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A New Synthetic Method for Haloalkyl Carboxylic Esters from the Radical Ring Cleavage of Cyclic Acetals with Haloform

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

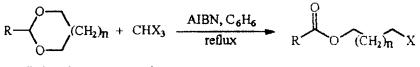
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ABSTRACT: A one-pot reaction of cyclic acetals with haloform catalyzed by AIBN(2,2'-azobisisobutyronitrile) provides a novel convenient way to prepare directly haloalkyl carboxylic esters in good yields.

The acetal is the most common protecting group for aldehydes and 1,3dioxolanes 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

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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., ¹HNMR 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.^(3,6)

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) [#]
8	$\langle 0 \rangle + \langle 0 \rangle$	CHCl ₃ CHBr ₃	Diona Dioner	84 92	9 5~9 7/1 102~105/1
b	\sim	CHCl ₃ CHBr ₃	Olora Olora	83 89	119~121/1 126~128/1
c	Me-O-C)	CHCl ₃ CHBr ₃	u -0 ¹ °~ ^{c1} u -0 ¹ °~ ^t	76 81	120~122/1 128~130/1
d	a-⊘-~°_)	CHCl ₃ CHBr ₃	i~~~a □i~~~a	74 80	145~147/1 152~154/1
e	$\langle O \rangle \langle J \rangle$	CHCl ₃ CHBr ₃	Jillan.	88 93	107~109/1 112~114/1
f	\$ - \$-\$	CHCl ₃ CHBr ₃	"~.~!@!~" •.~!@!~*	85 ^{**} 93 ^{**}	94~93 (mp) 96~99 (mp)
g	$\sim \sim \circ$	CHCl ₃ CHBr ₃	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	70 82	78~80/1 84~86/1
h	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	CHCl ₂ 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)

305

105°C/1mmHg; IR.(cm⁻¹): **3030**, 1725, 1525, 1150, 600; ¹HNMR(CCL, 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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