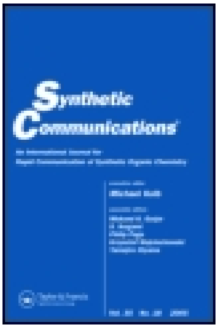

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Synthesis of Aldehydes from Carboxylic Acids via 2-Imidazolines

Zhen Shi [a] & Huan Gu [a]
[a] Department of Chemistry, Northwest University, Xi'an Shaanxi, 710069, China

To cite this article: Zhen Shi & Huan Gu (1997): Synthesis of Aldehydes from Carboxylic Acids via 2-Imidazolines, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 27:15, 2701-2707

To link to this article: http://dx.doi.org/10.1080/00397919708004139

SYNTHETIC COMMUNICATIONS, 27(15), 2701-2707 (1997)

SYNTHESIS OF ALDEHYDES FROM CARBOXYLIC ACIDS VIA 2-IMIDAZOLINES

Zhen Shi * and Huan Gu

Department of Chemistry, Northwest University, Xi'an Shaanxi 710069, China

Abstract: The use of readily available 2-substituted-2-imidazolines as precursors to 2-hydroxy aldehyde, unsaturated aldehyde and a variety of functionalized aldehydes is reported. It provides a novel method for the preparation of aldehydes from carboxylic acids via 2-substituted-2-imidazolines.

Methods for converting carboxylic acids into aldehydes generally make use of the controlled partial reduction of secondary or tertiary amides derived from carbazole, N-methylaniline, imidazole, dihydro-1,3-oxazines, or N,N'-carbonyl-diimidazole with lithium aluminum hydride, partial reduction of esters or cyanides using diisobutylaluminum hydride, or partial reduction of acid chlorides with lithium tri-t-butoxy-aluminum hydride.[1,2,3] These methods are not suitable for industrial application due to their expensive materials, inconvenient conditions. The need for an efficient preparation of aldehydes prompted us to develop the new synthetic method of aldehydes from carboxylic acids via 2-imidazolines.

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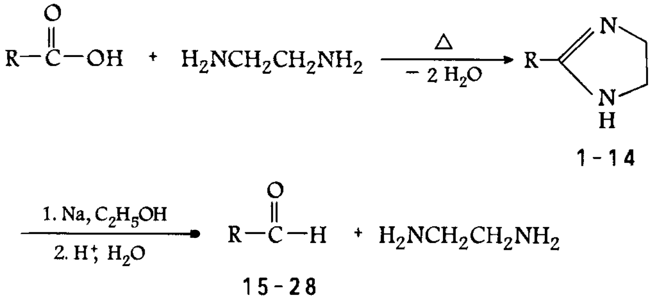
* To whom correspondence should be addressed.



Scheme

The conversion of carboxylic acids into 2-substituted-2-imidazolines is easily achieved in high yields by the reaction of carboxylic acids with ethylenediamine. The products are readily purified by crystallization (acetone or alcohol), vacuum sublimation, or chromatography on silica gel. 2-n-Octyl-2-imidazoline was chosen as the substrate to examine the effects of reaction temperatures and ratios of sodium to 2-substituted-2-imidazoline on the reduction of 2-substituted-2-imidazolines. For all practical purposes, it was found that the reduction should be performed at 0 ~ 5 ℃, the ratio of sodium to 2-substituted-2-imidazoline should be 2.5 : 1.0. In these conditions, the best results were obtained. 2-Substituted-2-imidazolidines derived from the reduction of 2-substituted-2-imidazolines were then subjected to acidic cleavage in either 1.2 mol/L hydrochloric acid or aqueous oxalic acid, the aldehydes derived from the hydrolysis of 2-substituted-2-imidazolidines were isolated and characterized (Table 1).

The most general method found for the hydrolytic cleavage of the 2-substituted-2-imidazolidines was steam distillation from oxalic acid solution. In this fashion, pure

Table 1 The Experimental Data of Compounds **15-28**

Comp	R	mp(℃)	Yield(%)
15	CH_3	[a]147-148(147)[4]	70.3
16	n-C_9H_{19}	[b]103-104(102)[5]	78.6
17	n-$C_{11}H_{23}$	[a]107-108(106)[6]	78.2
18	n-$C_{15}H_{31}$	34-35(34)[7]	76.4
19	C_6H_5	[a]235-236(237)[4]	65.6
20	$C_6H_5CH_2$	[a]121-122(120-121)[4]	70.1
21	4-$O_2NC_6H_4$	104-105(103-105)[7]	68.6
22	4-ClC_6H_4	46-48(45-47)[7]	63.1
23	4-$CH_3OC_6H_4$	[a]253-254(253)[4]	62.4
24	2-$O_2NC_6H_4$	42-43(42-43)[7]	48.7
25	3,4-$(CH_3O)_2C_6H_3$	153-154(153-154)[7]	54.2
26	$CH_3CH(OH)$	105(105)[7]	74.6
27	$C_6H_5CH(OH)$	136-138(134-137)[8]	72.3
28	(Z)-$CH_3(CH_2)_7CH{=}CH(CH_2)_7$	36(36)[9]	72.4

[a] The m.p. of 2,4-dinitrophenylhydrazone [b] The m.p. of semicarbazone

aldehydes were distilled off directly, leaving the ethylenediamine segment of the 2-substituted-2-imidazolidine in the distillation flask as the nonvolatile oxalate salt.

For aldehydes which were insufficiently volatile to make steam distillation practical, reflux of the oxalic acid solution for 90 min usually served the purpose, with the aldehydes being removed by extraction. It was found that this method sometimes would result in the decomposition of acid- or heat-sensitive aldehydes. In this cases, the aqueous acetic acid method at room temperature could be employed. Other means for releasing aldehydes involved refluxing an ethanolic solution with semicarbazide hydrochloride or 2,4-dinitrophenylhydrazine hydrochloride. The latter method, of course, converted the aldehyde directly to its semicarbazone or 2,4-dinitrophenylhydrozone derivatives.

EXPERIMENTAL SECTION

Synthesis of 2-substituted-2-imidazolines

The following general procedure, which represents a modification of Hans S. Mnnhelmer's protocol, was used in preparing the compounds **1-14**.

2-n-Octyl-2-imidazoline 2. One mol of n-capric acid and 1.2 mol of ethylenediamine were mixed and heated in an inert solvent such as toluene in amounts sufficient to dissolve them. This solution was maintained at the temperature of approximately 110℃. The water derived from the reaction was removed. When 0.9 mol of water was collected, the vessel was evacuated (4.0KPa) and the temperature was gradually raised to about 230℃ over 2 h during which all solvent and an additional mole of water were removed. The crude product was crystallized from acetone to give 2-n-octyl-2-imidazoline, m.p. 74-75℃(liter[10]:74-75℃).

The experimental data of compounds **1-14** are listed in Table 2.

Reduction of 2-substituted-2-imidazoline

To a 250 mL 3-necked flask equipped with an addition funnel with a nitrogen inlet

Table 2 The Experimental Data of Compounds **1-14**

Comp	R	mp(℃)	Yield(%)
1	CH_3	102-103(104)[11]	68.5
2	n-C_9H_{19}	74-75(74-75)[10]	85.3
3	n-$C_{11}H_{23}$	82-83(82-83)[10]	84.9
4	n-$C_{15}H_{31}$	90-92(92-93)[10]	82.4
5	C_6H_5	100-101(101)[12]	78.8
6	$C_6H_5CH_2$	66-67(66-68)[12]	80.2
7	4-$O_2NC_6H_4$	190-191(191-192)[13]	64.6
8	4-ClC_6H_4	187-189(187)[11]	62.1
9	4-$CH_3OC_6H_4$	138(138-139)[12]	60.6
10	2-$O_2NC_6H_4$	99-100(98)[12]	45.6
11	3,4-$(CH_3O)_2C_6H_3$	158-159(158-159)[12]	47.8
12	$CH_3CH(OH)$	93(92-94)[14]	78.2
13	$C_6H_5CH(OH)$	143-144(142-146)[14]	80.6
14	(Z)-$CH_3(CH_2)_7CH{=}CH(CH_2)_7$	73-75(74)[9]	88.4

was added 100 mL of absolute alcohol, 0.2 mol of 2-substituted-2-imidazoline and 0.45 mol of sodium. The mixture was stirred at 0 ~ 5℃ for 30 ~ 40 min.The solvent was removed and the residue extracted with hexane(3 × 50mL) under nitrogen. The hexane extracts were dried over magnesium sulfate and evaporated to give the crude 2-substituted-2-imidazolidine.

Cleavage of 2-substituted-2-imidazolidine to aldehyde

A: Steam distillation. To a 150 mL flask equipped with a distillation head and an addition funnel with a nitrogen inlet was added 0.2 mol of hydrated oxalic acid and 80 mL of water, steam was introduced into the solution and 0.05 mol of 2-substituted-2-imidazolidine was added dropwise over a period of 30 min. The addition funnel was then washed with 30 mL of 1M oxalic acid. The steam distillation was continued until the distillate was free of organic materials. The distillate was extracted with three 25 mL portions of pentane or ether. The extracts were dried over anhydrous sodium sulfate and the solvent was removed to give the pure aldehyde.

B: Oxalic acid hydrolysis. In cases where the aldehyde was water soluble or insufficiently volatile to make steam distillation practical the following procedure was used. The crude 2-substituted-2-imidazolidine (0.05mol) was added to the oxalic acid solution prepared above and heated to reflux for 90 min. The solution was extracted with ether, benzene, pentane, or dichloromethane (depending on the nature of the aldehyde), the extracts were washed with 5% sodium bicarbonate solution and dried (Na_2SO_4). Concentration of the solution was followed by either distillation or recrystallization.

C. Direct conversion of 2-substituted-2-imidazolidine to semicabarzone or 2,4-dinitrophenylhydrazone. A solution of 0.02mol 2-substituted-2-imidazolidine in 40 mL of absolute ethanol was treated with 0.1 mol of semicarbazide hydrochloride or 2,4-dinitrophenylhydrazine hydrochloride and heated under reflux for 2.5-3h. The solution was poured into 100 mL of cold 1M hydrochloric acid. The crystalline portion was recrystallized from ethanol and water.

REFERENCES

1. House, H.O. "Modern Synthtic Reactions", 2nd edition, W.A. Benjamin Inc., Menlo Park: California, **1972**, pp.73-82;
2. Thomas, A.F. "Deuterium Labeling in Organic Chemistry", Appleton-Century-Crofts, New York, **1971**, pp. 243;
3. Meyers, A.I.; Nabeya, A.; Adickes, H.W. *J. Org. Chem.*, **1973**, *38(1)*, 36;
4. Fales, H.M. *J. Am. Chem. Soc.*, **1955**, *77*, 5118;
5. Pickard, K. J. *J. Chem. Soc.*, **1913**, *103*, 1947;
6. Davies, R.R.; Hodgson, H.H. *J. Chem. Soc.* **1943**, 84;
7. Bejing Chemical Agent Com. "The Catalogue Handbook of Chemical Agents", Beijing Industry University Press, Beijing, **1993**, pp. 846;
8. Oldenziel, O.H. *Tetra. Lett.*, **1974**, *2*, 167;
9. Richard, N.M.; Chowdhury, A.K. *J. Am. Chem. Soc.*,**1983**, *105*, 2197;
10. Butler, R. N.; Thornton, J. D.; Oregan, C. B. *J. Chem. Soc., Perkin Transaction,* **1983**, *9*, 2197;
11. Levesque, G.; Gressier, J.C. *Synthesis*, **1981**, *10*, 963;
12. Oxley, P.; Short, W.F. *J. Chem. Soc.,* **1947**, *1*, 479;
13. Piskov, V.B. *Zh. Org. Khim.*,**1978**,*14(4)*, 820;
14. Neilson, D.G.; Peters, D.A.; Roach, L.H. *J. Chem. Soc.,* **1962**, 2272.

(Received in the UK 24 January 1997)