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Carbon-Carbon Double Bond Formation Between α-Haloketones and Aldehydes Mediated by SnCl<sub>2</sub>/Na<sub>2</sub>So<sub>3</sub>; Synthesis of (E) - α, β -Unsaturated Ketones

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## CARBON-CARBON DOUBLE BOND FORMATION BETWEEN $\alpha$ -HALOKETONES AND ALDEHYDES MEDIATED BY SnCl<sub>2</sub>/Na<sub>2</sub>SO<sub>8</sub>: SYNTHESIS OF (E) - $\alpha$ , $\beta$ -UNSATURATED KETONES

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ABSTRACT: One-pot reactions of  $\alpha$ -haloketones with aldehydes in the presence of excess SnCl<sub>2</sub>/Na<sub>2</sub>SO<sub>8</sub> or SnCl<sub>2</sub> alone in THF at reflux were found to afford (E) -  $\alpha$ ,  $\beta$ -unsaturated ketones in fair to good yields.

Several dehalogenating reagents of  $\alpha$ -haloketones have been found which could promote carbon-carbon single or double bond formation between α-haloketones and aldehvdes Cela or CeCla/NaI, 1 AlCla/KI or efficiently, such as TiCl<sub>4</sub>/KI, <sup>3</sup> Sml<sub>2</sub><sup>3</sup> and Sml<sub>8</sub><sup>4</sup> Some tin compounds, such as SnF<sub>2</sub>,<sup>5</sup> Sn (OTf) 2<sup>6.7</sup> as well as tin metal<sup>8</sup> have also been used as reagents for the reactions of  $\alpha$ -halocarbonyl compounds with aldehydes or ketones via tetravalent or divalent tin SnC1<sub>2</sub> in combination with CeCla<sup>1</sup> or enolates. Sometimes, Et<sub>2</sub>AlCl<sup>®</sup> has been employed in aldol or Reformatsky-type reactions of *α*-halocarbonyl with carbonyl compounds compounds, but SnCl<sub>2</sub> alone at room temperature has not been

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applied in the aldol reactions between  $\alpha$ -haloketones and aldehydes<sup>1</sup>. Previously, the combined reagent SnCl<sub>2</sub>/Na<sub>2</sub>SO<sub>8</sub>, as as SnCl<sub>2</sub> alone was to be well found <u>a n</u> effective dehalogenating reagent of  $\alpha$ -haloketones<sup>10</sup>. Now both the combined reagent SnCl<sub>2</sub>/Na<sub>2</sub>SO<sub>8</sub> and SnCl<sub>2</sub> alone are reported to be also efficient reagents for carbon-carbon double bond formation between α-haloketones and aldehydes in anhydrous THF solvent under reflux to afford (Ε) - α, β -unsaturated ketones selectively.

SnC1<sub>2</sub>/Na<sub>2</sub>SO<sub>8</sub>

Ar COCH<sub>2</sub>Bt+RCHO  $\longrightarrow$  Ar COCH=CHR or SnCl<sub>2</sub>

Treatment of equimolar mixture of α-bromoketones and aldehydes with excess anhydrous SnCl<sub>2</sub> and Na<sub>2</sub>SO<sub>8</sub> in the ratio of 1:1:4:1 in dry THF under reflux for 4-6h gave the corresponding (E) -  $\alpha$ ,  $\beta$  -unsaturated ketones in fair to good With  $\alpha$ ,  $\beta$ -unsatured aldehydes, vields. вuch 88 cinnamaldehyde and acrolein, the reactions also gave buta-1, 3-dienyl ketones in moderate yields. However, the reactions of a -bromophenyl ketones with p-and m-nitrobenzaldehydes did not give the desired  $\alpha$ ,  $\beta$ -unsaturated ketones, unknown being formed instead, probably because deep red mixtures of reduction of nitro group with SnCl<sub>2</sub>. Moreover, with ketones, the desired cabon-carbon bond formation did not occur, even with prolonged reaction time.

Treatment of ethyl bromoacetate and p-chlorobenzaldehyde with an excess of the combined reagent SnCl<sub>2</sub>/Na<sub>2</sub>SO<sub>8</sub> gave no Reformatsky-type product.

In the carbon-carbon double bond formation reactions. excess SnCl<sub>2</sub> was used to obtain satisfactory yields of the products. When the molar ratio of  $\alpha$ -haloketone; aldehyde ; SnCl<sub>2</sub>; Na<sub>2</sub>SO<sub>8</sub> was changed from 1:1:4:1 to 1:1:2:1. the reactions gave only traces of the product. In the absence of SnCl<sub>2</sub>, no reaction was occurred. In contrast, in the absence of Na<sub>2</sub>SO<sub>8</sub>, the reactions still gave satisfactory yields of the  $\alpha$ ,  $\beta$ -unsaturated ketones, though the yields of the products were reduced when compared with those in the presence of excess SnCl<sub>2</sub>/Na<sub>2</sub>SO<sub>8</sub>. These results suggest that the reducing reagent SnCl<sub>2</sub> plays an key role in the reactions. Å۹

## CARBON-CARBON DOUBLE BOND FORMATION

N	∝-Haloketone	Aldehyde	Product	Yield (%) <sup>b</sup>
1	CeHsCOCH2Br	C <sub>e</sub> H <sub>e</sub> CHO	CeHeCH=CHCOCeHe	73
2	CeHsCOCH2Br	3-C1C.H.CHO	3-C1C <sub>o</sub> H <sub>4</sub> CH=CHCOC <sub>o</sub> H <sub>5</sub>	83 (78)
3	CeHsCOCH2Br	4-BrC.H.CHO	4 - Br C <sub>o</sub> H <sub>4</sub> CH=CHCOC <sub>o</sub> H <sub>5</sub>	84 (81)
4	CeHsCOCH2Br	4-CH.OC.H.CHO	4 - CH <sub>2</sub> OC <sub>6</sub> H₄CH≈CHCOC <sub>6</sub> H <sub>6</sub>	71
5	C.H.COCH2B1	4-HOC <sub>s</sub> H <sub>4</sub> CHO	4-HOC <sub>0</sub> H <sub>4</sub> CH=CHCOC <sub>6</sub> H <sub>0</sub>	52
6	C.H.COCH2Br	4-Me2NCeH4CHO	4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> =CHCOC <sub>6</sub> H <sub>5</sub>	62
7	CeHsCOCH2Br	C <sub>s</sub> H <sub>s</sub> CH=CHCHO	C.H.SCH=CHCH=CHCOC.H.S	72
8	CeHeCOCH2Br	CH2=CHCHO	CH3=CHCH=CHCOC6H8	47
9	4-BrC.H.COCH2Br	CeHe CHO	C <sub>e</sub> H <sub>e</sub> CH=CHCOC <sub>e</sub> H <sub>e</sub> Br-4	76
10	4-BrCeH4COCH2Br	4-C1CaH4CHO	4-C1C <sub>o</sub> H <sub>4</sub> CH=CHCOC <sub>o</sub> H <sub>4</sub> Br-4	85 (83)
11	4-BrCeH4COCH2Br	4-HOC.H.CHO	4-HOC.H.CH=CHCOC.H.Br-4	55
12	4-BrCeH4COCH2Br	4-CH#OCeH4CHO	4 - CH <sub>2</sub> OC <sub>2</sub> H <sub>4</sub> CH=CHCOC <sub>2</sub> H <sub>4</sub> Br - 4	79
13	4-BrCeH4COCH2Br	4-Me_NC_H_CHO	4-Me2NC.H.CH=CHCOC.H.Br-4	65

Table 1. Carbon-Carbon Double Bond Formation between α-Haloketones and Aldehydes Promoted by SnCl<sub>2</sub>/Na<sub>2</sub>SO<sub>8</sub> or SnCl<sub>2</sub>

a. A mixture of α-haloketone(2mmol), aldehyde(2mmol), SnCl<sub>2</sub>(8mmol), Na<sub>2</sub>SO<sub>4</sub>(2mmol), was stirred at r.t. for 2h, then at reflux for 4h.

b. Isolated yields. The data in parentheses were the yields of reactions in the absence of Na<sub>2</sub>SO<sub>3</sub>.

previously, it was reported described that at 1000 temperature, the use of SnCl<sub>2</sub> alone gave no carbon-carbon bond formation product. Nevertherless, we found that the reactions took place with either excess SnCl<sub>2</sub> /Na<sub>2</sub>SO<sub>8</sub> 01 excess SnCl<sub>2</sub> alone with a longer reaction time and a higher reaction temperature. The results were listed in Table 1. The physical constants and spectral data of the products are shown in Table 2.

N.	M. P. (°C) (Lit) <sup>2</sup>	<sup>1</sup> H NMR 8 (ppm)	IR v max(cm <sup>-1</sup> )
1	56-57 (57-58)	7.24-8.0(10H, m) 8.08(2H, m)	1670 (в) 1615 (в)
2	75.5 (76)	7. 25-7. 28 (1H, m) 7. 44-7. 93 (7H, m)   7. 98 (1H, m) 8. 00-8. 10 (2H, m)	1670 (s) 1615 (s) 680 (s)
3	123 (123. 5)	7. 13-7. 24 (2H, m) 7. 27-7. 69 (7H, m) 8. 01-8. 08 (2H, m)	1670 (s) 1610 (s)
4	76-77.5 (77-78)	3. 85 (3H, s) 6. 75 (2H, m) 7. 15-7. 78 (7H, m) 7. 80-8. 10 (2H, m)	1670 (s) 1610 (s) 1270 (s)
5	103-104	6. 80-7. 03 (2H, m) 7. 15-7. 79 (7H, m) 7. 81-8. 07 (2H, m) 9. 92 (1H, S)	1665 (s) 1605 (s) 1595 (s)
6	112-114 (114)	3. 00 (8H, s) 6. 60 (2H, m) 7. 10-7. 78 (7H, m) 7. 90-8. 10 (2H, m)	3450 (m) 2920 (m) 1660 (s) 1610 (s)
7	100-102 (101-102)	6. 75-7. 05 (2H, m) 7. 12-7. 55 (10h, m) 7. 80-8. 10 (2H, m)	3040 (m) 1665 (s) 1585 (s)
8	47-48 (48)	1. 85 (3H, d, J=5HZ) 6. 05-6. 75 (3H, m) 7. 15-7. 45 (4H, m) 7. 70-8. 00 (2H, m)	1680 (s) 1620 (s)
9	112-113 (113)	7. 50-8. 20 (11H, m)	1665 (s) 1670 (s) 685 (s)
10	166-167	7. 48-8. 17 (10H, m)	1670 (s) 1615 (s) 1255 (s)
11	184. 5-186	6. 79-6. 89 (2H, m) 6. 67-8. 10 (8H, m) 10. 19 (1H, s)	1675 (s) 1620 (s) 1610 (s)
12	144-145	3. 87 (3H, s) 6. 80 (2H, m) 7. 25-7. 80 (6H, m) 7. 90-8. 15 (2H, m)	1660 (s) 1615 (s)
18	142-144	3. 03 (6H, s) 6. 74-6. 85 (2H, m)	1665 (s) 2620 (s)

Table 2. phsical constants and spectral data of products

By analogy with the mechanism of cabon-carbon bond between  $\alpha$ ,  $\alpha'$ -dibromophenylketones and aldehydes formation using stannous fluoride  $(SnF_2)$ <sup>5</sup>, the reactions of α -bromoketones and aldehydes in the presence of excess SnCl<sub>2</sub> /Na<sub>2</sub>SO<sub>8</sub> or SnCl<sub>2</sub> alone seem to proceed via tetravalent tin enolates, generated in situ by the reductive insertion of  $SnCl_2$  into the  $\alpha$ -bromoketones, reaction with the aldehydes, and subsequent dehydration to afford the  $\alpha$ ,  $\beta$ -unsaturated ketones. probably, Na<sub>2</sub>SO<sub>8</sub> promotes the debromination of α -bromoketones by SnCl<sub>2</sub> to form tin enclates.

## EXPERIMENTAL

Reactions of α-Haloketones with Aldehydes in the Presence of Excess SnCl<sub>2</sub>/Na<sub>2</sub>SO<sub>8</sub>—General Procedure:

Under anhydrous conditions, a mixture of a - bromophenyl ketone (2mmol), aldehyde (2mmol), SnCl<sub>2</sub> (8mmol, 1.53g) and Na<sub>2</sub>SO<sub>8</sub> (2mmol, 0. 25g) in anhydrous THF (20ml) was stirred at room temperature for 2h, then at reflux fot 4h. The reaction mixture was filtered to remove inorganic salts. The solid was washed with ether. To the filterate, brine (5ml) was added, and the mixture was then extracted with ether. The combined extracts were washed with brine, dried with anhydrous MgSO<sub>4</sub>, filtered and evaporated under reduced pressure. The crude product was purified by recrystallization. All products had physical data and spetral characteristics (IR and H-NMR) in agreement with literature data and new compounds also gave satisfactory elemental analyses.

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