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LETTERS

Novel Photochemical Addition of Aromatic Aldehydes to Ketene Dithioacetal *S,S*-Dioxides and Its Application to Organic Synthesis

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Abstract: On irradiation (>290 nm) in the absence or presence of benzophenone, various aromatic aldehydes add to ketene dithioacetal *S,S*-dioxides to give the corresponding 1:1 adducts, which were shown to be synthetic precursors of indanone derivatives. © 1998 Elsevier Science Ltd. All rights reserved.

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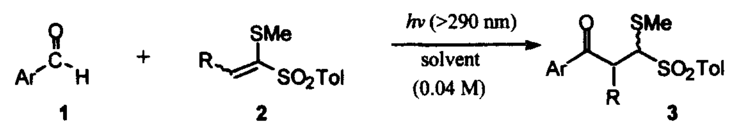
The C-C bond formation that occurs by radical addition of reagents across the double bonds of olefins is important in organic synthesis and referred to as the Kharasch addition reaction.[1] Generally, aliphatic aldehydes add via a radical chain mechanism to electron-deficient olefins such as α,β-unsaturated ketones or esters to yield the corresponding 1:1 adducts in good to excellent yields (eq. 1).[2]

(1)

(2)

However, the addition reaction of aromatic aldehydes to olefins (eq. 2), which have appeared in only a few literatures, seems to occur with less efficiency.[2a,2d,3] Since a variety of aromatic aldehydes are easily available, the exploitation of an efficient reaction for eq. 2 is promising for the development of new and useful methods for organic synthesis. In this letter, we report a novel photochemical reaction of aromatic aldehydes (**1**) with ketene dithioacetal *S,S*-dioxides (**2**)[4] to give 2-aroylalkanal dithioacetal *S,S*-dioxides (**3**) as well as their utilization in synthesizing indanone derivatives.



(3)

When a solution of 1-methylthio-1-(*p*-tolylsulfonyl)-1-butene (**2a**) (1.0 mmol) and benzaldehyde (**1a**) (5.0 mmol) in benzene (25 mL) was irradiated with a high-pressure Hg arc

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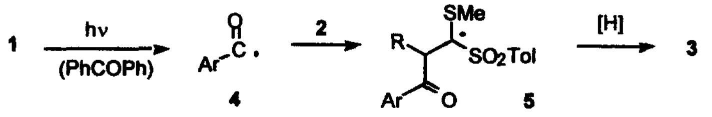
lamp (100 W) at room temperature under N_2 atmosphere for 2 h, the expected adduct (**3**; R=Me, Ar=Ph) was produced as a diastereomeric mixture (52:48) in 77% yield along with a small amount (10%) of the unchanged **2a**. This reaction also took place in chlorobenzene or acetonitrile. As summarized in Table 1, various benzaldehyde derivatives except for *p*-methoxybenzaldehyde gave the corresponding **3**. In any case, the conversion yield based on unrecovered **2** was high.

Table 1. Photochemical Addition of Aromatic Aldehydes (**1**) to **2**.[a]

R	ArCHO	[equiv.][b]	Solvent	Ph_2CO/equiv.	Yield/%[c]	(d.r.)[d]
Et	C_6H_5CHO	[5.0]	benzene		77 [86]	(52:48)
Et		[5.0]	MeCN		58 [68]	(61:39)
Et		[5.0]	chlorobenzene		75	(54:46)
Me		[5.0]	benzene		81	(55:45)
^{i}Pr		[5.0]	benzene[e]		61 [95]	(53:47)
Me	*p*-(AcO)C_6H_4CHO	[5.0]	chlorobenzene		57 [65]	(50:50)
Me		[3.0][f]		2.0	69 [84]	(52:48)
Me	*p*-(MeO)C_6H_4CHO	[5.0]	chlorobenzene		--[g]	---
Me		[3.0][f]		2.0	60 [74]	(51:49)
Me	*p*-MeC_6H_4CHO	[5.0]	chlorobenzene		59 [93]	(53:47)
Me		[3.0][f]		2.0	83 [97]	(56:44)
Me	*m*-MeC_6H_4CHO	[5.0]	chlorobenzene		65 [82]	(53:47)
Me		[3.0][f]		2.0	67 [82]	(54:46)
Me	*p*-FC_6H_4CHO	[5.0]	chlorobenzene		68 [76]	(54:46)
Me		[3.0][f]		2.0	69 [84]	(56:44)

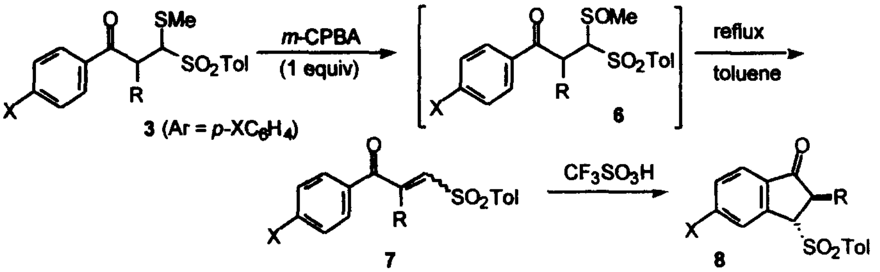
[a] Irradiated with a 100 W high-pressure Hg arc lamp for 2.0 h unless otherwise noted.
[b] Mol-equivalent to **1**. [c] The value in brackets is based on the unrecovered **2**. [d] The diastereomeric ratio of **2**. [e] Irradiated for 3.0 h. [f] Benzophenone (2.0 mol equiv) was added. [g] The starting material (68%) was recovered.

The coexistence of benzophenone (2 mmol) accelerated the reaction so that the amount of **1** was reduced to 3 mmol without decreasing the yield. It is noteworthy that *p*-methoxybenzaldehyde did not produce the expected adduct on direct irradiation without benzophenone, but the yield of 60% was attained in the presence of benzophenone. These results are probably due to the fact that the lowest excited state of *p*-methoxybenzaldehyde is not (n,π^*), but (π,π^*). The present addition reaction is initiated by hydrogen abstraction from the aromatic aldehyde (**1**) by the (n,π^*) excited state of **1** itself[6] or benzophenone to produce an aroyl radical (**4**) which adds efficiently to **2**. The driving force for the efficient addition of **4** to **2** is thought to be the stabilization of the resulting radical (**5**) by a synergistic (captodative) effect of an electron-donating methylthio group and an electron-withdrawing *p*-tolylsulfonyl group.[8]



(4)

The present addition can be characterized by the indispensable amount of **1** that is 3-5 mol-equivalents to **2**. This is in sharp contrast to the addition reaction of a 1-hydroxyalkyl radical to **2**. As reported in our previous papers,[9] the alcohol which is the source of the 1-hydroxyalkyl radical has to be utilized in large excess, usually as a solvent. Hence, the present addition of **1** to **2** seems to be a more practical process. In order to utilize the aroyl adducts (**3**) for organic synthesis, we planned a novel route leading to 2-substituted indanone derivatives (**8**) via β-aroyl-α,β-unsaturated sulfones (**7**). A key to success in the conversion of **3** to **8** is the Nazarov-type cyclization[10] of **7** because the Nazarov cyclization of aryl vinyl ketones possessing a strongly electron-withdrawing group (*p*-tolylsulfonyl) at the β-position of the vinyl part is unprecedented.



(5)

Oxidation of **3** with *m*-chloroperbenzoic acid (1.0 mol-equiv.) followed by pyrolysis in refluxing toluene gave **7** (Table 2). For the Nazarov-type cyclization of **7** (X=H, R=Me), we surveyed various acids such as polyphosphoric acid, conc. sulfuric acid, chlorosulfonic acid, trifluoroacetic acid, trifluoromethanesulfonic acid, and 12 tungsto(VI)phosphoric acid n-hydrate. Among them, trifluoromethanesulfonic acid gave the best result: When a solution of **7** (X=H, R=Me) in trifluoromethanesulfonic acid was allowed to stand at room temperature for 2 d, the Nazarov-type cyclization occurred to give **8** (X=H, R=Me)[11] in 58% yield. Other results are summarized in Table 2, which shows that an electron-withdrawing substituent retards the reaction to require either a longer reaction time or a higher reaction temperature. Under the present conditions, *p*-hydroxyl and *p*-methoxyl substituents seem to behave as an electron-withdrawing group because of protonation of their oxygen lone pair. We also found that 1-(methylthio)-1-propen-2-yl phenyl ketone easily polymerized at room temperature in trifluoromethanesulfonic acid. Therefore, it seems that the presence of a *p*-tolylsulfonyl group at the 3-position inhibits the acid-catalyzed polymerization of the α,β-unsaturated carbonyl moiety to make the Nazarov reaction tolerant of severe conditions.

Table 2. Transformation of **3** into **8** via **7**.

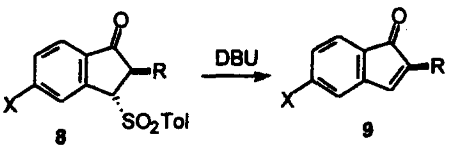
X	R	**3** → **7**	**7** → **8**	
		yield (*E*:*Z*)	temp./time	yield/% [a]
H	Me	83 (60:40)	rt / 2 d	58
H	^{i}Pr	89 (58:42)	rt / 2 d	63
F	Me	77 (65:35)	rt / 7 d	23 [62]
Me	Me	77 (63:37)	rt / 3 d	61
MeO	Me	86 (61:39)	50 °C/ 1 d	49 [61]
AcO	Me	81 (58:42)	70 °C/ 2.5 h	44[b]
OH	Me	--- [c]	50 °C/ 2 d	58

[a] The value in brackets means the yield based on the unrecovered **7**.

[b] **8** (X=OH, R=Me) was given.

[c] **7** (X=OH, R=Me) obtained by acidic hydrolysis of **7** (X=OAc, R=Me) was subjected to the transformation to **8**.

In any case, the Nazarov-type cyclization of **7** was achieved in moderate yields by treatment with trifluoromethanesulfonic acid. Since they possess a tolylsulfonyl group at the 3-position, the indanone derivatives (**8**) are anticipated to be useful for synthesizing various derivatives of indanone. One example is the conversion of **8** to 2-substituted indenones (**9**): Treatment of **8** (R= X=Me) with DBU (2 equiv.) in THF at room temperature gave 2-methylindenone (**9**; R= X=Me) in 91% yield.



8 **9**

In conclusion, we have found that, on irradiation with a high-pressure Hg lamp, various aromatic aldehydes (**1**) added to ketene dithioacetal *S,S*-dioxides (**2**) to afford the Kharasch-type adducts (**3**). In some cases, the reaction was accelerated by the coexistence of benzophenone. In addition, the adducts (**3**) were shown to be useful for synthesizing indanone derivatives. Now we are studying the addition of aliphatic aldehydes to **2** in elaboration of the present addition reaction.

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