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# CuCl/bpy-Promoted Unusual Z-stereoselective Synthesis of Trichloroacetic Acid Phenyl Ester for Hirshfeld Surface Analysis and DFT Study

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A simple trichloromethyl ester underwent stereoselective synthesis of Z-2,3-dichloro-but-2-enedioic acid diphenyl ester with 2 mol equiv CuCl/bpy in reflux benzene under inert N<sub>2</sub> condition. The Z-stereochemistry of the product was confirmed by X-ray diffraction spectroscopy of Z-2,3-dichloro-but-2-enedioic acid dinaphthalen-1-yl ester which selectively formed from one of the two positional isomer of trichloro-acetic acid naphthalen-1- and 2-yl ester. The stability and stereochemistry was interpreted by Hirshfeld surface analysis and computationally using Density Functional Theory at B3LYP/6-311G(d,p) level of theory. The study revealed that the thermodynamically stable E-isomer is predominated by kinetically controlled Z-isomer.

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## CuCl/bpy-Promoted Unusual Z-stereoselective Synthesis of Trichloroacetic Acid Phenyl Ester for Hirshfeld Surface Analysis and DFT Study

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**Abstract:** A trichloromethyl ester devoid of suitably substituted C=C bond, any leaving group or a Hatom at the  $\beta$ -position to the radical, which are otherwise known for ATRA/ATRC, 1,2-rearrangement/ fragmentation or simple 1,2-H shift respectively, in a reaction of trichloro-acetic acid phenyl ester with 2 mol equiv CuCl/bpy in reflux DCE or benzene under inert N<sub>2</sub> condition resulted to stereoselective synthesis of Z-2,3-dichloro-but-2-enedioic acid diphenyl ester and/or formation of reductive dechlorination side product. The Z-stereochemistry of the product was confirmed by X-ray diffraction spectroscopy of Z-2,3-dichloro-but-2-enedioic acid dinaphthalen-1-yl ester which crystalizes in monoclinic system of P21/c symmetry elements. Hirshfeld surface analysis of experimentally established structure of Z-2,3-dichloro-but-2-enedioic acid diphenyl ester unrevealed the intermolecular interactions showing both H-bonding and short contacts. The stereochemistry was also interpreted computationally using Density Functional Theory at B3LYP/6-311G(d,p) level of theory. The calculated energies, energy gap and balance between the electrostatic potential on the molecular surface were computed which revealed unusual formation of less stable Z-isomer. **Key Words: 1.** CuCl/bpy **2.** Z-Stereoselective **3.** Z-Diphenyl 2.3-dichloromaleate **4.** DET study **5.** 

**Key Words: 1.** CuCl/bpy, **2.** Z-Stereoselective, **3.** Z-Diphenyl 2,3-dichloromaleate, **4.** DFT study, **5.** Hirshfeld Surface Analysis.

Introduction: The trichloromethyl group containing compounds are classically known for the free radical reactions under transition metal salt and their salts complexed with nitrogen containing ligands. The trichloromethyl group containing compounds easily form free radicals by homolysis of an activated C-CI bond with the help of UV-light, radical initiators, redox active metal salts or its complexes.<sup>1</sup> The study and behaviour of dichloromethyl radical variously substituted at the  $\beta$ -position generated under redox condition of Cu(I) salts and its complexes with nitrogen based ligands were extensively studied by Ram et al (Scheme 1). The results revealed that generated radicals normally undergo intermolecular addition and/or intramolecular cyclization (Path 1) on to suitably substituted carbon-carbon double bond, which may be free or hindered by bulky groups.<sup>2-5</sup> However, radicals substituted by weak or strong nucleofugal groups at the β-position underwent predominantly rearrangement (Path 2) and/or fragmentation (Path 3) through the intermediate formation of contact ion pair (CIP) which was extensively explored and established by inter or intramolecular tandem nucleophilic attack followed by radical cyclization experiments.<sup>6-7</sup> In two extreme cases the β-position of radical substituted by hydrogen and oxy group underwent 1,2-H shift via intermediate formation of a copper-carbenoid species and Z-stereoselective radical dimerization to ene-1,4-diones (Path 4).<sup>8-9</sup> Based on these observations it was thought to check the behaviour of trichloromethyl esters under this reaction condition (Path 5).



Scheme 1 Study of dichloromethyl radical under redox condition of Cu(I)

Stereoselective-alkenes are highly appraised functional groups used in chemical transformations for the development of pharmaceutical products and essential building blocks of biomolecules.<sup>10</sup> The stereo-chemical outcome of any alkene reaction decide the fate of the products. Both Z & E isomers of alkene possesses unique property, hence stereo defined alkene are much demanding. The survey of the literature revealed that Z-alkenes are important starting molecules for the synthesis of biologically active molecules and are usually found in natural products, medicinal values such as (Z)-tamoxifen, (Z)-vinylic sulfides, etc.<sup>11</sup> However, the counter E-isomer has limited use in medicine. Also, the transfat in food possesses E-alkenes which are considered harmful to the human health but not the counter Z-isomer.<sup>12</sup> As long as the stability of alkene is considered, the formation of Ealkene is relatively easy, and thus in majority of cases, the synthesis of E-alkene predominates over Z-alkene owe to its thermodynamic stability. Thus, the synthesis of stereoselective and/or stereo defined alkenes remains a thrust area of research in organic synthesis. Recently Ram and Tittal have reported synthesis of Z-stereoselective ene-1,4diones and the synthesis of Z & E-trisubstituted alkenes.<sup>13,3</sup> The formation of counter Eisomer was either present in very less amount which cannot be ascertained or might have transformed to Z-form. This observation prompted the author to further investigate the predominance of the stereochemistry of these alkene with the help of more reliable computational method using DFT calculations. Herewith author is presenting the stereochemistry of E- and Z-ene-1,4-diones.

Results and Discussion: The starting material trichloro-acetic acid naphthalen-1-yl ester 1a and its positional isomer trichloro-acetic acid naphthalen-2-yl ester 1b were easily prepared by the trichloro acetylation of commercially available 1- and 2-naphthol with trichloroacetyl chloride using triethylamine as base in dry diethylether by following reported procedure with little modofications.<sup>14</sup> The reaction of starting material **1a** and **1b** was performed with CuCl/bpy in 1:1 molar ratio in dry benzene under inert nitrogen atmosphere. The reaction of 1a completed in 2h with the consumption of 2 equivalents of copper complex CuCl/bpy. The reaction mixture was worked up as per the usual procedures adopted until earlier.<sup>3,5,13</sup> The characterization of the final major product revealed it to be a Z-2,3-dichloro-but-2-enedioic acid dinaphthyl ester 2a, which was successfully characterized by IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and HRMS and finally supported by the X-ray crystallographic data. The formation of Z-2,3dichloro-but-2-enedioic acid dinaphthyl ester **Z-2a** was thought to be by the stereoselective radical dimerization of initially formed dichloromethyl radical from trichloro-acetic acid naphthalen-1-yl ester 1 with the help of CuCl/bpy along with the formation of small amount of monochloro reduction product as shown in Scheme 2. The survey of literature revealed that no other similar Z-2,3- dichloro-but-2-enedioic acid dinaphthyl ester Z-2a molecule and dimerization reaction reported so far except our recent report on similar radical dimerization of 2,2,2-trichloro-1-phenyl-ethanones to stereoselective Z-ene-1,4-diones.<sup>13</sup>



Scheme 2 Reaction of trichloro-acetic acid naphthalen-1-yl ester 1a and 1b with CuCl/bpy (1:1 mol ratio)

The prolonged heating of **1b** starting material underwent hydrolysis of trichloroester completely along with the reduction of chlorine atom(s) to form corresponding 2-naphthol along with the formation of chloro-acetic acid naphthalene-2-yl ester. The probable reason for the selective radical dimerization with **1a** may be due to the stabilization of dichloromethyl radical of **1a**. However, 2-naphthoxide is more stable than the dichloromethyl radical of **1b**. The unusual formation of Z-2,3-dichloro-but-2-enedioic acid dinaphthyl ester **Z-2a** selectively from one of the two positional isomer of trichloro-acetic acid naphthalen-1-and 2-yl ester is the unique feature of this study. The importance of this kind of alkene realizes in organic synthesis like dimethyl maleate, maleic anhydride, and fumarates which may be used as the electron-poor alkene ligands for the synthesis and characterization of zero valent platinum complexes and also been used as catalysts in the hydrosilylation of styrene with triethylsilane.<sup>15-16</sup>

The molecular structure of **Z-2a** crystalized in monoclinic system with (P21/c) symmetry element and displayed a single molecule in the asymmetric unit. The ORTEP diagram of **Z-2a** is given in **Fig. 1**. In an asymmetric unit the two aromatic rings are orthogonal to the carbonyl groups displaying a torsion angle of  $0.0(5)^{\circ}(O_3-C_{14}-O_4-C_{15}) & 9.0(5)^{\circ}(O_2-C_{11}-O_1-C_1)$ ,



Fig. 1 The ORTEP diagram of Z-2.

where the carbonyl group was almost coplanar with the aromatic rings. This difference may be attributed to the different type of carbonyl group present in the crystal structures. However, the torsion angle displayed by the central atoms ( $C_{11}$ - $C_{12}$ - $C_{13}$ - $C_{14}$ ) was found to be almost similar to the torsion angle observed in the reported crystal structures of (*Z*)-2,3dichloro-1,4-bis(4-chlorophenyl)but-2-ene-1,4-dione; Crystal structure of (*Z*)-2,3-dichloro-1,4bis(4-methoxyphenyl)but-2-ene-1,4-dione and other (*Z*)-ene-1,4-diones recently reported by Ram and Tittal.<sup>13</sup> The mean plane of the two naphthyl units displayed a torsion angle of 42.38(10)° and 14.16(8)° with respect to each other. Unlike the reported crystal structure of the similar molecules by Tittal et al. and Ram & Tittal, no intermolecular hydrogen bonding of C-H...O observed in the crystal packing diagram of the title compound. However, crystal packing diagram reveals short contact (which is a sum of Van der Waals radii) at C-H...O and Cl...Cl type intermolecular contacts and intramolecular hydrogen bonding between C=O...O (**Fig. 2 a**) & **b**). Also, short intermolecular  $\pi$ ... $\pi$  contacts were observed between





**Fig. 2 a)** A crystal packing view of **Z-2** along b axis showing short contacts C-H...O and Cl...Cl.; **b)** A crystal packing view of **Z-2** along b axis showing intramolecular H-bond at C=O...O.

the naphthyl units, Cg to Cg 3.702 Å (+x,-1 + y,+z) (**Fig. 3**) and 3.843 Å (+x,-1 + y,+z). Similar  $\pi$ ... $\pi$  stacking of aromatic rings as well as C-H...O interactions were reported by Subramanian et al wherein  $\pi$ - $\pi$  stacking interactions between the aromatic rings and imidazole rings and intermolecular  $\pi$ - $\pi$  stacking interactions of aromatic groups observed.<sup>17</sup>





Fig. 3 A partial crystal packing view of the title compound showing  $\pi$ ... $\pi$  intermolecular contacts.

The data collection and structure refinement details are summarized in **Table 1**. All the hydrogen atom connected to the aromatic carbon atom were placed at 0.93 Å and refined using riding model with  $U_{iso}(H) = 1.2U_{eq}$ .

 Table 1. Experimental and data collection details of crystal cell Z-2

Experimental details of Crystal data Z-2	
Chemical formula	$C_{24}H_{14}CI_2O_4$
<i>M</i> <sub>r</sub>	437.25
Crystal system, space group	Monoclinic, P2 <sub>1</sub> /c
Temperature (K)	273
a, b, c (Å)	20.308 (8), 4.5337 (17), 22.738 (8)
β()	108.029 (6)
$V(Å^3)$	1990.8 (13)
Z	4
Radiation type	Μο <i>Κ</i> α
$\mu (mm^{-1})$	0.36
Crystal size (mm)	0.32 × 0.12 × 0.11
Data collection	
Diffractometer	CCD area detector
Absorption correction –	18321, 3709, 3489
No. of measured, independent and	
observed $[l > 2\sigma(l)]$ reflections	
R <sub>int</sub>	0.037
$(\sin \theta / \lambda)_{max} (\dot{A}^{-1})$	0.606
Refinement	0.071, 0.145, 1.25
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	
No. of reflections	3709
No. of parameters	271
H-atom treatment	H-atom parameters constrained
$\Delta \rho_{max}, \Delta \rho_{min} (e \AA^{-3})$	0.43, -0.18

**Hirshfeld surface analysis:** The intermolecular interactions in the title compounds were analysed using Hirshfeld surface analysis.<sup>18</sup> The asymmetric unit present in the crystal structure of **Z-2** was used to obtain the Hirshfeld surface. The Hirshfeld surface mapped

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using d<sub>norm</sub> indicated the presence of a short contact by displaying intense red color spots as shown in **Fig. 4** a). Further analysis of the Hirshfeld surface indicated that the dark red stops are due to the presence of C-H...O (**Fig. 4** b)) and Cl...Cl (**Fig. 4** c)) contacts. The 2-D fingerprint plots of **Z-2** were generated using this asymmetric unit. The fingerprint plot produced a quantitative picture of intermolecular interactions of compound **Z-2** are listed in **Table 2** and represented in **Fig. 5**. The 2-D fingerprint plots indicated that the C-H... $\pi$  (H...H



**Fig. 4 a)** The Hirshfeld surface of the title compound mapped with d<sub>norm</sub>.; **b)** The Hirshfeld surface showing C-H...O interaction.; **c)** The Hirshfeld surface showing C-H...O and Cl...Cl interactions.

and C...H) interactions provide highest contribution (53.4%) to the total Hirshfeld surface. The Cl...Cl interactions contribute 6.1% to the total Hirshfeld surface, while the Cl...H and Cl...C interactions contribute 10.1% and 4.3%, respectively to the total Hirshfeld surface, which indicated that the halogen interaction also plays an important role in stabilization of the crystal packing. The intermolecular O...H interactions contribute 12.5% to the total Hirshfeld surface. The C...C ( $\pi$ ... $\pi$ ) interactions contribute 7.6% to the total Hirshfeld surface. The other intermolecular interactions are listed in the **Table 2**.



Fig. 5 (a-k) The two-dimensional fingerprint plots showing (a) complete Hirshfeld surface (b) H...H interactions (c) C...H interactions (d) C...C interactions (e) O...O interactions (f) C...O interactions (g) O...H interactions (h) Cl...H interactions (i) Cl...C interactions (j) Cl...O interactions (k) Cl...Cl interactions.

<b>Table 2.</b> The Percent contributions of the different interatomic contacts to the total Hirshfeld surfaces of 2.	able 2. The Percent contributions of th	e different interatomic contacts	s to the total Hirshfeld	d surfaces of Z-2
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Contact	(%) Contribution
НН	35.2
СН	18.2
CC	7.6
00	1.6
CO	2.5
OH	12.5
ClH	10.1
ClC	4.3
ClO	2.0
ClCl	6.1

To investigate the predominance of Z-ene-1,4-dione obtained in experimental results over Ecounterpart under our reaction conditions, we thought to calculate their energies, band gap, and electrostatic potential balance on the molecular surface. The study was conducted on E and Z-isomers of 2,3-dichloro-but-2-enedioic acid dinaphthalen-1-yl ester **1** and 2,3-Dichlorobut-2-enedioic acid dinaphthalen-2-yl ester **2**. With the help of density functional theory (DFT) calculations using the Gaussian 09 program,<sup>19</sup> the configurations of the structures **Z-1**, **Z-2**, **E-1** and **E-2** were optimized by using B3LYP/6-311G(d,p) level of theory. The optimized structures of these E-and Z- isomers are shown in **Fig. 6**.



Fig 6. (a-d) B3LYP/6-311G(d,p) optimized structures of Z-1, Z-2, E-1 and E-2.

The optimized DFT calculations on the configurations of these isomers showed surprising result and reveal that the E-isomer is slightly stable than the Z-isomer with the relative energy of 0.54 kcal/mol as shown in **Table 3**. We have used the energy gap between HOMO and LUMO to assess the stability of the Z and E isomers.<sup>20</sup> In general, the narrower energy gap allows, the easier electron transition and reduces the molecular stability. The predicted energy gap values for **Z-1** and **E-1** are 3.57 eV and 4.16 eV, respectively representing E isomer more stable. The contour surfaces of the frontier molecular orbitals are shown in **Figures 2** and **3**. In **Z-1** isomer, the HOMO is delocalized over the whole (O)CIC=CCI(O) group. By contrast, the LUMO is located over the aromatic ring only. A similar trend observed in the case of **E-1** isomer also.

Table 3. Calculated energies, HOMO and LUMO for Z-1 and E-1 isomers.

S. No.	Molecule	Energy (a.u.)	HOMO (a.u.)	LUMO (a.u.)
1.	Z-1	-2144.262897	-0.22969	-0.09830

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Fig 8. a: Optimized structure of E-1, b: HOMO E-1 and c: LUMO E-1.

Politzer et al. correlated the charge imbalance with a sensitivity of energetic materials.<sup>21</sup> The imbalance in the charge distribution on molecular surface can be linked with the molecular stability. The *v* is the effective balance between positive and negative surface potentials which may reach a maximum value of 0.250, when  $\sigma_+^2 = \sigma_-^2$ . Where,  $\sigma_+^2 \& \sigma_-^2$  indicates the variabilities of both positive and negative surface potential on molecular surface by following equation,

$$v = \frac{\sigma_+^2 \sigma_-^2}{(\sigma_+^2 + \sigma_-^2)^2}$$

The imbalance in surface potential, *v* as shown in **Table 4** has been correlated with the stability of the molecule. The significant variation from 0.250 values represents the decreased stability. The calculated values of *v* for **Z**- and **E-1** isomers are 0.2020 and 0.2116, reveal that Z isomer has higher imbalance and thus lower molecular stability. The Z and E-1 isomers contain the naphthalene rings, chlorine and ester groups, responsible for electron withdrawing and create the imbalance in surface potentials. In both the isomers, we observed that the negative regions are stronger than the positive regions ( $\sigma_{-}^2 > \sigma_{+}^2$ ). **Figure 9** represents the calculated electrostatic potentials on the 0.001 electron/bohr<sup>3</sup> molecular surface of **Z** and **E-1** isomers.

Table 4. Calculated energies, HOMO and LUMO for Z- and E-1 isomers.

S. No.	Molecule	$\sigma_+^2$	$\sigma_{-}^{2}$	V
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		(kcal/mol) <sup>2</sup>	(kcal/mol) <sup>2</sup>	
1	Z-1	25.66	65.68	0.2020
2	E-1	34.30	78.51	0.2116

The structural parameters of **Z-1** isomer negative than 11. The structural parameters of **Z-1** isomer obtained at the B3LYP/6-311G(d,p) level of theory gave good agreement with experimental data of **Z-1** as shown in **Table 5**. However, experimental results supported by X-ray crystallography data of **Z-1** and the same category of radical dimerization of trichloromethyl ketones under similar condition to Z-ene-1,4-diones formation reported very



Experimen	tal data of <b>Z-1</b>	E	33LYP/6-311G(d,p) dat	a of <b>Z-1</b>
S. No.	Description	Bond length (Å)	Description	Bond length (Å)
1	C9-O11	1.421	C9-O11	1.393 (2.0)
2	O11-C12	1.339	O11-C12	1.361 (1.6)
3	C12-O13	1.182	C12-O13	1.202 (1.6)
4	C12-C14	1.490	C12-C14	1.496 (0.4)
5	C14-Cl16	1.718	C14-Cl16	1.740 (1.2)
6	C14-C15	1.323	C14-C15	1.346 (1.7)
7	C15-Cl17	1.715	C15-Cl17	1.732 (0.9)
8	C15-C18	1.504	C15-C18	1.525 (1.3)
9	C18-O22	1.179	C18-O22	1.192 (1.1)
10	C18-O19	1.336	C18-O19	1.355 (1.4)
11	C23-O19	1.422	C23-O19	1.400 (1.5)
S. No.	Description	Bond angle (°)	Description	Bond angle (°)
1	C9-O11-C12	117.29	C9-O11-C12	123.17 (4.7)
2	011-C12-O13	125.64	O11-C12-O13	119.93 (4.7)
3	O11-C12-C14	111.16	O11-C12-C14	118.69 (6.3)
4	O13-C12-C14	123.20	O13-C12-C14	121.25 (1.6)
5	O12-C14-CI16	117.40	O12-C14-Cl16	119.50 (1.7)
6	Cl16-C14-C15	124.74	CI16-C14-C15	121.14 (2.9)
7	C14-C15-Cl17	122.94	C14-C15-Cl17	121.87 (0.8)
8	CI17-C15-C18	112.66	CI17-C15-C18	111.19 (1.3)
9	C15-C18-C20	124.10	C15-C18-C20	119.75 (3.6)
10	O20-C18-O19	125.84	O20-C18-O19	120.92 (4.0)
11	C18-O19-C23	117.13	C18-O19-C23	123.42 (5.0)

**Fig 9**. Calculated electrostatic potentials on the 0.001 electron/bohr<sup>3</sup> molecular surface of **Z-2a** and **E-2a**. White circles denote the positions of atoms in a molecule. Color range (in kcal/mol): red greater than 13; yellow within 13 and 12; green within 12 and 11; blue more negative than 11.

recently supported the Z-steroselective formation of ene-1,4-diones. The optimization of Z-ene-1,4-diones by DFT calculations at the B3LYP/6-311G(d,p) level of theory is under progress which would be communicated with full results.

 Table 5. Comparison of experimental and theoretical structural parameters of Z-1.

Values in parenthesis shows % deviation relative to experimental results.

After ramrod study and the positive results for the stereoselective formation of 2,3-dichlorobut-2-enedioic acid dinaphthyl ester **Z-2a** from trichloro-acetic acid naphthalen-1-yl ester **1a** under CuCl/bpy mediated reaction condition prompted the authors to explore their formation from other derivatives to generalize the process and check the tolerance of other functional groups under this reaction condition. Thus, other trichloroacetic acid aryl ester **1** (**Scheme 3**) were prepared by the simple trichloroacetylation of the corresponding phenols by following



Scheme 3. Synthesis of aryl trichloroacetates (1a-h).

reported procedure as discussed earlier.<sup>14</sup> In the same way, other trichloroesters **1b-h** were prepared, and all of them showed the satisfactory IR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra. It has been observed that these aryltrichloroesters were very unstable and were prone to hydrolysis, especially O-acetyl and P-acetyl aryltrichloroesters 1d-e which readily hydrolysed to corresponding phenols. The so formed aryl trichloroacetates 1a-h, when allowed to react under the non-reducing condition of CuCl/bpy (1 mol equiv) in refluxing DCE under inert N<sub>2</sub> atmosphere, the reaction did not complete even after prolonged reflux time of 12 hrs. However, when one more equivalent of CuCl/bpy was added to the reaction mixture, it completed in an hr. Thus, the completion of reaction required two equivalent of CuClcomplex. The study of reaction products showed it did not give any decarboxylation, rearrangement or fragmentation products rather the reaction of 1a gave Z-alkene 2a (Scheme 4), in 50 and 60% isolated yield in dry DCE and benzene solvents along with the formation of 35% and 20% of mono-reduction product 3a respectively. Other relevent information are listed in **Table 1**. However, the reaction of **1b** as discussed earlier did not give the formation of any alkene dimer via radical dimerization. However, the reaction product after purification showed the formation of di-reduction product 4 in 30 and 40% isolated yield in DCE and benzene, respectively. The formation of Z-alkene 2c in 60 and 65% isolated vield was found in dry DCE and benzene, respectively in case of trichloroacetic acid phenyl ester 1c but the corresponding reduction product was not isolated. These results showed that the benzene is little better choice of solvent for supporting the formation of Zalkene and suppressing the formation of reduction products. The reaction of 1d-e did not resulted to the radical dimerization to form corresponding Z-alkene, rather hydrolysed readily to the corresponding phenol. The completion of reaction requires two equivalent of CuCl/bpy (1:1 mol ratio each). The products were successfully characterized by IR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra and the stereochemistry was supported by X-ray crystallographic data.<sup>22</sup>



a: 1-C<sub>10</sub>H<sub>7</sub>; b: 2-C<sub>10</sub>H<sub>7</sub>; c:C<sub>6</sub>H<sub>5</sub>; d: *O*-CH<sub>3</sub>CO-C<sub>6</sub>H<sub>4</sub>; e: *P*-CH<sub>3</sub>CO-C<sub>6</sub>H<sub>4</sub>; f: *P*-CI-C<sub>6</sub>H<sub>4</sub>; g: *P*-Me-C<sub>6</sub>H<sub>4</sub>; h: *P*-MeO-C<sub>6</sub>H<sub>4</sub>;

S. No.	1a-h	Solvent	Time (h)	Yield(%) <sup>b</sup>			
				Phenol	2	3	4
1	<b>a</b> , 1-C <sub>10</sub> H <sub>7</sub>	DCE	1.5	5	50	35	-
2	<b>a</b> , 1-C <sub>10</sub> H <sub>7</sub>	benzene	2	-	60	20	-
3	<b>b</b> , 2-C <sub>10</sub> H <sub>7</sub>	DCE	1	50	С	-	30
4	<b>b</b> , 2-C <sub>10</sub> H <sub>7</sub>	benzene	2	45	С	-	40
5	<b>c</b> , C <sub>6</sub> H <sub>5</sub>	DCE	1.5	15	60	-	-
6	<b>c</b> , C <sub>6</sub> H <sub>5</sub>	benzene	2	22	65	- (	-
7	<b>d</b> , 2-CH <sub>3</sub> CO-C <sub>6</sub> H <sub>4</sub>	DCE	1	70	a	-	-
8	<b>d</b> , 2-CH <sub>3</sub> CO-C <sub>6</sub> H <sub>4</sub>	benzene	1	64	a		-
9	<b>e</b> , 4-CH <sub>3</sub> CO-C <sub>6</sub> H <sub>4</sub>	DCE	1	78	d		× -
10	<b>e</b> , 4-CH <sub>3</sub> CO-C <sub>6</sub> H <sub>4</sub>	benzene	1	72	d		-
11	f, 4-CI-C <sub>6</sub> H <sub>4</sub>	DCE	1.5	12	55	20	-
12	f, 4-CI-C <sub>6</sub> H <sub>4</sub>	benzene	2	10	60	15	-
13	<b>g</b> , 4-Me-C <sub>6</sub> H <sub>4</sub>	DCE	1	05	50	30	-
14	<b>g</b> , 4-Me-C <sub>6</sub> H <sub>4</sub>	benzene	2	-	62	20	-
15	<b>h</b> , 4-MeO-C <sub>6</sub> H <sub>4</sub>	DCE	1.5	07	65	10	-
16	<b>h</b> , 4-MeO-C <sub>6</sub> H <sub>4</sub>	benzene	2	-	72	20	-

<sup>a</sup>The reaction performed with 0.003 mol of **1** & 0.006 mol of CuCl/bpy in 20 mL DCE or benzene under inert N<sub>2</sub> atm. <sup>b</sup>Yield(%) refer to purified products after column chromatography.

<sup>c</sup>The dimer product was not obtained.

<sup>d</sup>Starting material is very unstable and hydrolysed readily to corresponding phenol.

Scheme 4 Reaction of aryl trichloroacetates 1a-h with 2 equiv. CuCl/bpy (1:1 mol ratio).

Table 6. Reaction of aryltrichloroacetates 1a-h with 2 equiv CuCl/bpy (1:1 mol ratio)<sup>a</sup>

In view of earlier observations attained while monitoring the progress of the reaction of 2,2,2trichloro-1-phenyl-ethanone with 2 mol equiv each of CuCl and bpy in refluxing DCE under a  $N_2$  atm and progress of reaction of trichloro-acetic acid phenyl ester under similar reaction condition, both underwent dimerization to Z-ene-1,4-dione and Z-2,3-dichloro-but-2- enedioic acid diphenyl ester, respectively along with formation of small amount of reductive dechlorination products.<sup>9</sup> On the basis of these observations following mechanism (**Scheme 5**) may be proposed to support the stereoselective radical dimerization under the same reaction condition.



Scheme 5. Proposed mechanism for stereoselective radical dimerization of aryl trichloroacetates.

In conclusions, the reaction of trichloro-acetic acid phenyl ester which is a one oxygen homolog of trichloromethyl ketone acquired similar Z-stereoselective radical dimerization with two mol equiv of CuCl/bpy in dry DCE or benzene to Z-2,3-dichloro-but-2-enedioic acid diphenyl ester. However, the information for the formation of counter E-isomer was not found, if formed may readily converted to Z-isomer. The observations revealed that the thermodynamically stable E-isomer is predominated by kinetically controlled Z-isomer. The products were successfully characterized by IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and finally supported by some HRMS data. However, the stereochemistry supported by the X-ray diffraction

spectroscopy of Z-2,3-dichloro-but-2- enedioic acid diphenyl ester **2a**. The unusual formation of Z-2,3-dichloro-but-2-enedioic acid dinaphthyl ester **Z-2a** selectively from one of the two positional isomer of trichloro-acetic acid naphthalen-1-and 2-yl ester is the unique feature of this study. The electron-poor alkene like **Z-2a** may be used for the development of Pt(0)-complexes of the type [Pt( $\eta$ 2-alkene)( $\eta$ 2-norbornene)<sub>2</sub>] by the reaction with [Pt( $\eta$ 2-norbornene)<sub>3</sub>]. The complex reported for the hydrosilylation reaction of styrene by triethylsilane.<sup>15</sup> Due to extended electronic conjugation, Z-2a can find applications in electro-optic devices, fluorescent probes, and dyes.

## **Experimental Section:**

General Method: In a two-neck round bottom flask fitted with a rubber septum and connected to a Schlenk tube through a condenser under inert N<sub>2</sub> atm charged with CuCl (0.60 g, 0.006 mol), 2,2'-bipyridine (0.94 g, 0.006 mol), and a magnetic bar under continuous flow of nitrogen. Then, 8 mL benzene was injected into the flask and the heterogeneous mixture was heated at 50 °C with stirring for 30 mi nutes to ensure the formation of the brown Cu-bpy complex. Then the Cu-complex was cooled to room temperature and a solution of the ester 1 (0.003 mol) in benzene (7 mL) was injected through the septum. The flask again evacuated and filled with nitrogen after cooling it in an ice bath. The ice bath removed and the reaction mixture heated at reflux with stirring under a slow and continuous flow of nitrogen. The progress of the reaction monitored by TLC and the initial brown color of the reaction mixture faded as the reaction progressed. After the completion of the reaction in 1-2 h as indicated by TLC, the greenish reaction mixture cooled and filtered through a celite pad. The insoluble green solid on the celite pad was washed thoroughly with benzene and the light brown filtrate then evaporated under reduced pressure on a rotary evaporator. The residual mass subjected to column chromatography using silica gel as the solid support and n-hexane and its mixtures with chloroform as the solvent system for elution. The Z-alkene (Z-2a,c,f-h) eluted first followed by the reduced esters 3 and 5 were obtained afterwards as a colourless thick liquid by elution with n-hexane-chloroform (95:5 v/v) mixture. In the last hydrolysed phenolic starting materials or their polymeric material recovered.

**Naphthalen-1-yl trichloroacetate** (1a): Colorless solid, mp 74 °C. 75 % yield. Gives positive Beilstein test for chlorine. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.03-8.00 (m, 1H), 7.93-7.90 (m, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.60-7.49 (m, 3H), 7.41 (d, J = 7.5 Hz, 1H) ppm; IR (KBr):  $v_{max}$  1772(s), 1632(m), 1596(m), 1504(m), 1462(m), 1389(s), 1222(s), 1069(s), 1027(s), 956(s), 872(s), 834(s), 756(s), 670(s) cm<sup>-1</sup>.

**Z-2,3-dichloro-but-2-enedioic acid dinaphthyl ester** (**2a**): White light weight foamy solid, mp 112 °C. 60 % yield. Gives positive Beilstein test for chlorine and KMnO<sub>4</sub> test for free double bond. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.98 (d, *J* = 7.9 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.54-7.39 (m, 3H), 7.33 (d, *J* = 7.4 Hz, 1H) ppm; <sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  159.8 (C), 145.8 (C), 134.7 (C), 131.4 (C), 128.0 (CH), 126.9 (CH), 126.7 (CH), 126.3 (C), 125.3 (CH), 120.8 (CH), 117.8 (CH) ppm; IR (KBr): *v*<sub>max</sub> 1756(s), 1731(s), 1633(m), 1593(s), 1507(m), 1391(s), 1257(s), 1157(s), 1080(s), 1036(s), 1011(s), 971(s), 813(m), 780(s) cm<sup>-1</sup>. HRMS [M+K]<sup>+</sup>: m/z cal. for C<sub>24</sub>H<sub>14</sub>Cl<sub>2</sub>O<sub>4</sub>K 474.9906, found 474.9928.

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- 22. CCDC No. of **Z-2a** is 619578.

# Highlights of the study:

- 1) The unusual stereoselective formation of Z-2,3-dichloro-but-2-enedioic acid diphenyl ester.
- 2) Thermodynamically stable E-isomer is predominated by kinetically controlled Z-isomer.
- 3) The products were successfully characterized by IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and HRMS data.
- 4) The stereochemistry of **Z-2a** was supported by the X-ray crystallographic data of Z-2,3-dichloro-but-2-enedioic acid dinaphthyl ester.
- 5) The stability of **Z-2a** was interpreted by Hirshfeld surface analysis and DFT at B3LYP/6-311G(d,p) level of theory.

Thank You,

Yours truly, Ram Kumar Tittal