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

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Lin Hai-xia [a] , Xu Liang-heng [b] & Huang Nai-ju [b]
[a] Department of Chemistry , Wen Zhou Normal College , WenZhou, 325003, China
[b] Department of Chemistry , Fudan University , Shanghai, 200433, China
Published online: 22 Aug 2006.

To cite this article: Lin Hai-xia , Xu Liang-heng & Huang Nai-ju (1997) A New Synthetic Method for Haloalkyl Carboxylic Esters from the Radical Ring Cleavage of Cyclic Acetals with Haloform, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 27:2, 303-306

To link to this article: http://dx.doi.org/10.1080/00397919708005032

SYNTHETIC COMMUNICATIONS, 27(2), 303-306 (1997)

A NEW SYNTHETIC METHOD FOR HALOALKYL CARBOXYLIC ESTERS FROM THE RADICAL RING CLEAVAGE OF CYCLIC ACETALS WITH HALOFORM

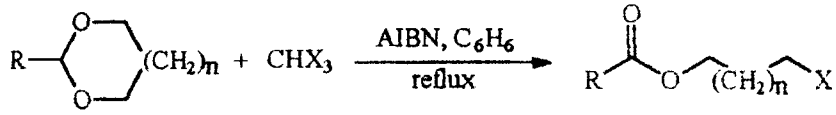
Lin Hai-xia[a*] Xu Liang-heng[b] Huang Nai-ju[b]

a(Department of Chemistry, WenZhou Normal College, WenZhou 325003, China)
b(Department of Chemistry, Fudan University, Shanghai 200433, China)

ABSTRACT: A one-pot reaction of cyclic acetals with haloform catalyzed by AIBN(2,2'-azobisisobutyronitrile) provides a novel convenient way to prepare directly haloalkyl carboxylic esters in good yields.

The acetal is the most common protecting group for aldehydes and 1,3-dioxolanes are the most commonly encountered type of acetal. It has been reported that cyclic acetals can be oxidized into β-hydroxyethyl carboxylates and β-bromoethyl carboxylates, respectively by t-BuOOH and NBS.[1,2] In a previous work, we demonstrated that cyclic acetals in the presence of neutral potassium permanganate can be oxidized to hydroxyalkyl carboxylates.[3] We now wish to report the use of haloform in benzene for the conversion of cyclic acetals to haloalkyl carboxylic esters, which is one of useful synthetic

*To Whom correspondence should be addressed



R = alkyl, aryl; n = 0, 1; X=Cl, Br

Scheme 1

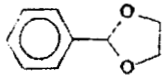
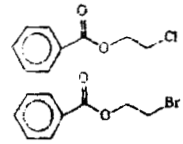
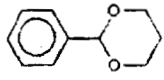
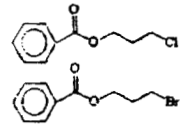
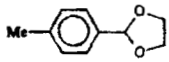
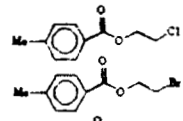
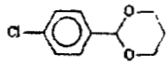
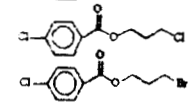
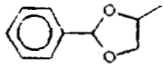
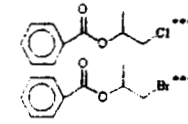
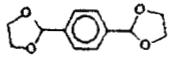
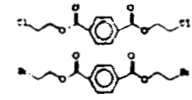
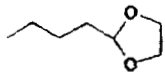
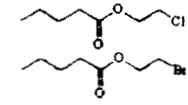
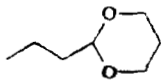
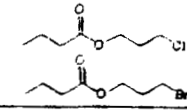
intermediates.[4] The synthetic sequence is shown in scheme 1 and the results of this study are summarized in Tab. 1.

All products are purified by distillation or recrystallization and characterized by IR., ^{1}HNMR and elemental analysis. As may be seen from the table 1, the radical cleavage proceeds with a wide range of acetals. The new modification can be used advantageously as one pot reaction and provides a facile and mild condition, easy performance and simple work-up for the synthesis of haloalkyl carboxylic esters with better yield than those reported elsewhere.[5,6]

EXPERIMENTAL

General Procedure(preparation of 2-bromoethyl benzoate): A mixture of 2-phenyl-1,3-dioxolane (0.05 mol, 7.5 g; prepared from benzldehyde (0.05 mol) and ethylene glycol (0.055 mol) at reflux in anhydrous benzene containing catalytic p-TsOH with water removal), bromoform (0.05 mol, 12.6 g), AIBN(0.1 g) and benzene (30 ml) was stirred and refluxed for about 5 hrs. After evaporation of the solvent, the residue was distilled under vacuum , the product was collected as a colorless liquid in 92% yield (10.5 g). b.p. 102-

Tab. 1. Conversion of Cyclic Acetals into Haloalkyl Carboxylic Esters

Entry	Acetal(1)	Haloform	Haloestre(2)	yield (%)*	b.p. of (2)#
a		$CHCl_3$ $CHBr_3$		84 92	95~97/1 102~105/1
b		$CHCl_3$ $CHBr_3$		83 89	119~121/1 126~128/1
c		$CHCl_3$ $CHBr_3$		76 81	120~122/1 128~130/1
d		$CHCl_3$ $CHBr_3$		74 80	145~147/1 152~154/1
e		$CHCl_3$ $CHBr_3$		88 93	107~109/1 112~114/1
f		$CHCl_3$ $CHBr_3$		85** 93**	94~93 (mp) 96~99 (mp)
g		$CHCl_3$ $CHBr_3$		70 82	78~80/1 84~86/1
h		$CHCl_3$ $CHBr_3$		73 79	60~62/2 68~71/2

*Yields of isolated products based on 1

**Recrystallized from methanol-water

***Contaminated with less than 5% of the regioisomer

#(°C/mmHg)

105°C/1mmHg; IR.(cm^{-1}): 3030, 1725, 1525, 1150, 600; ^{1}HNMR(CCl_4, ppm): 8.2(m, 2H), 7.6(m, 3H), 4.7(t, J=6Hz, 2H), 3.7(t, J=6Hz, 2H).

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(Received in The Netherlands 16 July 1996)