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An evidence of contact ion pair in β-(acyloxy)alkyl radical heterolysis during copper(I)-mediated synthesis of trisubstituted alkenes

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ABSTRACT

The first evidence for a unified mechanism of heterolysis in β-(acyloxy)alkyl radical involving contact ion pair (CIP) is presented for both fragmentation and rearrangement of the acyloxy group in the reaction of 1-alkoxy-2,2,2-trichloroethyl acetate with 2 mol equiv each of CuCl and bpy in refluxing DCE under a N_2 atmosphere and availed this reaction for the synthesis of *Z*-stereoselective trisubstituted alkenes. The stereochemistry of the trisubstituted alkenes was assigned by the uniform pattern of the chemical shift values of some relevant signals in ^1H and ^{13}C NMR spectra. This assignment was further supported by the X-ray diffraction spectroscopy of *Z*-1-chloro-2-(4-nitrobenzyloxy)vinyl acetates.

The pioneering work by Beckwith et al.[1] suggested that the rearrangement of β-acyloxy alkyl radical and its close relatives β-phosphatoxy, β-sulfatoxy- and β-nitroxy-alkyl radicals involves the migration of an ester group to the adjacent position by a common mechanism involving initial fragmentation to alkene radical cation–ester anion pair intermediate followed by its collapse to the rearranged radical. In this sequence, Newcomb and co-workers added a milestone by establishing the nature of the alkene radical cation–ester anion pair intermediate that varies from a tight contact ion pair (CIP) to diffusively free fragments to a solvent separated ion pair (SSIP) depending on the stability of the alkene radical cation and the ester anion fragments as well as the polarity of the medium.[2] The β-phosphatoxyalkyl radical cation has been detected by spectroscopy[3] and also intercepted by inter- or intramolecular tandem nucleophilic attack followed by radical cyclization even in solvents of low polarity, such as benzene to constitute an elegant methodology for the synthesis of tetrahydrofurans[4] and nitrogen-heterocycles.[5] Also the radical cation formed by mesylate heterolysis was convincingly demonstrated by laser flash photolysis kinetic studies as well as by trapping studies with thiophenol. It indicated that the acyclic alkene radical cation readily equilibrates with one or more cyclic distonic radical cation, whereby thiophenol trapping gave respective acyclic and cyclic products.[6]

However, in case of β-acyloxyalkyl radical, the alkene radical cation has not been detected or trapped or a stable alkene radical fragmentation product isolated during the rearrangement even when the reaction was performed in polar solvents and a cation stabilizing α-alkoxy substituent was present on the radical.[7] Therefore, the possibility of a concerted 1,2-acyloxy migration through a 5-centre 5-electron or 3-centre 3-electron transition state could not be ruled out.[1a] Further the β-acyloxy radicals were mostly generated by the reaction of β-acyloxyalkyl halides with an organotin hydride to investigate this rearrangement. However, direct reduction of the halide was a serious side reaction, which necessitated the reaction to be conducted by slow addition of the organotin hydride under dilute condition in order to minimize the side reaction.[8]

Further, transition-metal catalyzed radical reactions have played a vital role in the formation of carbon—carbon and carbon—heteroatom bonds and are treated as highly efficient tools in organic synthesis. These tools are very effective for the synthesis of a variety of complex molecules including natural products due to their mildness and wide range of functional group tolerance. Other advantages include low cost, non-hazardous nature, easy work-up, catalytic nature and the reaction can be performed at relatively higher concentrations without the risk of direct reduction.[1]

Ram and Meher reported CuCl/bpy-promoted generation of β-(acyloxy)alkyl radical by dechlorinative 1,2-acetoxy migration under non reducing condition from 2,2,2-trichloroethyl carboxylate. Under these conditions, the β-(acyloxy)alkyl radical underwent an efficient dechlorinative 1,2-acyloxy migration in a

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contra-thermodynamic direction to radical and afforded rearranged product 1-chloroethyl carboxylate. A concerted mechanism involving copper-complexed three- or six-member cyclic transition states were proposed for this CuCl/bpy-promoted dechlorinative 1,2-acyloxy migration.[9] No sign of the formation of diffusively free alkene radical cation was discerned when the reaction was conducted by us during the reaction of 2,2,2-trichloroethyl benzoate in more polar 1:1 v/v mixture of DCE and MeOH.

In view of overwhelming evidence for the formation of alkene radical cation in the rearrangement and fragmentation reaction of β-phosphatoxyalkyl radical and the uncertainty about the mechanism of β-acyloxyalkyl radical rearrangement, it was considered worthwhile to investigate the effect of the substituent that favours the formation of the alkene radical cation on the reaction of β-acyloxyalkyl radical in order to gain further insight into the mechanism of the reaction under these conditions. This would enable the synthesis of variously substituted, synthetically important trisubstituted alkenes, having all three heteroatom substituents, which are otherwise very difficult to synthesize.

The trisubstituted alkenes are an important part of many natural products (such as hennoxazole A,[10] discodermolide[11] and ratjadone[12]) and have also been used as precursors for the synthesis of other type of organic molecules and materials. Most of the methods relied on synthesis of the thermodynamically more stable *E*-alkenes with very good selectivity.[13] In a majority of cases either a mixture of alkenes favouring *E*-isomer was obtained as the final reaction product[14] or the *Z*-isomer formed at the initial stage which quickly gets transformed to the more stable *E*-isomer.[15] Only a few methods provided direct synthesis of thermodynamically less stable *Z*-alkenes, though *Z*-alkenes are commonly found in natural products[16] and have great scope in synthesis. In order to overcome the thermodynamically dominated selectivity, a directing group strategy has been used to access less stable *Z*-isomer.[17] Advances in catalyst design have put forward some of the *Z*-selective olefin metathesis with Mo and W catalysts,[18] Ru-phosphine catalysts,[19] and Ru containing NHC ligand.[19–22] Other methods include the reduction of alkynes over a poisoned catalyst,[23] Wittig olefination,[24] cross-coupling of *Z*-vinyl halides or *Z*-vinyl organometallic reagents,[25] Still–Gennari modification to the Horner Wadsworth–Emmons olefination,[26] and some other *Z*-selective olefin metathesis.[18a,20a] Very recently Weix and co-workers have reported the selective isomerization of terminal alkene to *Z*-stereoselective internal alkenes by the action of sterically demanding cobalt(II) catalyst.[27] Zhu and co-workers contributed much[28] and recently reported the regio- and stereoselective synthesis of (*Z*)-1-thio- and (*Z*)-2-thio-1-alkenyl boronates by Cu-catalyzed selective α- and β-borylation of thioacetylenes. This method represents the first method of its kind for generating all possible regio- and stereoisomers of trisubstituted alkene.[29]

It has been observed that the stereoselective synthesis of the trisubstituted alkene of the type α-haloenol acetates is very difficult. Ferreira described the selective and efficient Hiyama coupling of α-silylenoate and α-silylenamides obtained from platinum-catalyzed hydrosilylation for selective and efficient synthesis of stereodefined trisubstituted alkenes.[30] Kim and Lee proposed gold(I)-catalyzed regio- and stereodefined synthesis of trisubstituted alkenes via hydrophosphoryloxylation of haloalkynes followed by transition-metal-catalyzed cross coupling reaction.[31] McElvain and Stammer,[32] O'Connor[33] and Pericas and Serratosa[34] reported use of strong bases like *t*-C_4H_9OK or KOH for the dehydrohalogenation of *trans*-substituted hydrogen and halogen from 1, 2-dihalo-1,2-dialkoxyethane. Mueller and Seyferth[35] showed the formation of *cis* and *trans* isomers of 1-chloro-1,2-diethoxyethylene during thermolysis of organomercurials in a total 49% yield along with other thermolysis products ethyl chloroacetate and ethyl ethoxychloroacetate. Griesbaum et al.[36] reported sulfur, oxygen and chlorine heteroatom containing trisubstituted alkenes by the ring opening reaction of *trans*-2,3-dichlorooxirane with dimethyl sulfide via the formation of sulfonium salt. Barluenga et al.[37] and Jiang and co-workers[38] have reported the preparation of haloenol acetates from terminal alkynes by stereoselective difunctionalization in the presence of tetrafloroborate. Kowalski and Haque[39] prepared bromoenol acetates from respective esters with dibromomethyllithium at −90 °C followed by reaction with *n*-butyl lithium and acetic anhydride. These bromoenol acetates are good precursors for the formation of α-keto dianions. Falck and co-workers[40] introduced $CrCl_2$-promoted *Z*-stereoselective transformation of trihalomethylcarbinol to (*Z*)-α-haloenol ester and (*Z*)-β-haloenol ether, a kind of trisubstituted alkene with O and Cl as two hetero atoms by intramolecular 1,2-shift of acyloxy and hydrogen atom, respectively.

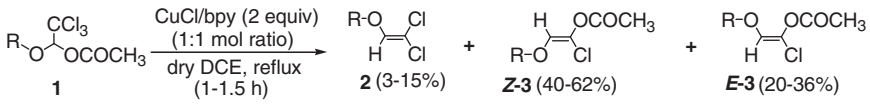
However, these methods have one or more drawbacks like use of strong basic conditions (*t*-C_4H_9OK, KOH, etc.), non friendly solvents (DMSO, DMF, etc.), costly reagents (Au, Pd-complexes, etc.), or modification of pre-existing alkenes and alkynes. Therefore, the selective formation of less stable *Z*-alkene having all the heteroatom substitutions under mild reaction condition, easy route and cheaply available reagents remains an unsolved problem. We report herewith the synthesis of *Z*-stereoselective trisubstituted alkene of the type α-haloenol ester having all the three heteroatom substituents under non-reducing and milder reaction condition wherein a range of functional groups have been survived.

Our results with Cu(I)/bpy promoted dechlorinative Surzur–Tanner rearrangement of 2,2,2-trichloroethyl carboxylates have motivated us to check the effect of various alkoxy substituted carboxylates under similar reaction condition. Some attempts have been made in this direction and the results are being presented here with, which indicate the formation of the alkene radical cation. Thus, the readily available 2,2,2-trichloro-1-benzyloxyethyl acetates **1** (Scheme 1) were treated with CuCl/bpy (1:1 molar ratio) in 1,2-dichloroethene (DCE) at reflux under a nitrogen atmosphere to meet the above expectations. Reaction smoothly completed with 2 equiv of Cu(I)-complex to give fragmentation products **2** (Table 1; see SI, p S-2) as well as rearranged products *Z*-**3** and *E*-**3**. Formation of these products together in the same reaction vessel strongly supports the dissociative mechanism involving heterolysis to contact alkene radical cation/anion pair (CIP). This CIP collapses to major rearranged products at one side and little solvation of CIP resulting in minor fragmentation product at other side.

The crude reaction mixture was purified by silica gel (60–120 mesh) column chromatography using *n*-hexane and ethyl acetate mixture in different proportions as the solvent for elution. The fragmentation products **2** were eluted first with *n*-hexane only in 3–15% chemical yield. The rearranged products *Z*-**3** were then eluted with 2–3% ethyl acetate in *n*-hexane followed by the other rearranged product *E*-**3** with 3–4% ethyl acetate in *n*-hexane in 40–62% and 20–36% yield, respectively. The rearrangement was found to be stereoselective with *Z*-**3** enol acetates.

Assignment of stereochemistry

The NOE experiments with *Z*-**3a**,**b**,**g** and *E*-**3a**,**b**,**g** were inconclusive for the determination of the configuration of the enol acetates. However, it was observed that the major enol acetates moved faster than the minor enol acetate on column chromatography in all the cases. It could be explained by assuming that the major enol acetates **3** had *Z* configuration and the minor had *E* configuration. Based on this crude method for the determination of configuration, presumably *Z*-**3** and *E*-**3** isomers were arranged along with the ^1H and ^{13}C NMR chemical shift values of some relevant signals as



R = **a.** $PhCH_2$, **b.** $Ph(CH_2)_2$, **c.** n-C_8H_{17}, **d.** $C_2H_5OCH_2CH_2$, **e.** $CH_3CH(CH_3)CH_2CH_2$, **f.** p-$MeOC_6H_4CH_2$, **g.** p-$NO_2C_6H_4CH_2$, **h.** p-$BrC_6H_4CH_2$, **i.** m-CH_3COO-$C_6H_4CH_2$, **j.** $C_5H_4NCH_2$

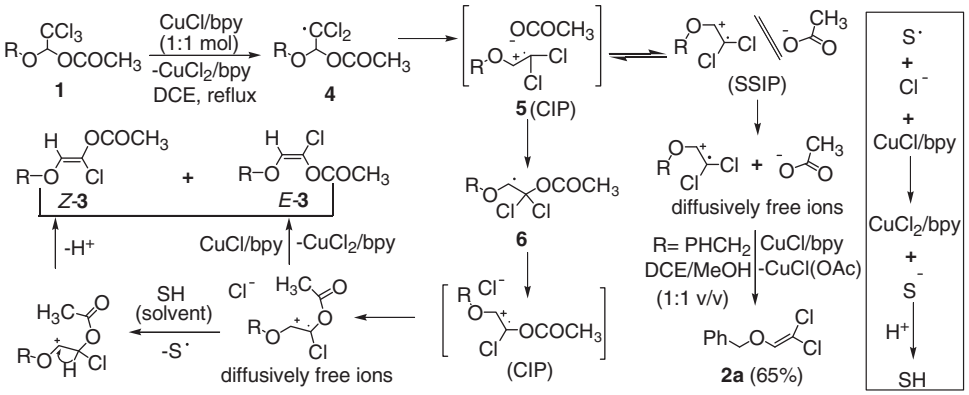
Scheme 1. Reaction of 2,2,2-trichloro-1-benzyloxyethyl acetate with CuCl/bpy.

shown in Tables 2 and 3 (see SI, p S-2). A uniform pattern in the chemical shift values of the olefinic CH and alkoxy CH_2 protons was observed in the ^1H NMR spectra. The uniform pattern in the δ values of the quaternary ester carbonyl carbon, olefinic quaternary carbon and alkoxy methylene carbon was also observed in ^{13}C NMR spectra of **3**. It was observed that the olefinic CH proton, carbon and the carbonyl carbon in *Z*-**3** appeared at considerably lower δ values than the corresponding proton and carbon of *E*-**3**, with the exception of **3i**,**j**. The shielding of the olefinic proton was observed to be 0.3 ppm or near. The alkoxy methylene protons in *Z*-**3** appeared at a slightly lower δ value than that in *E*-**3**, with the exception of **3i** in which protons appeared at nearly the same δ value. Accordingly, the olefinic CH carbons in *Z*-**3** were shielded by δ 2.0–2.6 ppm as compared to the olefinic CH in *E*-**3**. Also, the carbonyl carbon in *Z*-**3** was observed to appear upfield by δ 1.6–1.9 ppm as compared to the carbonyl carbon in *E*-**3**, except in *E*-**3j**. In this case, the difference in the δ value was only 0.1 ppm. However, a comparison of the alkoxy methylene of *Z*-**3** and *E*-**3** indicated that they had similar configuration. The significant shielding of the olefinic methine proton and carbon in olefinic quaternary carbons appeared at nearly the same respective positions in both the isomers. This similarity could be due to the uninhibited electron-donating resonance effect of the acetate group as suspected earlier. Finally, this assignment of the configuration was supported by X-ray diffraction spectroscopy of one of the enol acetates **3g** (major) which was the only solid product obtained. The single crystal X-ray diffraction spectroscopy showed the structure of this major isomer ((*Z*)-2-(4-nitro benzyloxy)-1-chlorovinyl acetate **3g**), as deduced earlier. The ORTEP diagram of *Z*-**3g** is shown in Figure 1 (SI, p S-13).[41]

Thus, the stereo chemical assignment of the major enol acetates **3**, earlier to have *Z* configuration, was supported by X-ray diffraction spectroscopy of *Z*-**3g** together with the similarity of the chemical shifts of the olefinic CH protons (Table 2) and carbons along with the ester carbonyl carbons (Table 3) of **3** with those of *Z*-**3g**. However, the stereo chemical assignment of the minor *E*-isomers was then a logical extension. But, in case of **3j**, where the difference in the chemical shift values was small, the stereochemistry could not be assigned conclusively.

Mechanistic consideration

A mechanism involving the intermediacy of the alkene radical cation/carboxylate anion pair **5** has been proposed for the formation of (*Z*/*E*)-2-(alkoxy)-1-chlorovinyl acetates **3** and 1-alkoxy-2,2-dichloroalkenes **3** from 1-alkoxy-2,2,2-trichloroethyl acetates **1** as shown in Scheme 2. The rearranged radical **6** also has a good leaving group (Cl^-) at the β-position. It is likely that this may also form a contact alkene radical cation/chloride anion pair, which may evolve into diffusively free ions more easily. The diffusively free radical cation may form the stable alkene product by accepting an electron from CuCl/bpy. Alternatively it may abstract a hydrogen atom from the medium to form a cation which would form the stable alkene product by deprotonation. As expected, an electron-donating alkoxy substituent slightly promoted the fragmentation of the initially formed radical **4** to the alkene radical cation–acetate anion pair **5**. This was evident by the formation of small amounts of 1-alkoxy-2,2-dichloroalkenes **2** in the reaction mixture even in a relatively less polar DCE solvent due to diffusion of the radical cation and acetate ion out of the solvent cage. The involvement of the contact radical cation/acetate anion pair has been further been supported by the formation of the 2,2-dichloro-1-benzyloxy ethene **2a** in significantly higher isolated yield (65%) along with small amounts of the rearranged products *Z*-**3a** and *E*-**3a** in more polar DCE/MeOH (1:1 v/v) solvent. This unified mechanism was preferred due to the proclaimed propensity of the β-(acyloxy)alkyl radical to fragment heterolytically. However, the involvement of electron-transfer to the initially formed radical intermediate **4** (Scheme 3; see SI, p S-3) from CuCl/bpy and elimination of resultant carbanion for the formation of the dichloroalkenes **2** could not be ruled out. It is also possible that the rearranged radical **6** forms the enol acetates *Z*-**3** and *E*-**3** in a similar manner. Alternatively, it may form the *gem*-dichloro intermediate **8** by transfer of a chlorine atom from $CuCl_2$/bpy, which may form the enol acetates *Z*-**3** and *E*-**3** as well as the dichloroalkene **2** by β-elimination using 2 equiv of CuCl/bpy. However, this mechanism is less likely to explain the formation of the dichloroalkene **2a** predominantly in more polar solvent DCE/MeOH (1:1 v/v). To the best of our information there is no precedent for the formation of



Scheme 2.

rearrangement and fragmentation products both from the reaction of a β-acyloxyalkyl radical under the same reaction conditions.

Takai et al. have reported a similar reaction of 2,2,2-trichloroethyl acetates and carbonates with $CrCl_2$ which is not a radical reaction but occurs by intermediacy of an organochromium species.[42]

In conclusion, a unified mechanism involving CIP in the heterolysis of β-(acyloxy)alkyl radical has been presented for the first time in the reaction of 1-alkoxy-2,2,2-trichloroethyl acetate whereby formation of both rearrangement and fragmentation products was obtained. The mechanism is supported by the formation of the fragmentation product in higher proportion in more polar DCE/MeOH (1:1 v/v) solvent. Small amounts of 1-alkoxy-2,2-dichloroalkenes were also formed by elimination involving dechlorodeacetoxylation. The *Z*-1-alkoxy-1-chlorovinyl acetates were isolated as the major products. The stereochemistry of the *Z* and *E* isomers was assigned on the basis of single crystal X-ray diffraction spectroscopy of a solid crystalline isomer and by similarity of its NMR spectra with others. These trisubstituted alkenes are highly substituted by electronegative groups at the carbon—carbon double bond which are otherwise difficult to prepare.

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Supplementary data

Supplementary data (IR, ^{1}H and ^{13}C NMR data of products **1a–j**, **2a–j**, *Z*-**3** and *E*-**3**, scan copies of ^{1}H and ^{13}C NMR spectra of 1-alkoxy-2,2,2-trichloroethyl acetates **1a–j**, 2,2-dichloroalkoxyalkenes **2a–j**, *Z*-2-alkoxy-1-chlorovinyl acetates *Z*-**3a–j** and *E*-2-alkoxy-1-chlorovinyl acetates *E*-**3a–j**, single crystal X-ray diffraction data (CIF files) and ORTEP diagram of *Z*-**3g**) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.06.008.

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