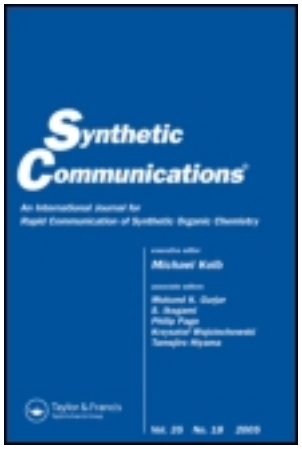

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Synthesis and Structure of Novel 1-Aryl-4,4,4-trichloro-1,3-butanediones

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SYNTHESIS AND STRUCTURE OF NOVEL 1-ARYL-4,4,4-TRICHLORO-1,3-BUTANEDIONES

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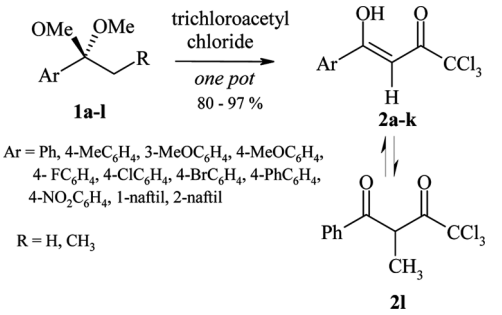
GRAPHICAL ABSTRACT



Abstract *Novel 1-aryl-4,4,4-trichloro-1,3-butanediones in good yields (80–97%) were synthesized in one pot through acetal acylation with trichloroacetyl chloride followed by acid hydrolysis. Structures of all compounds were elucidated by elemental analysis, mass spectrometry, and* $^{1}H/^{13}C$ *nuclear magnetic resonance (NMR) measurements. The* $^{1}H/^{13}C$ *NMR data showed that trichloromethyl-β-diketones* ***2a–k*** *in solution are predominantly ketoenol. However, the spectroscopic data from 4,4,4-trichloro-2-methyl-1-phenyl-1,3-butabedione (****2l****) with methyl substituent between carbonyls showed a bias toward the diketo form in solution. X-ray diffraction of monocrystals from* ***2g*** *and* ***2i*** *showed that these compounds are* cis*-ketoenol tautomers.*

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Keywords Acetal acylation; β-diketones; keto–enol equilibrium; trichloromethyl-β-diketones

INTRODUCTION

1,3-Diketones have interesting properties and have been widely studied both experimentally and theoretically because they are important organic reagents.[1–3]

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They are extensively used as versatile heterocyclic precursors[4–6] and chelating reagents for metal ions.[7–9] Many studies have reported the synthesis of 1,3-diketones.[10–12] The most common method employs the Claisen condensation of ketone enolates and an ester.[2,13–16] However, only a limited number of procedures for this method has been reported: 1,3-diketones synthesized from metal enolate acylation show poor chemoselectivity because their α-hydrogens are more acidic than those of the starting ketones.[17] In addition, the alkaline medium in metal enolate acylation limits the scope to unreactive alkali sidechains for the resultant 1,3-diketones. Because of the importance of this class of compound, we have applied the acetal acylation method to C-C bond formation in a β-alkoxyvinyl trihalomethyl ketone building block and have been studying hydrolysis to the respective β-dicarbonyl derivatives.[18,19] As a result, we have developed a convenient procedure for the synthesis of novel trichloromethyl-β-diketones. Although we previously demonstrated the synthesis of trichloroacetyl-cycloalkanones and 4,4,4-trichloro-1-heteroaryl-1,3-butanediones, a review of the literature on the trichloromethyl-β-diketones revealed that they are still uncommon. At the same time, 1-aryl-4,4,4-trifluoro-1,3-butanediones have been widely used for the synthesis of coordination complexes[20–22] and trifluoromethylated heterocyclic compounds.[23,24]

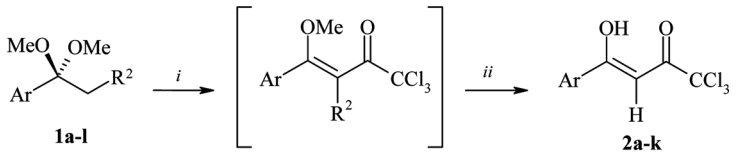
Based on our previous experience, we continued our search for new trichloromethyl containing β-diketones that can be used in coordination chemistry and organic synthesis. Herein, we report the synthesis and structure of novel 1-aryl-4,4,4-trichloro-1,3-butanediones, as well as their direction of enolization.

RESULTS AND DISCUSSION

The 1-aryl-1,1-dimethoxyethanes **1a–k** and 1,1-dimethoxy-1-phenyl-propane **1l** were prepared using a previously reported procedure.[18] Acetals **1a–l** reacted with trichloroacetyl chloride in pyridine without solvent. Acetal acylation and subsequent hydrolysis of the β-alkoxyvinyl trichloromethyl ketone were carried out in one reaction (Scheme 1). Hydrolysis was performed in 1mol L^{-1} sulfuric acid solution for 2h at room temperature. The diketones **2a–l** were obtained as crystalline solids, whose colors varied from white to yellow depending on the aryl substituent (see the experimental section).

The $^{1}H/^{13}C$ nuclear magnetic resonance (NMR) spectra of all products showed signals attributed to trichloromethyl-β-diketones. β-Diketones have two forms, the keto–enol and diketo forms. The NMR analyses of 1-aryl-4,4,4-trichloro-1,3-butanediones (**2**) revealed that, except for **2l**, they were all in enolic form. An important feature of the ^{1}H NMR spectra of compounds **2a–k** was the presence of a broad singlet in the region of 14.0 ppm, resulting from the enolic hydrogen. Another feature was the presence of a singlet in the region of 6.7–6.8 ppm from vinylic hydrogen predominantly in the *keto–enol* form. However, for compound **2l**, the ^{1}H NMR spectrum showed only signals of diketone form as a quartet at 4.0 ppm from the coupling of the H2 with the α-methyl substituent ($J_{HH} = 7$ Hz) and the respective methyl as a doublet at 1.63 ppm. Thus, **2l** was assigned as entirely diketo in form.

The $^{13}C(H)$ NMR spectra for compounds **2a–k** showed a signal at 89–95 ppm, typical of vinylic C-sp^2 in the *keto–enol* form. For compound **2l**, a signal in the range

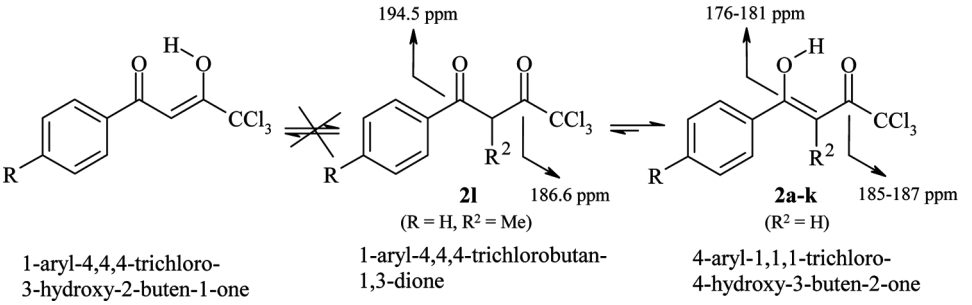


	a	b	c	d	e	f
Ar	Ph	4-MeC_6H_4	3-$MeOC_6H_4$	4-$MeOC_6H_4$	4-FC_6H_4	4-ClC_6H_4
R^2	H	H	H	H	H	H

	g	h	i	j	k	l
Ar	4-BrC_6H_4	4-PhC_6H_4	4-$NO_2C_6H_4$	1-naphtyl	2-naphtyl	Ph
R^2	H	H	H	H	H	Me

Scheme 1. Synthesis of 1-aryl-4,4,4-trichloro-1,3-butanediones.

of 47 ppm for C-α confirmed the diketo structure (e.g., compare Figs. S5 and S32, available online in the supplementary information). The ^{13}C NMR data for carbonyl carbons showed chemical shifts for carbonyls near the trichloromethyl group (C2) for products **2a–l**, at around 185–187 ppm. However, the chemical shifts from carbonyl carbons near the aromatic substituent were considerably different between *cis*-keto–enols **2a–k** at around 176–181ppm and diketo **2l**, which showed a chemical shift at 194 ppm. Based on these data, the *cis*-keto–enols **2a–k** were assigned the structure 4-aryl-1,1,1-trichloro-4-hydroxy-3-buten-2-one, because no signals were observed for diketo 1-aryl-4,4,4-trichlorobutan-1,3-dione or *cis*-ketoenol 1-aryl-4,4,4-trichloro-3-hydroxy-2-buten-1-one (Scheme 2).



Scheme 2. Tautomeric equilibrium for β-diketones **2a–l**.

Compounds **2g** and **2i** were subjected to single-crystal x-ray analysis (Tables 1, 2, and 3), which confirmed the solid-state molecular structure *cis*-keto–enol proposed for compounds **2a–k** with a *Z*-configuration on the alkene moiety and the intramolecular hydrogen bond O3—H1−N1 (Fig. 1). In the solid state, the enolenone fragments [O(21) = C(2)–C(3) = C(4)–O(41)] were nearly planar, with root mean square (rms) deviations from the plane of 0.0056 and 0.0024 Å for compounds **2g** and **2i**, respectively. The C(2) atom deviated most, by −0.0069 (17) and −0.0035 (12) Å for **2g** and **2i**, respectively. Planarity was confirmed by the torsion angles O(21)=C(2)–C(3)=C(4), which were −0.8(4)° and −0.9(3)° in **2g** and **2i**, respectively, and the torsion angles C(2)–C(3) = C(4)–O(41), which were −0.6(4)° and −0.7(3)° in

Table 1. General and crystal data and summary of intensity data collection and structure refinement for compounds **2g** and **2i**

Compound	**2g**	**2i**
Formula	$C_{10}H_6BrCl_3O_2$	$C_{10}H_6Cl_3NO_4$
Mr	344.41	310.51
CCDC[a]	733496	733495
Temperature (K)	302(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space Group	P2(1)/n	P21/c
Unit cell parameters		
a (Å)	13.5020 (11)	6.7037 (14)
b (Å)	6.7499 (5)	16.899 (4)
c (Å)	13.7410 (11)	11.470 (3)
α (°)	90	90
β (°)	91.149 (5)	102.403 (8)
γ (°)	90	90
V (Å^3)	1252.06 (17)	1269.0 (5)
Z	4	4
Density (calculated) (g cm^{-3})	1.827	1.625
Absorption coefficient (mm^{-1})	3.903	0.726
F (000)	672	624
Crystal size (mm)	0.58 × 0.55 × 0.41	0.75 × 0.25 × 0.18
θ range for data collection (°)	2.97 to 31.58	2.18 to 31.03
h,*k*,*l* range	−19 ≤ h ≤ 19	−9 ≤ h ≤ 9
	−9 ≤ k ≤ 9	−24 ≤ k ≤ 24
	−20 ≤ l ≤ 15	−16 ≤ l ≤ 16
T_{max}/T_{min}	1.0000/0.5080	0.89358/0.74739
Reflections collected	17965	15927
Independent reflections	4080 [R(int) = 0.0841]	4041 [R(int) = 0.0343]
Data/restraints/parameters	4080/0/145	4041/0/163
Absorption correction	Gaussian	Gaussian
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Final R indices [I > 2σ(I)]	R1 = 0.0402, wR2 = 0.1054	R1 = 0.0452, wR2 = 0.1083
R indices (all data)	R1 = 0.0934, wR2 = 0.1147	R1 = 0.0828, wR2 = 0.1319
Goodness of fit on F^2	0.855	1.048
Largest diff. peak and hole (eÅ^{-3})	0.756 and −0.697	0.441 and −0.467

[a]CCDC 733495 (**2i**) and 733496 (**2g**) contain the supplementary crystallographic data for this paper. These data are available free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting CCDC.

Table 2. Select geometric parameters (Å, °) obtained experimentally for **2g** and **2i**

	2g	**2i**
Bond lengths (Å)		
C(1)–C(2)	1.558(4)	1.548(3)
C(2)–C(3)	1.416(3)	1.433(3)
C(3)–C(4)	1.358(4)	1.359(3)
C(2)-O(21)	1.222(3)	1.224(2)
C(4)-O(41)	1.328(3)	1.326(2)
C(1)-Cl(1)	1.756(3)	1.766(2)
C(4)–C(41)	1.477(3)	1.482(3)
C(44)–Br	1.902(3)	—
C(44)–N(44)	—	1.486(3)
N(44)–O(45)	—	1.212(3)
N(44)–O(46)	—	1.215(3)
Bond angles (°)		
C(1)–C(2)–C(3)	117.9(2)	118.19(17)
C(2)–C(3)–C(4)	120.9(2)	120.20(19)
O(21)–C(2)–C(3)	125.2(2)	124.01(19)
C(3)–C(4)–O(41)	122.9(2)	122.80(18)
C(3)–C(4)–C(41)	124.5(2)	124.79(19)
O(21)–C(2)–C(1)	116.9(2)	117.80(17)
O(41)–C(4)–C(41)	112.6(2)	112.41(18)
C(43)–C(44)–Br	119.4(2)	—
C(43)–C(44)–N(44)	–	118.7(2)
C(44)-N(44)–O(45)	—	118.4(3)
O(45)–N(44)–O(46)	—	124.0(2)

2g and **2i**, respectively. For C(1)=C(2)=C(3)=C(4), the enolenone had a torsion angle of 179.9(2)° in **2g** and 179.41(19)° in **2i**, indicating that the C(1) atom (a member of the trichlormethyl group) was almost in the same plane as the enaminone fragment. The geometry of the enolenone system was similar to that reported in the literature.[25] The least-squares plane angles between the enolenone and the phenyl group were 11.15(14)° and 4.23(12)° for **2g** and **2i**, respectively. The interatomic distances between the proton acceptor and proton donor oxygen atoms, O(41)···O(21), were 2.611(3) and 2.576(2) Å in molecules **2g** and **2i**, respectively, confirming the presence of the intramolecular hydrogen bond.[26]

CONCLUSION

In conclusion, our methodology can be used to prepare various 1-aryl-4,4,4-trichloro-1,3-butanediones. To the best of our knowledge, this series of compounds

Table 3. Hydrogen bonding geometry in **2g** and **2i** (Å, °)

Compound	D-H···A	D-H	H···A	D···A	D-H···A	Symmetry codes
2g	O(41)–H(41)···O(21)	0.82	1.90	2.611(3)	145.0	
	O(41)–H(41)···O(21)	0.82	2.35	2.981(3)	134.7	$-x+1, -y, -z+1$
2i	O(41)–H(41)···O(21)	0.82	1.86	2.576(2)	145.8	
	O(41)–H(41)···O(21)	0.82	2.36	2.999(2)	135.7	$-x+3, -y+1, -z+2$

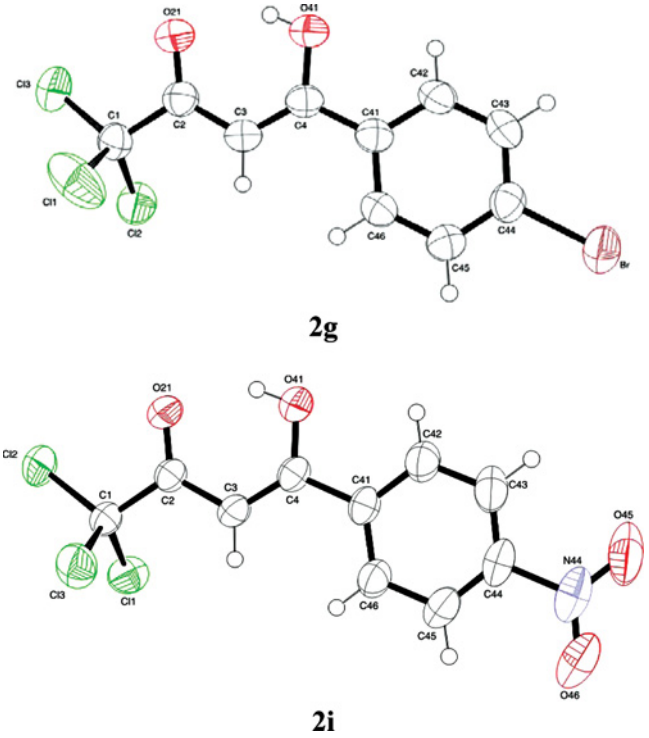


Figure 1. Molecular structure of compounds **2g** and **2i**, with ellipsoids for nonhydrogen atoms, drawn at the 50% probability level. H atoms are drawn as arbitrary spheres. (Figure is provided in color online.)

has never been reported, with the exception of compounds **2a** and **2l**.[19] Ten novel trichloromethyl-1,3-diketones were synthesized in good yields. The β-trichloromethyl-β-diketones **2a–k** were in *cis*-keto–enol form in solution, as revealed by NMR spectroscopy. In contrast, the novel trichloromethyl-β-diketone **2l** was found only in the diketo form in solution. Based on the NMR and x-ray data, the different aryl substituents did not affect keto–enol equilibrium in the 1-aryl-4,4,4-trichloro-1,3-butanediones. The x-ray data revealed that trichloromethyl-β-diketones are *cis*-keto–enols in the solid state too.

EXPERIMENTAL

The synthesis of 1-aryl-1,1-dimethoxyacetals has been reported elsewhere.[20] Trichloroacetyl chloride and pyridine were used as obtained from commercial suppliers; chloroform was purified before use. A $1\,mol\,L^{-1}$ solution of H_2SO_4 was prepared by dissolving 98% H_2SO_4 in 100 mL distilled water. The yields of the isolated compounds were measured. Melting points were determined using a Reichert Thermovar apparatus and were uncorrected. The ^1H and ^{13}C spectra were recorded at 298 K on a Bruker DPX 400 spectrometer (^1H at 400.13 MHz, ^{13}C at 100.63 MHz) with a digital resolution of ±0.01 ppm. All chemical shifts were expressed in parts per

million (ppm), and ^{1}H and ^{13}C were reported with respect to internal tetramethylsilane (TMS). Solutions of 0.1mol L^{-1} $CDCl_3$ were used. H-H and C-F coupling constants were measured in hertz (Hz). Mass spectra were registered using an HP 5973 mass selective detector connected to an HP 6890 GC and interfaced with a Pentium PC. The GC was equipped with a split–splitless injector, auto-sampler, and cross-linked HP-5 capillary column (30 m, 0.32mm internal diameter), and helium was used as the carrier. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer (São Paulo University, São Paulo, Brazil). Diffraction measurements were made using graphite-monochromatized Mo Kα radiation with $\lambda = 0.71073$ Å on a Bruker SMART CCD diffractometer.[27] The structures were solved by direct methods using the SHELXS-97 program,[28] and refined on F^2 using a full-matrix least-squares package by SHELXL97.[29] Absorption correction was performed using Gaussian methods.[30] Anisotropic displacement parameters for nonhydrogen atoms were applied. The hydrogen atoms were placed at calculated positions of 0.96 Å (methyl CH3), 0.97 Å (methylene CH_2), 0.98 Å (methine CH), and 0.93 Å (aromatic CH) using a riding model. Hydrogen isotropic thermal parameters were kept equal to Uiso(H) $= xU$eq (carrier C atom), with $x = 1.5$ for methyl groups and $x = 1.2$ otherwise. The valence angles C-C-H and H-C-H of the methyl groups were set to 109.5°, and H atoms were allowed to rotate around the C-C bond. Molecular graphics were prepared using ORTEP3 for Windows.[31]

General Procedure for the Synthesis of 1-Aryl-4,4,4-trichlorobutan-1,3-dione

A solution of trichloroacetyl chloride (7.0 mL, 60 mmol) in chloroform (20 mL) was added dropwise to a stirred solution of 1-aryl-1,1-dimethoxyethanes **1a–k,** pyridine (5.2 mL, 60 mmol), and 1,1-dimethoxy-1-phenylpropane **1l** (30 mmol) in chloroform (50 mL) kept at 0 °C. The mixture was stirred for 8 h at 0–25 °C, quenched with a 2 mol L^{-1} sulfuric acid solution (30 mL), and then stirred for 2h at 40 °C. The organic layer was dried with sodium sulfate, the solvent was evaporated, and products were obtained with good purity. The crystalline compounds were purified by recrystallization from hexane.

Data

1,1,1-Trichloro-1-hydroxy-4-phenyl-1-buten-2-one (2a). Yield 85%, oil; IR (film) ν_{max}/cm^{-1}: 3400 (OH), 3089 (C=CH), 2926, 2878 (C=C), 1592, 1568 (O=C-C=C), 1493, 1455 (C-O), 1255, 1081; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.8 (s, 1H, H3), 7.5 (m, 2H, Ph), 7.6 (m, 1H, Ph), 7.9 (m, 2H, Ph), 14.3 (s, br, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.2 (C2), 180.8 (C4), 133.4, 132.5, 128.9, 127.2 (Ph), 95.0 (C1), 89.6 (C3); MS (70 eV) m/z 268 ($M^+ + 4$, 4), 266 ($M^+ + 2$, 12), 264 (M^+, 12), 203 (16), 201 (25), 147 (100), 105 (100), 77 (100), 69 (100). Anal. calcd. for $C_{10}H_7Cl_3O_2$: C, 45.24; H, 2.66. Found: C, 45.27; H, 2.68.

1,1,1-Trichloro-4-hydroxy-4-(4-toluil)-1-buten-2-one (2b). Yield 88%, mp: 55–57 °C; IR (KBr) ν_{max}/cm^{-1}: 3447 (OH), 3093 (C=CH), 2930, 2885 (C=C), 1611, 1585 (O=C-C=C), 1561, 1507 (C-O), 1434, 1238, 1121; ^{1}H NMR (400 MHz, $CDCl_3$):

δ 2.4 (s, 3H, 4-CH_3), 6.7 (s, 1H, H3), 7.3 (m, 2H, Ar), 7.8 (m, 2H, Ar), 14.4 (s, br, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.9 (C2), 181.2 (C4), 144.5, 129.7, 129.6, 127.2 (Ar), 99.9 (C1), 89.0 (C3), 21.7 (4-CH_3); MS (70 eV) m/z 282 ($M^+ + 2$, 4), 280 (M^+, 4), 217 (10), 215 (12), 161 (100), 119 (65), 91 (30), 69 (50). Anal. calcd. for $C_{11}H_9Cl_3O_2$: C, 47.26; H, 3.25. Found: C, 47.5; H, 3.4.

1,1,1-Trichloro-4-hydroxy-4-(3-methoxyphenyl)-1-buten-2-one (2c). Yield 85%, mp: 41–43 °C; IR (KBr) ν_{max}/cm^{-1}: 3445 (OH), 3065, 3015 (C=CH), 2955 (C=C), 1760, 1670 (O=C-C=C), 1596, 1577 (C-O), 1451, 1353, 1279, 1214, 1100, 972; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.88 (s, 3H, 3-OCH_3), 6.79 (s, 1H, H3), 7.13 (m, 1H, Ar), 7.4 (m, 1H, Ar), 7.45 (m, 1H, Ar), 7.50 (m, 1H, Ar) 14.8 (s, br, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.1 (C2), 180.7 (C4), 159.9, 133.9, 129.9, 119.6, 119.2, 112.2 (Ar), 94.9 (C1), 89.9 (C3), 55.5 (3-OCH_3); MS (70 eV) m/z 298 ($M^+ + 4$, 11), 296 ($M^+ + 2$, 28), 294 (M^+, 35), 233 (10), 231 (18), 177 (100), 135 (100), 109 (70), 92 (20), 69 (100). Anal. calcd. for $C_{11}H_9Cl_3O_3$: C, 44.70; H, 3.07. Found: C, 44.50; H, 3.0.

1,1,1-Trichloro-4-hydroxy-4-(4-methoxyphenyl)-1-buten-2-one (2d). Yield 82%, mp: 58–60 °C; IR (KBr) ν_{max}/cm^{-1}: 3437 (OH), 3067 (C=CH), 2936, 2840 (C=C), 1602, 1599 (O=C-C=C), 1562, 1511 (C-O), 1465, 1309, 1251, 1177, 1026; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.89 (s, 3H, 4-OCH_3), 6.75 (s, 1H, H3), 6.98 (m, 2H, Ar), 7.92 (m, 2H, Ar), 14.6 (s, br, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.4 (C2), 181.2 (C4), 164.0, 129.4, 124.7, 114.3 (Ar), 95.0 (C1), 88.3 (C3), 55.5 (4-OCH_3); MS (70 eV) m/z 298 ($M^+ + 4$, 4), 296 ($M^+ + 2$, 10), 294 (M^+, 10), 233 (10), 231 (15), 177 (100), 135 (85), 109 (20), 92 (20), 69 (30). Anal. calcd. for $C_{11}H_9Cl_3O_3$: C, 44.70; H, 3.07. Found: C, 44.85; H, 3.1.

1,1,1-Trichloro-4-(4-fluorophenyl)-4-hydroxy-1-buten-2-one (2e). Yield 82%, mp: 75–76 °C; IR (KBr) ν_{max}/cm^{-1}: 3424 (OH), 3072 (C=CH), 2966, (C=C), 1594, 1576 (O=C-C=C), 1508, 1437 (C-O), 1437, 1330, 1230, 1170, 1076; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.7 (s, 1H, H3), 7.2 (m, 2H, Ar), 7.9 (m, 2H, Ar), 14.3 (s, br, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.1 (C2), 179.7 (C4), 165.9 $J_{CF} = 254$, 129.7 $J_{CF} = 9.2$, 128.7 $J_{CF} = 3.0$, 116.2 $J_{CF} = 21.6$ (Ar), 94.9 (C1), 89.3 (C3); MS (70 eV) m/z 284 ($M^+ + 2$, 2), 282 (M^+, 2), 221 (5), 219 (12), 165 (100), 123 (70), 95 (30), 69 (35). Anal. calcd. for $C_{10}H_6Cl_3FO_2$: C, 42.37; H, 2.13. Found: C, 42.2; H, 2.1.

1,1,1-Trichloro-4-(4-chlorophenyl)-1-buten-2-one (2f). Yield 86%, mp: 69–71 °C; IR (KBr) ν_{max}/cm^{-1}: 3422 (OH), 3052 (C=CH), 2960, (C=C), 1646, 1586, 1583, 1558 (O=C-C=C), 1486, 1427 (C-O), 1319, 1212, 1092, 1074, 1011; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.7 (s, 1H, H3), 7.5 (m, 2H, Ar), 7.8 (m, 2H, Ar), 14.2 (s, br, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.3 (C2), 179.3 (C4), 139.7, 130.9, 129.3, 128.4 (Ar), 94.9 (C1), 89.7 (C3); MS (70 eV) m/z 302 ($M^+ + 4$, 4), 300 (M^+, 6), 298 (4), 239 (2), 237 (5), 235 (8), 183 (25), 181 (100), 139 (70), 111 (20), 69 (35). Anal. calcd. for $C_{10}H_6Cl_4O_2$: C, 40.04; H, 2.02. Found: C, 40.1; H, 2.0.

4-(4-Bromophenyl)-1,1,1-trichloro-4-hydroxy-1-buten-2-one (2g). Yield 83%, mp: 65–67 °C; IR (KBr) ν_{max}/cm^{-1}: 3422 (OH), 1702, 1646, 1589, 1556 (O=C-C=C), 1486, 1430 (C-O), 1211, 1186, 1152, 1076, 1011; ^{1}H NMR

(400 MHz, $CDCl_3$): δ 6.7 (s, 1H, H3), 7.6 (m, 2H, Ar), 7.8 (m, 2H, Ar), 14.2 (s, br, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.3 (C2), 179.4 (C4), 132.2, 131.3, 128.5, 128.3 (Ar), 94.8 (C1), 89.7 (C3); MS (70 eV) m/z 348 ($M^+ + 4$, 1), 346 ($M^+ + 2$, 5), 344 (M^+, 6), 342 (4), 283 (4), 281 (10), 227 (95), 225 (100), 185 (60), 183 (65), 157 (20), 155 (18), 109 (20), 89 (15), 69 (70). Anal. calcd. for $C_{10}H_6BrCl_3O_2$: C, 34.87; H, 1.76. Found: C, 34.85; H, 1.90.

4,4,4-Trichloro-4-hydroxy-4-(4,4′-biphenyl)-1-buten-2-one (2h). Yield 76%, mp: 74–76 °C; IR (KBr) ν_{max}/cm^{-1}: 3427 (OH), 3058, 3031 (C=CH), 2986, 2959 (C=C), 1680, 1603, 1597, 1589 (O=C-C=C), 1553, 1513, 1485 (C-O), 1423, 1402, 1262, 1195, 1120, 1078; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85 (s, 1H, H3), 7.45–7.50 (m, 3H, Ph), 7.62–7.67 (m, 2H, Ph), 7.70–7.75 (m, 2H, Ar), 7.99–8.10 (m, 2H, Ar), 14.3 (s, br, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.1 (C2), 180.5 (C4), 146.1, 139.5, 131.2, 129.0, 128.4, 127.7, 127.5, 127.2 (Ar), 95.0 (C1), 89.5 (C3); MS (70 eV) m/z 298 ($M^+ + 4$, 4), 296 ($M^+ + 2$, 10), 294 (M^+, 10), 233 (10), 231 (15), 177 (100), 135 (85), 109 (20), 92 (20), 69(30). Anal. calcd. for $C_{16}H_{11}Cl_3O_2$: C, 56.25; H, 3.25. Found: C, 56.5; H, 3.5.

1,1,1-Trichloro-4-hydroxy-4-(4-nitrophenyl)-1-buten-2-one (2i). Yield 78%, mp: 79–82 °C; IR (KBr) ν_{max}/cm^{-1}: 3442 (OH), 3127 (C=CH), 2986, 2935 (C=C), 1652, 1605, 1573 (O=C-C=C), 1522, 1490 (C-O), 1426, 1341, 1320, 1213, 1153, 1073; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.7 (s, 1H, H3), 8.0 (m, 2H, Ar), 8.2 (m, 2H, Ar), 13.8 (s, br, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.8 (C2), 176.6 (C4), 150.3, 138.0, 128.0, 124.0 (Ar), 94.7 (C1), 91.6 (C3); MS (70 eV) m/z 311 ($M^+ + 2$, <1), 309 (M^+, <1), 248 (2), 246 (5), 192 (100), 150 (40), 104 (15), 89 (10), 69(18). Anal. calcd. for $C_{10}H_6Cl_3NO_4$: C, 38.68; H, 1.95. Found: C, 38.8; H, 2.0.

1,1,1-Trichloro-4-hydroxy-4-(1-naftyl)-1-buten-2-one (2j). Yield 82%, mp: 74–75 °C; IR (KBr) ν_{max}/cm^{-1}: 3451 (OH), 3029, 3040 (C=CH), 1621, 1579 (C=O), 1394, 1366, 1325, 1245, 1188, 1145, 839, 779; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.65 (s, 1H, H3), 7.45–7.60 (m, 4H, Ar), 7.77 (m, 1H, Ar), 7.88 (m, 1H, Ar), 7.98 (m, 1H, Ar), 8.37 (m, 1H, Ar), 14.3 (s, br, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.7 (C2), 184 (C4), 133.8, 132.8, 131.6, 130, 128.7, 127.9, 127.7, 126.6, 125.1, 124.8 (Ar), 95.0 (C3), 94.9 (CCl_3); MS (70 eV) m/z 318 ($M^+ + 4$, 6), 316 ($M^+ + 2$, 15), 314 (M^+, 17), 210 (20), 197 (100), 155 (57), 127 (47), 69 (22). Anal. calcd. for $C_{14}H_9Cl_3O_2$: C, 53.28; H, 2.87. Found: C, 53.5; H, 2.90.

1,1,1-Trichloro-4-hydroxy-4-(2-naftyl)-1-buten-2-one (2k). Yield 86%, mp: 79–81 °C; IR (KBr) ν_{max}/cm^{-1}: 3451 (OH), 3109 (C=CH), 1618, 1600, 1584, 1563 (C=O), 1404, 1386, 1398, 1337, 1265, 1190, 1142, 1132, 837, 822, 777, 766; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97 (s, 1H, H3), 7.63 (m, 2H, Ar), 7.91 (m, 1H, Ar), 7.94 (m, 1H, Ar), 7.99 (m, 1H, Ar), 8.54 (m, 1H, Ar), 14.4 (s, br, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.1 (C2), 180.7 (C4), 135.6, 132.6, 129.7, 129.5, 128.8, 128.7, 127.8, 127.1, 122.7 (Ar), 95.1 (C1), 89.9 (C3). Anal. calcd. for $C_{14}H_9Cl_3O_2$: C, 53.28; H, 2.87. Found: C, 53.5; H, 2.90.

4,4,4-Trichloro-2-methyl-1-phenylbutan-1,3-dione (2l). Yield 90%, mp: 97–98 °C; IR (KBr) ν_{max}/cm^{-1}: 3059 (C=CH), 2983, 2935 (C=C), 1810 (C=O),

1715 (C=O), 1642, 1495 (C-C), 1398, 1325, 1260, 1239, 1150, 1092, 1015; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.63 (d, J_{HH} 7.2Hz, 3H, CH_3), 5.41 (q, J_{HH} 7.2Hz, 1H, H2), 7.52 (m, 2H, Ph), 7.63 (m, 1H, Ph), 8.05 (m, 2H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.5 (C2), 186.6 (C4), 134.2, 134.0, 129.1, 128.8, (Ar), 95.8 (CCl_3), 47.3 (C3), 16.6 (CH_3); MS (70 eV) m/z 161 (13), 105 (100), 77 (30), 51 (8). Anal. calcd. for $C_{11}H_9Cl_3O_2$: C, 47.26; H, 3.25. Found: C, 47.5; H, 3.4.

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