



NOTE

Synthesis of Aliphatic Aldehydes

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An easy procedure for synthesis of aliphatic aldehydes has been realized in heterogeneous medium from dimethyl sulfoxide, halides and bicarbonate anions. The mixture was irradiated with microwave for a short time and led to desired products. A number of aliphatic aldehydes were obtained in mild conditions with a good yield.

Key Words: Heterogeneous medium, Aldehydes, DMSO, Halides, Microwaves.

The Kornblum oxidation of halides with DMSO gives carbonyl compounds^{1,2}. This reaction has a great importance in organic synthesis as *viz.*, morphine alkaloid synthesis³, preparation of nitronyl nitroxides compounds^{4,5}, synthesis of asymmetric ligands used as catalysts⁶, synthesis of histrionitocotoxin⁷, synthesis of potential plant protecting compound on the basis of 2,3-dihydrothiazol-2-thione⁸, synthesis of polynitrodiols⁹.

The conventional synthesis of aliphatic aldehydes with the help of Kornblum reaction necessitates a long time, room-temperature conditions to afford a convenient yield^{1,2,6}. An improvement of Kornblum reaction was obtained involving the ultrasound activation⁷.

As well as ultrasounds, the microwave could quite probably exert a favourable effect on the Kornblum oxidation. To prove this hypothesis we studied aldehydes synthesis by Kornblum oxidation in heterogeneous medium and assisted by microwave.

Alkyl bromide, DMSO and sodium bicarbonate are commercially available substances. The resulting product was identified by TLC (silica gel, Et₂O), elemental analysis and IR spectra. The infrared spectra were recorded on compound's thin liquid, with the help of a Perkin-Elmer 1600 spectrometer. An Optiquick Y71 microwave oven operating at 300 W was employed. Elemental analyses were carried out with a Carlo Erba model 1106 apparatus. Boiling points were measured by distillation.

General procedure of synthesis: A mixture of 4 mmol of alkyl bromide, 5 mmol of DMSO and 8 mmol of sodium bicarbonate were added in a 25 mL pyrex beaker. The mixture

was irradiated in a microwave oven ($\lambda = 12.2$ cm) for required time. The resulting mixture was put in 50 mL ice-water and extracted with 2 × 50 mL ether. The organic layer was dried on anhydrous sodium sulfate for removing traces of water and then was filtered off. After evaporation of the solvent at room pressure, a liquid resulted. Distillation of the resulting liquid under vacuum and temperature digital control in a BOECO RVO 400SD apparatus give the pure synthesized aldehydes (Table-1).

The organic halides and dimethyl sulfoxide are polar reagents which absorb strongly in the microwave. For this reason the synthesis of aldehyde from halides which are oxidized with DMSO could be possible by microwave activation. Keeping this in mind we implemented an advantageous proceeding for synthesis of several aliphatic aldehydes in heterogeneous medium. The DMSO, alkyl bromide and potassium bicarbonate were put together in a beaker and well mixed. The resulting mixture was irradiated 2-4 min and then the aldehyde was extracted with diethyl ether (Table-1).

The purity of the products, few minutes irradiation time, easy experimental installation and the high yields are the principal benefits of this method. These results could be explained considering that reaction between alkyl halides and DMSO take place on the surface of the bicarbonate granules by a lower energy transition state¹⁰.

Conclusion

The aliphatic aldehydes were synthesized in attractive conditions with the help of microwaves. The reactions are quick and the yields are over 85 %.

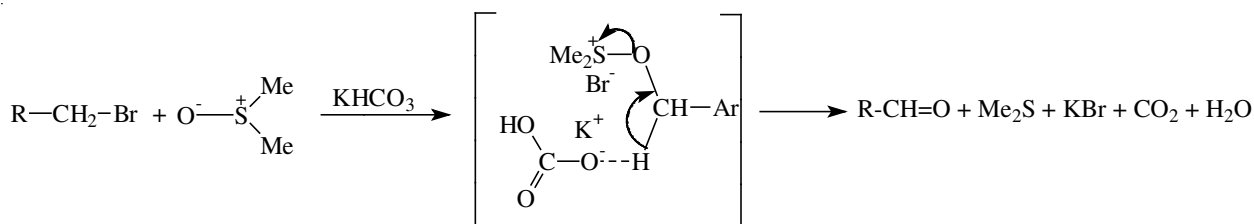


TABLE-1
ALDEHYDES SYNTHESIZED BY KORNBLUM OXIDATION UNDER MICROWAVES
 $R-CH_2Br + Me_2SO + KHCO_3 \rightarrow R-CHO + Me_2S + KBr + H_2O + CO_2$

N ^o	R	Elemental analysis (%): Calcd. (found)		$\nu(C=O)$ (cm ⁻¹)	Time (s)	Yield (%)	b.p. (°C)
		C	H				
1	<i>t</i> -Bu	69.76 (69.64)	11.62 (11.57)	1726	129	91	75-76/760Torr ¹¹ (77)
2	<i>i</i> -BuCHMe	73.68 (73.61)	12.28 (12.19)	1718	131	90	138-142/760Torr ¹² (139-141)
3	MeC≡C	70.58 (70.42)	5.88 (5.79)	1692	125	97	55/15Torr ¹³ (54)
4	<i>n</i> -BuCHMe	73.68 (76.59)	12.28 (12.23)	1711	175	91	38-39/9Torr ¹⁴ (37-38)
5	Me(CH ₂) ₃ CHMe	76.05 (75.98)	12.67 (12.60)	1709	238	89	95/5Torr ¹⁵ (94-95)
6	Me(CH ₂) ₈ CHMe	78.26 (78.18)	13.04 (13.01)	1706	205	92	145/20Torr ¹⁶ (145-146)
7	<i>i</i> -PrCH ₂	69.76 (69.67)	11.62 (11.53)	1719	125	93	90-92/760Torr ¹⁷ (91)
8	<i>n</i> -PrCH ₂	69.76 (69.59)	11.62 (11.52)	1720	130	95	55-57/12Torr ¹⁸ (56)
9	<i>i</i> -Pr(CH ₂) ₃	73.68 (76.58)	12.28 (12.12)	1712	197	88	80-85/100Torr ¹⁹ (83)
10	<i>i</i> -Pr(CH ₂) ₄	75.00 (74.85)	12.50 (12.43)	1715	205	87	50-55/8Torr ²⁰ (52-54)
11	Me(CH ₂) ₆	75.00 (74.93)	12.50 (12.39)	1712	230	89	171/760Torr ²¹ (170.5)
12	Me(CH ₂) ₇	76.05 (75.96)	12.67 (12.56)	1710	237	86	190/760Torr ²² (190)
13	Me(CH ₂) ₈	76.92 (76.83)	12.82 (12.76)	1707	240	85	207-208/760Torr ²³ (206-207)

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