{14}H_{14}ClNO_2S_2$: C 51.29, H 4.30, N 4.27; found: C 51.39, H 4.31, N, 4.22.

3cc: yellowish solid, mp 144–146 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.15 (s, 3H), 4.14 (m, 4H), 7.15–7.30 (m, 14H), 7.25 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.0, 39.2, 41.5, 121.3, 128.1, 128.5, 128.8, 129.4, 130.7, 135.8, 136.8, 143.6, 146.2, 149.3, 162.2, 198.0; IR (KBr, neat): ν = 3321, 1665, 1315, 1246, 826 cm^{-1}; anal. calcd. for $C_{25}H_{22}ClNO_2S_2$: C 64.16, H 4.74, N 2.99; found: C 64.24, H 4.69, N, 3.03.

Acknowledgements

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