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First synthesis of 1-aryl-4,4-dichlorobut-3-en-1-ones. The electrochemical reduction of 1-aryl-4,4,4-trichlorobut-2-en-1-ones as a key step

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Abstract—The first method for the synthesis of 1-aryl-4,4-dichlorobut-3-en-1-ones is reported. Treatment of acetophenones with anhydrous chloral leads to 1-aryl-4,4,4-trichloro-3-hydroxybutan-1-ones in near quantitative yields. These compounds were efficiently dehydrated with either sulfuric or *p*-toluenesulfonic acid to give 1-aryl-4,4,4-trichlorobut-2-en-1-ones, which were selectively converted to the title compounds in fair to quantitative yields by electrochemical reduction. The X-ray crystallographic structure of 4,4-dichloro-1-(4-methoxyphenyl)but-3-en-1-one has been determined. The preferential formation of β,γ-unsaturated ketones with total exclusion of the corresponding α,β-unsaturated isomers has been discussed with the aid of HF and B3LYP density functional theory methods.

1. Introduction

The synthesis of β,γ-unsaturated ketones has received considerable attention since these have significant synthetic utility.[1] Owing to a notable proclivity of these compounds to undergo isomerization towards conjugated α,β-unsaturated isomers,[2] mild experimental conditions and exclusion of strong acidic or basic catalysts are considered essential factors in developing fine preparative methods on this topic. The most usual synthetic procedures for β,γ-unsaturated ketones include acylation of allylic organometallics of a variety of elements,[2,3] whereas reaction between aldehydes and some of these organometallic compounds followed by oxidation of the corresponding allyl alcohols is also an exploitable preparative process.[4] Some other less general reactions yielding β,γ-unsaturated ketones have also been described.[5]

Chloral is an inexpensive multipurpose starting material for organic synthesis.[6] Direct reactions of chloral with certain compounds can provide derivatives bearing a trichloromethyl group of a high electrosynthetic potential. In this reaction we recognized the starting point of different routes for preparing new heterocyclic compounds and synthetic intermediates of significant interest.[7]

As a further result of working on this project, we recently communicated the first synthesis of 3-aryl-5-dichloromethyl-2-pyrazolines based on using 1-aryl-4,4-dichlorobut-3-en-1-ones **5** as key intermediates.[8] We have also found that **5** are able to provide novel 5-dichloromethylisoxazolines in good yields.[9] In these cases compounds **5** exhibit a chemical behaviour of a significant preparative interest since reactions with dinucleophilic agents can promote cyclization processes associated with a simultaneous generation of dichloromethyl groups. In this manner, pre-chlorinated synthons derived from chloral are highly effective in overcoming severe obstacles of chemical incompatibility caused by the indiscriminate action of the reagents most used to generate dichloromethyl groups.[10]

Given the synthetic interest of compounds **5**, we now report full details of this highly efficient synthetic approach as well as spectral and X-ray crystallographic structural data for this class of substances.

An optimal reaction route for preparing products **5** has been established through a sequence of chemical and electrochemical steps, as shown in Scheme 1. Preparations of chloral-acetophenones **2** have been described by arylation

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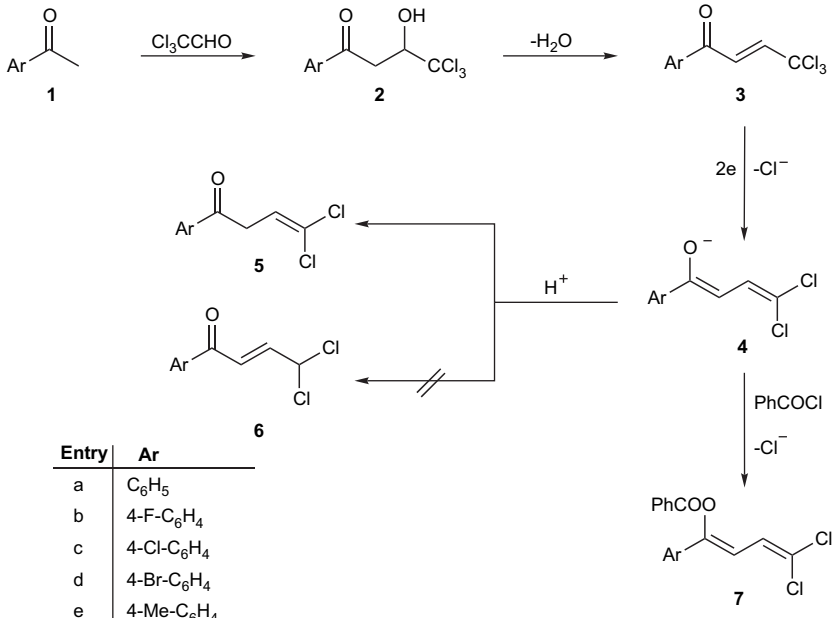

Entry	Ar
a	C_6H_5
b	4-F-C_6H_4
c	4-Cl-C_6H_4
d	4-Br-C_6H_4
e	4-Me-C_6H_4
f	4-MeOC_6H_4
g	4-$NO_2C_6H_4$
h	2,4-$Me_2C_6H_3$
i	4-Ph-C_6H_4
j	2-$C_{10}H_7$

Scheme 1.

processes involving ring opening of β-trichloromethyl-β-propiolactones,[11] and by reaction of chloral with acetophenone derivatives[12] such as imines and trimethylsilyl enol ethers. A few old examples of direct reactions between chloral and acetophenones yielding products **2** were reported[13] but they omit fundamental details such as experimental conditions, yields and physical and analytical properties for these products. For this reason, precise preparative experimental conditions and physical and analytical data for these compounds have been included here as Supplementary data.

2. Results and discussion

Direct preparation of chloralacetophenones **2** was attempted by reaction between acetophenones **1** and chloral hydrate but these processes yielded small amounts of reaction products that were isolated and identified as the desired compounds **2**. However, much more efficient were the reactions with anhydrous chloral, which in general, provided fair to high yields (70–89%). In order to attempt a straightforward generation of the targeted compounds **5** from compounds **2** they were treated with zinc metal in hot acetic acid. The formation of **5** was found to be unsatisfactory due to a conjunction of adverse factors such as the requirement of large excess of reducing reagent, low yields, incompatibility with the presence of nitro groups and a remarkable difficulty in the isolation and purification of products. It should also be noted that the electrochemical reduction of compounds **2** failed completely, leading to the formation of complex mixtures of unidentifiable products instead of products **5**. In the search for an effective method for preparing the desired compounds we had successful results on the basis of highly selective electrochemical reductions of intermediates **3**.

In order to prepare 1-aryl-4,4,4-trichlorobut-2-en-1-ones **3**, chloralacetophenones **2** were dehydrated with either thionyl chloride or phosphorus pentoxide. These reactions occurred with moderate efficiency. Their results were compared with those arising from dehydration promoted by acidic catalysis with either sulfuric or *p*-toluenesulfonic acids. These other processes, in general, were found to be much more efficient but in some cases yields were found to be remarkably dependent on the acidic reagent used. Results are given for the most proficient acid to provide each of the compounds **3**.

Cathodic reductions of solutions of compounds **3** in acetonitrile–acetic acid–lithium perchlorate at a mercury pool cathode were carried out under a constant potential. The electricity consumption was always 2 F/mol of **3**. At the end of the electrolyses, the catholyte solutions were checked by TLC and GC showing a complete transformation of starting materials to single products, which were easily isolated by evaporation of the solvent under reduced pressure, addition of the residue onto cold water and filtration of the precipitated solid. Highly pure products were isolated in this manner and were crystallized and identified by IR, MS, high field NMR spectroscopy and microanalyses as 1-aryl-4,4-dichlorobut-3-en-1-ones **5**. Yields were almost quantitative. Advantageously, these results were found to be reproducible by changing the cathodic material from mercury to graphite. Advantageously, it has been established that lithium perchlorate can be replaced by sodium tetrafluoroborate, leading to the same results. Worthy of note is

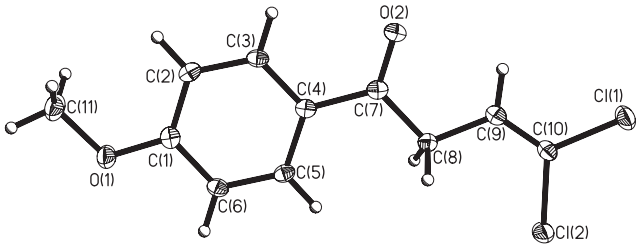

Figure 1. Molecular structure of **5f**, showing the crystallographic numbering system used.

the total selectivity of these electrochemical processes with the generation of conjugated isomers **6** being fully avoided.

Geometrical characteristics of compounds of type **5** were determined by X-ray crystallography of **5f**. The molecular structure found is illustrated in Figure 1. A noteworthy feature of this structure is its near planarity.

Concerning the electrogeneration of products **5** from compounds **3** (Scheme 1) it seems reasonable to postulate a two-electron transfer process leading to dienolates **4**, which undergo specific α-protonation to give the final products. An

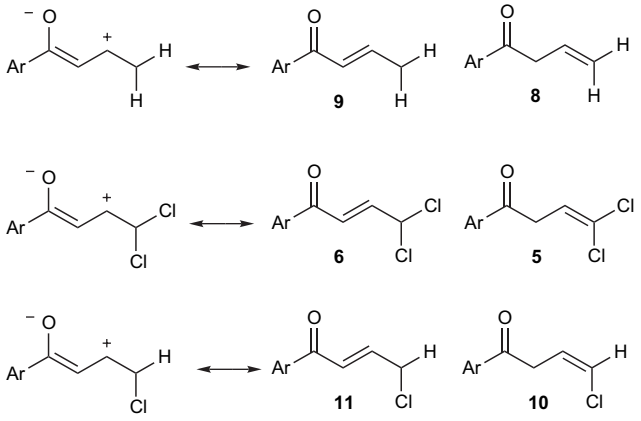

Figure 2. α,β-Unsaturated and β,γ-unsaturated isomeric ketone pairs.

evidence for the generation of species **4** was established by carrying out the cathodic reduction of **3d** in the presence of benzoyl chloride instead of acetic acid since the formation of the corresponding dienol benzoate **7c** in high yield instead of product **5c** occurred in this case. As far as we know there are no precedents for halogenated derivatives of types **5** and **7**.

It should be noted that the formation of products **5** can be explained by C-α protonation of intermediates **4** whereas conjugated products **6** would be originated in the case of C-γ protonation. However, all experiments led to the formation of non-conjugated ketones **5** with total exclusion of their conjugated isomers **6**. In view of these peculiar results, we focused interest on a comparative study concerning the relative stabilities of chlorinated and non-chlorinated series of analogous compounds (Fig. 2) by applying computational methods. With this purpose, these procedures were tested firstly by computing fully optimized geometries obtained by using HF and B3LYP density functional theory methods[16] and compared with X-ray structural data of **5f**. Table 1 shows selected bond lengths and bond angles of crystal and calculated structures at the B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) levels of theory. An excellent agreement can be appreciated since differences between bond lengths are lower than 0.03 Å, whereas between bond angle differences are less than 0.6°, which could be attributed to molecular distortion in the crystal structure forced by packing. As mentioned above, a peculiar feature of this structure is its near planarity. Interplanar angles are listed in Table 2, where angles between the reference plane C(1)–C(3)–C(5) and planes in this table are lower than 3.1°. Optimized structures at the B3LYP/6-31G(d), HF/6-31G(d) and HF/6-311+(d,p) have also been determined, and the results for bond lengths and bond angles are within ±0.01 Å and ±0.3° for the different models. Next, relative energies (ΔE_0) for isomeric ketone pairs were computed at the B3LYP/6-311++G(d,p)// B3LYP/6-31G(d) level of theory. The ΔE_0-values evidence that non-chlorinated α,β-unsaturated ketones **9** are notoriously more stable ($\Delta E_0 \approx 5.4$ kcal/mol) than their β,γ-unsaturated isomers **8** (Fig. 3, series A). The electronic effect exerted by the ring substituents over the corresponding energy differences seems to be of little importance.

Table 1. Selected bond lengths and bond angles of crystal and calculated structures in crystal structure of **5f** and their difference

Bond	Crystal structure (Å)	Calculated structure (Å)[a]	Δ (Å)	Calculated structure (Å)[b]	Δ (Å)
C(9)–C(10)	1.316(2)	1.327	−0.011	1.312	0.004
C(8)–C(9)	1.497(2)	1.499	−0.002	1.503	−0.006
C(7)–C(8)	1.520(2)	1.532	−0.012	1.523	−0.003
C(4)–C(7)	1.487(2)	1.489	−0.002	1.492	−0.005
O(2)–C(7)	1.221(2)	1.218	0.003	1.192	0.029
Cl(2)–C(10)	1.726(2)	1.750	−0.024	1.735	−0.009
Cl(l)–C(10)	1.732(2)	1.745	−0.013	1.731	0.001
Angle	**Crystal structure (°)**	**Calculated structure (°)[a]**	**Δ (°)**	**Calculated structure (°)[b]**	**Δ (°)**
O(2)–C(7)–C(4)	120.80(13)	121.28	−0.48	121.07	−0.27
O(2)–C(7)–C(8)	121.16(13)	120.70	0.46	120.94	0.22
C(4)–C(7)–C(8)	118.03(12)	118.03	0.00	118.00	0.03
C(9)–C(8)–C(7)	112.24(12)	112.63	−0.39	112.81	−0.57
C(10)–C(9)–C(8)	124.29(13)	124.88	−0.59	124.41	−0.12
C(9)–C(10)–Cl(2)	123.34(12)	123.18	0.16	123.36	−0.02
C(9)–C(10)–Cl(1)	122.89(12)	122.82	0.07	122.71	0.18
Cl(2)–C(10)–Cl(1)	113.76 (8)	114.00	−0.24	113.92	−0.16

[a] Geometry optimized at the B3LYP/ó-311++G(d,p) level of theory.
[b] Geometry optimized at the HF/6-311++G(d,p) level of theory.

Table 2. Interplanar angles of crystal and calculated structures in crystal structure of **5f** and their difference

Plane	Crystal structure (°)	Calculated structure (°)[a]	Δ (°)
C(11)–C(2)–C(6)	0.7	0.2	0.5
O(1)–C(2)–C(6)	1.0	0.1	0.9
C(7)–C(2)–C(6)	0.5	0.1	0.4
O(2)–C(2)–C(6)	2.0	0.2	1.8
C(8)–C(2)–C(6)	2.1	0.1	2.0
C(9)–C(2)–C(6)	2.7	0.1	2.6
C(10)–C(2)–C(6)	3.1	0.2	2.9
Cl(1)–C(2)–C(6)	3.3	0.3	3.0
Cl(2)–C(2)–C(6)	3.3	0.2	3.1

The angles are between the selected planes and the plane of reference C(1)–C(3)–C(5).

[a] Angles calculated from geometry optimized at the B3LYP/5-311++G(d,p) level of theory.

By contrast, dichlorinated ketones **6** and **5** exhibit small differences in energy ($\Delta E_0 \approx 0.5$ kcal/mol) (series C). The electronic influence due to the ring substituents is also unimportant. This energy equalization is understandable considering that the +M-effect of the chlorine atoms in isomers **5** compensates the −M-effect of the carbonyl group in compounds **6**. The intermediate location of monochlorinated ketone pairs **11** and **10** ($\Delta E_0 \approx 2.4$ kcal/mol) (Fig. 3, series B) is fully consistent with this explanation.

It should be noted that the natural[14] charge-values at the β-carbon atoms for ketones **9a** (series A), **11a** (series B) and **6a** (series C), computed at B3LYP/6-31G(d) level of theory are −0.108, −0.154 and −0.189 (values in electrons), respectively. This means that the contribution of dipolar canonical structures to resonance hybrids placing a positive charge density on C-β (Fig. 2) is being inhibited by interaction with the vicinal electron-withdrawing groups (CH_2Cl and $CHCl_2$).

Taking into account the above results, it seems reasonable to conclude that the observed total priority towards the formation of products **5** in detriment to formation of products **6** should not be due to thermodynamic control but should be driven by a remarkably efficient kinetic control. An evidence of this was found by attempting a base-catalyzed isomerization of **5e** to **6e** by refluxing in ethanol–pyridine solution for a sufficient time to provide fully equilibrated mixtures of both isomers. The result of this experiment was the formation of a mixture of compounds **5e** and **6e** (ratio ≈ 1:1), as expected from the calculated Gibbs free energies of the two isomeric ketones ($\Delta G^0 = -0.13$ kcal/mol at the B3LYP/6-31G(d) level of theory). This conclusion also finds support in different studies on the base-catalyzed deconjugation of α,β-unsaturated ketones where results point towards kinetically controlled protonation of the involved dienolate anion intermediates.[15]

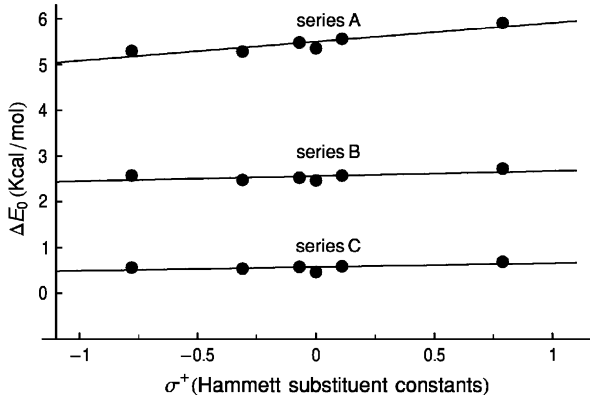

Figure 3. Values of $\Delta E_0 = E_0$(β,γ-unsaturated ketone) − E_0(α,β-unsaturated isomer) for the non-chlorinated (series A), monochlorinated (series B) and dichlorinated isomeric ketone pairs (series C) computed at the B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) level of theory and including ZPE corrections calculated at the same level as geometry optimization.

In conclusion, an effective method for the synthesis of a previously unattainable family of compounds, which can be used for preparing a variety of dichloromethylated heterocyclic compounds, is reported. Versatility, good yields, easy availability of starting materials, mildness and simple experimental procedure are noteworthy advantages of this synthetic methodology.

3. Experimental

3.1. General

NMR spectra were determined on Bruker AV-200, Bruker AV-300 or Bruker AV-400 with tetramethylsilane as internal reference. Electron-impact mass spectra were obtained on Thermoquest trace MS spectrometer under an ionizing voltage of 70 eV. FAB^+ data were obtained on Autospec 5000 VG spectrometer. IR spectra (Nujol emulsions) were recorded on a Nicolet Impact 400 Spectrometer. Microanalyses were performed on a Carlo Erba EA-1108 analyzer. Melting points were determined on a Büchi Melting point B-540, and are uncorrected. Electrochemical experiments were performed with an Amel 552 potentiostat coupled to an Amel 721 integrator.

All computations were performed with the Spartan'04 package program.[16] The most stable conformers were determined by using the MMFF molecular mechanics method.[17] Next, these conformers were used as input for ab initio molecular orbital and density functional theory calculations of geometry optimizations at the Hartree–Fock and B3LYP[18] levels of theory with the 6-31G(d) basis set. Selected geometry optimizations were also carried out at these levels of theory with the 6-311+G(d,p) and 6-311++G(d,p) bases. There were no significant differences between the results obtained with the different basis sets. Frequency calculations were performed at the same level of theory as the geometry optimizations to characterize the stationary points as local minima (equilibrium structures) and to evaluate the zero-point energy (ZPE). No scaling procedures were used. Single-point energies were calculated with the 6-311++G(d,p) basis.

3.2. Preparation of 1-aryl-4,4,4-trichlorobut-2-en-1-ones (3)

Compounds **3a**–**d**, method A: The appropriate ketone **2** (35 mmol) in sulfuric acid (100 mL) was stirred at room temperature for 2 h. The reaction product was isolated by dropping the reaction mixture into ice water (400 mL) and filtering the yellow solid precipitated, which was air-dried and crystallized in the appropriate solvent.

Compounds **3e–j**, method B: The appropriate ketone **2** (33 mmol), *p*-toluenesulfonic acid monohydrate (17 mmol) and toluene (300 mL) were refluxed with a Dean–Stark water separator until a total conversion of the starting material **2** was observed by TLC (silica gel/ethyl acetate–petroleum ether, ratio 1:9). Then the solvent was removed under reduced pressure, the residue was dissolved in chloroform and washed with aqueous sodium bicarbonate and water. The organic layer was dried over anhydrous magnesium sulfate and chloroform was removed in vacuo leaving a solid residue that was crystallized in the appropriate solvent.

3.2.1. 4,4,4-Trichloro-1-phenylbut-2-en-1-one (3a). Yield 94%. White plates, mp 101–102 °C (ethanol), (lit.:[13b] mp 100 °C). ^{1}H NMR δ ($CDCl_3$, 400 MHz): 7.26 (d, 1H, J=14.5 Hz), 7.40 (d, 1H, J=14.5 Hz), 7.51 (t, 2H, J=7.4 Hz), 7.62 (tt, 1H, J=7.4 Hz, J=1.2 Hz), 7.97 (dd, 2H, J=7.4 Hz, J=1.2 Hz); ^{13}C NMR δ ($CDCl_3$, 100.8 MHz): 93.04 (CCl_3), 124.25 (CH), 128.80 (CH), 128.97 (CH), 133.91 (CH), 136.90 (C), 145.51 (CH), 188.84 (CO); MS, *m*/*z* (%): 252 (M^++4, 1), 250 (M^++2, 2), 248 (M^+, 2), 149 (14), 105 (100), 77 (37); IR (Nujol): 1674, 1626, 1594, 1341, 1277, 1011, 953, 876, 767, 739 cm^{-1}. Anal. Calcd for $C_{10}H_7Cl_3O$: C, 48.14; H, 2.83. Found: C, 48.60; H, 2.91.

3.2.2. 4,4,4-Trichloro-1-(4-fluorophenyl)but-2-en-1-one (3b). Yield 95%. White plates, mp 117–119 °C (hexane), (lit.:[13c] mp 117–118 °C). ^{1}H NMR δ ($CDCl_3$, 200 MHz): 7.20 (t, 2H, J=8.8 Hz), 7.27 (d, 1H, J=14.6 Hz), 7.39 (d, 1H, J=14.6 Hz), 8.04 (dd, 2H, J=8.8 Hz, J=5.4 Hz); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 92.87 (CCl_3), 116.22 (d, J=22.1 Hz) (CH), 123.71 (CH), 131.54 (d, J=9.5 Hz) (CH), 133.24 (d, J=2.8 Hz) (C), 145.67 (CH), 166.25 (d, J=256.9 Hz) (C), 187.18 (CO); MS, *m*/*z* (%): 270 (M^++4, 4), 268 (M^++2, 10), 266 (M^+, 11), 231 (16), 196 (12), 203 (37), 205 (27), 123 (100), 95 (53), 75 (34); IR (Nujol): 1672, 1621, 1591, 1333, 1420, 1212, 1162, 962, 880, 814, 758 cm^{-1}. Anal. Calcd for $C_{10}H_6Cl_3FO$: C, 44.90; H, 2.26. Found: C, 44.70; H, 2.11.

3.2.3. 4,4,4-Trichloro-1-(4-chlorophenyl)but-2-en-1-one (3c). Yield 90%. Pale yellow prisms, mp 116–117 °C (ethanol) (lit.:[13c] mp 115–116 °C). ^{1}H NMR δ ($CDCl_3$, 200 MHz): 7.26 (d, 1H, J=14.6 Hz), 7.35 (d, 1H, J=14.6 Hz), 7.50 (d, 2H, J=8.8 Hz), 7.93 (d, 2H, J=8.8 Hz); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 92.83 (CCl_3), 123.59 (CH), 129.34 (CH), 130.19 (CH), 135.12 (C), 140.57 (C), 145.89 (CH), 187.59 (CO); MS, *m*/*z* (%): 286 (M^++4, 17), 284 (M^++2, 31), 282 (M^+, 23), 247 (25), 249 (26), 219 (65), 221 (67), 185 (77), 139 (100), 141 (65), 111 (78), 73 (64); IR (Nujol): 1674, 1623, 1589, 1279, 1211, 1182, 1091, 1015, 961, 873, 776 cm^{-1}. Anal. Calcd for $C_{10}H_6Cl_4O$: C, 42.30; H, 2.13. Found: C, 42.49; H, 2.22.

3.2.4. 1-(4-Bromophenyl)-4,4,4-trichlorobut-2-en-1-one (3d). Yield 84%. Pale yellow needles, mp 122 °C (ethanol) (lit.:[13c] mp 119–120 °C). ^{1}H NMR δ ($CDCl_3$, 400 MHz): 7.27 (d, 1H, J=14.5 Hz), 7.36 (d, 1H, J=14.5 Hz), 7.67 (d, 2H, J=8.6 Hz), 7.85 (d, 2H, J=8.6 Hz); ^{13}C NMR δ ($CDCl_3$, 100.8 MHz): 92.81 (CCl_3), 123.52 (CH), 129.35 (C), 130.24 (CH), 132.33 (CH), 135.51 (C), 145.93 (CH), 187.82 (CO); MS, *m*/*z* (%): 330 (M^++4, 19), 328 (M^++2, 30), 326 (M^+, 15), 265 (33), 229 (14), 183 (100), 185 (98), 149 (45), 75 (36); IR (Nujol): 1662, 1621, 1578, 1398, 1322, 1278, 1101, 1069, 1006, 962, 766 cm^{-1}. Anal. Calcd for $C_{10}H_6BrCl_3O$: C, 36.57; H, 1.84. Found: C, 36.46; H, 1.72.

3.2.5. 4,4,4-Trichloro-1-(4-tolyl)but-2-en-1-one (3e). Yield 89%. White plates, mp 89–90 °C (ethanol). ^{1}H NMR δ ($CDCl_3$, 300 MHz): 2.44 (s, 3H), 7.25 (d, 1H, J=14.7 Hz), 7.31 (d, 2H, J=8.1 Hz), 7.41 (d, 1H, J=14.7 Hz), 7.89 (d, 2H, J=8.1 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 21.85 (CH_3), 93.13 (CCl_3), 124.24 (CH), 128.97 (CH), 129.69 (CH), 134.39 (C), 145.07 (C), 145.21 (CH), 188.36 (CO); MS, *m*/*z* (%): 266 (M^++4, 28), 264 (M^++2, 75), 262 (M^+, 76), 227 (24), 102 (69), 163 (70), 145 (45), 128 (39), 119 (100), 91 (74), 73 (44); IR (Nujol): 1668, 1604, 1408, 1330, 1284, 1183, 1124, 1097, 959, 1014, 959, 872, 758 cm^{-1}. Anal. Calcd for $C_{11}H_9Cl_3O$: C, 50.13; H, 3.44. Found: C, 50.26; H, 3.41.

3.2.6. 4,4,4-Trichloro-1-(4-methoxyphenyl)but-2-en-1-one (3f). Yield 80%. Pale yellow prisms, mp 66–68 °C (ethanol). ^{1}H NMR δ ($CDCl_3$, 400 MHz): 3.89 (s, 3H), 6.99 (d, 2H, J=8.9 Hz), 7.25 (d, 1H, J=14.5 Hz), 7.41 (d, 1H, J=14.5 Hz), 7.99 (d, 2H, J=8.9 Hz); ^{13}C NMR δ ($CDCl_3$, 100.8 MHz): 55.65 (CH_3), 93.23 (CCl_3), 114.23 (CH), 124.20 (CH), 129.92 (C), 131.27 (CH), 144.87 (CH), 164.33 (C), 187.02 (CO); MS, *m*/*z* (%): 282 (M^++4, 54), 280 (M^++2, 54), 278 (M^+, 54), 243 (24), 245 (18), 217 (74), 215 (62), 208 (25), 179 (74), 145 (60), 135 (100), 92 (74), 77 (64); IR (Nujol): 1670, 1597, 1570, 1425, 1327, 1264, 1176, 1099, 1015, 872, 840, 762, 719 cm^{-1}. Anal. Calcd for $C_{11}H_9Cl_3O_2$: C, 47.26; H, 3.25. Found: C, 47.36; H, 3.34.

3.2.7. 4,4,4-Trichloro-1-(4-nitrophenyl)but-2-en-1-one (3g). Yield 82%. Yellow prisms, mp 109 °C (ethanol), (lit.:[13e] mp 102–103 °C). ^{1}H NMR δ ($CDCl_3$, 200 MHz): 7.33 (d, 1H, J=14.4 Hz), 7.40 (d, 1H, J=14.4 Hz), 8.16 (d, 2H, J=8.8 Hz), 8.38 (d, 2H, J=8.8 Hz); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 92.45 (CCl_3), 123.23 (CH), 124.19 (CH), 129.80 (CH), 141.25 (C), 146.94 (CH), 150.73 (C), 187.59 (CO); MS, *m*/*z* (%): 260 (48), 258 (65), 230 (28), 184 (36), 150 (100), 104 (47), 92 (29), 76 (50); IR (Nujol): 1707, 1686, 1625, 1599, 1514, 1209, 1092, 1011, 963, 855, 780, 770 cm^{-1}. Anal. Calcd for $C_{10}H_6Cl_3NO_3$: C, 40.78; H, 2.05; N, 4.76. Found: C, 40.62; H, 1.98; N 4.67.

3.2.8. 4,4,4-Trichloro-1-(2,4-dimethylphenyl)but-2-en-1-one (3h). Yield 85%. Yellow plates, mp 72–73 °C (cyclohexane). ^{1}H NMR δ ($CDCl_3$, 400 MHz): 2.38 (s, 3H), 2.49 (s, 3H), 7.14 (d, 1H, J=14.7 Hz), 7.06 (d, 1H, J=14.7 Hz), 7.11 (br s, 2H), 7.52 (d, 1H, J=8.2 Hz); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 21.55 (CH_3), 21.10 (CH_3), 93.03 (CCl_3), 126.52 (CH), 127.70 (CH), 129.67 (CH), 132.95 (CH), 134.31 (C), 139.10 (C), 142.88 (C), 145.18 (CH), 192.39 (CO); MS, *m*/*z* (%): 177 (6), 159 (11), 146 (9), 133 (100), 105 (19), 77 (7); FAB$^+$: 277 (M+H$^+$); IR (Nujol): 1699, 1609, 1312, 1281, 1138, 1008, 973, 770, 760, 718 cm^{-1}. Anal. Calcd for $C_{12}H_{11}Cl_3O$: C, 51.92; H, 3.99. Found: C, 52.03; H, 4.07.

3.2.9. 1-(4-Biphenylyl)-4,4,4-trichlorobut-2-en-1-one (3i). Yield 75%. Pale yellow plates, mp 120–121 °C (ethanol). ^{1}H NMR δ ($CDCl_3$, 400 MHz): 7.30 (d, 1H,

J=14.5 Hz), 7.40–7.50 (m, 4H), 7.63 (d, 2H, J=7.5 Hz), 7.73 (d, 2H, J=8.3 Hz), 8.06 (d, 2H, J=8.3 Hz); ^{13}C NMR δ ($CDCl_3$, 100.8 MHz): 93.08 (CCl_3), 124.16 (CH), 127.37 (CH), 127.58 (CH), 128.93 (CH), 129.10 (CH), 129.45 (CH), 135.54 (C), 139.62 (C), 145.45 (CH), 146.68 (C), 188.31 (CO); MS, m/z (%): 328 (M^++4, 18), 326 (M^++2, 49), 324 (M^+, 50), 261 (22), 225 (50), 191 (32), 181 (100), 152 (73), 127 (20); IR (Nujol): 1673, 1621, 1603, 1404, 1096, 1005, 960, 779, 772, 750, 696 cm^{-1}. Anal. Calcd for $C_{16}H_{11}Cl_3O$: C, 59.02; H, 3.41. Found: C, 58.97; H, 3.37.

3.2.10. 4,4,4-Trichloro-1-(naphthalen-2-yl)but-2-en-1-one (3j). Yield 87%. Pale yellow plates, mp 98–99 °C (ethanol). ^{1}H NMR δ ($CDCl_3$, 200 MHz): 7.33 (d, 1H, J=14.6 Hz), 7.56 (d, 1H, J=14.6 Hz), 7.53–7.67 (m, 2H), 7.86–8.06 (m, 4H), 8.46 (br s, 1H); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 93.10 (CCl_3), 124.07 (CH), 127.16 (CH), 127.95 (CH), 129.02 (CH), 129.13 (CH), 129.77 (CH), 130.85 (CH), 132.43 (C), 134.19 (C), 135.92 (C), 145.44 (CH), 188.55 (CO); MS, m/z (%): 302 (M^++4, 17), 300 (M^++2, 50), 298 (M^+, 52), 235 (19), 199 (19), 181 (33), 165 (47), 155 (100), 127 (93), 77 (22); IR (Nujol): 1673, 1623, 1593, 1314, 1190, 1126, 1097, 954, 862, 776, 761, 742, 681 cm^{-1}. Anal. Calcd for $C_{14}H_9Cl_3O$: C, 56.13; H, 3.03. Found: C, 55.92; H, 2.97.

3.3. Electrogeneration of 1-aryl-4,4-dichlorobut-3-en-1-ones (5)

Reductive electrolyses of compounds **3** were carried out under a constant cathodic potential in a concentric cylindrical cell with two compartments separated by a circular glass frit (medium) diaphragm. A mercury pool (diameter 5 cm; tip of the Luggin-capillary situated on the edge of the pool) was used as the cathode and a platinum plate as the anode. The catholyte was magnetically stirred. The temperature was kept at approximately 18 °C by external cooling. The reductions were performed in MeCN (60 mL)–AcOH (10 mL)–$LiClO_4$ 0.47 M; 55 mL and 15 mL were placed in the cathodic and the anodic compartments, respectively. Sodium acetate (1 g) was placed in the anode compartment. Solutions of **3** (5 mmol) were electrolyzed under the following cathodic potentials,[19] which were selected in order to provide operative current intensities (close to 220 mA at the beginning and 10 mA at the end): **3a** (−0.20); **3c**,**d**,**i** (−0.30); **3g** (−0.40); **3b**,**f** (−0.50); **3j** (−0.60); **3e** (−0.72); **3h** (−0.80) V versus SCE. The electricity consumption was 2 F/mol. Isolation of products **5** was carried out by removing the solvent in vacuo, adding water (150 mL) and collecting the resulting solid by filtration.[20]

These syntheses were found to be reproducible when following a procedure like the above but using graphite (area 12 cm^2) instead of mercury as cathodic material, and platinum (area 8 cm^2) as cathodic material with an operating potential of −1.00 V versus SCE, except in the reduction of **3g**, in which the electrolysis was carried under a potential of −0.55 V versus SCE. The current intensity was about 100 mA at the beginning, and 20 mA at the end. The electricity consumption was 2 F/mol. Analogous results were obtained in experiments under these electrolysis conditions but working in MeCN (60 mL)–AcOH (10 mL)–H_2O (5 mL)–$NaBF_4$ 0.45 M.

3.3.1. 4,4-Dichloro-1-phenylbut-3-en-1-one (5a). Yield 95%. Pale yellow prisms, mp 50–51 °C (petroleum ether). ^{1}H NMR δ ($CDCl_3$, 200 MHz): 3.99 (d, 2H, J=6.8 Hz), 6.34 (t, 1H, J=6.8 Hz), 7.44–7.53 (m, 2H), 7.56–7.65 (m, 1H), 7.94–8.00 (m, 2H); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 39.26 (CH_2), 122.61 (CH), 122.74 (CCl_2), 128.23 (CH), 128.85 (CH), 133.71 (CH), 136.07 (C), 195.02 (CO); MS, m/z (%): 105 (100), 77 (47); FAB$^+$: 215 (M+H$^+$); IR (Nujol): 1684, 1625, 1594, 1580, 1347, 1248, 1073, 992, 904, 814, 690, 608 cm^{-1}. Anal. Calcd for $C_{10}H_8Cl_2O$: C, 55.84; H, 3.75. Found: C, 55.62; H, 3.81.

3.3.2. 4,4-Dichloro-1-(4-fluorophenyl)but-3-en-1-one (5b). Yield 96%. Chromatography (silica gel/ethyl acetate–hexane, ratio 1:1) gave yellow powder, mp 32–34 °C. ^{1}H NMR δ ($CDCl_3$, 400 MHz): 3.88 (d, 2H, J=6.6 Hz), 6.33 (t, 1H, J=6.6 Hz), 7.16 (t, 2H, J=8.6 Hz), 8.00 (dd, 2H, J=8.6 Hz, J=5.3 Hz); ^{13}C NMR δ ($CDCl_3$, 100.8 MHz): 39.15 (CH_2), 116.01 (d, J=22.1 Hz) (CH), 122.37 (CH), 122.88 (CCl_2), 130.91 (d, J=9.3 Hz) (CH), 132.46 (d, J=2.9 Hz) (C), 166.01 (d, J=255.7 Hz) (C), 193.41 (CO); IR (Nujol): 3055, 1684, 1625, 1600, 1057, 1242, 1203, 1160, 992, 905, 841, 802, 639 cm^{-1}. Anal. Calcd for $C_{10}H_7Cl_2FO$: C, 51.53; H, 3.03. Found: C, 51.40; H, 3.12.

3.3.3. 4,4-Dichloro-1-(4-chlorophenyl)but-3-en-1-one (5c). Yield 97%. Chromatography (silica gel/ethyl acetate–hexane, ratio 1:9) gave white powder, mp 58–59 °C. ^{1}H NMR δ ($CDCl_3$, 200 MHz): 3.87 (d, 2H, J=6.6 Hz), 6.32 (t, 1H, J=6.6 Hz), 7.47 (d, 2H, J=8.6 Hz), 7.92 (d, 2H, J=8.6 Hz); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 39.22 (CH_2), 122.23 (CH), 123.04 (CCl_2), 129.19 (CH), 129.63 (CH), 134.37 (C), 140.23 (C), 193.79 (CO); IR (Nujol): 1673, 1630, 1590, 1341, 1210, 1093, 996, 894, 812, 788 cm^{-1}. Anal. Calcd for $C_{10}H_7Cl_3O$: C, 48.14; H, 2.83. Found: C, 47.82; H, 2.84.

3.3.4. 1-(4-Bromophenyl)-4,4-dichlorobut-3-en-1-one (5d). Yield 98%. White plates, mp 79–80 °C (petroleum ether). ^{1}H NMR δ ($CDCl_3$, 400 MHz): 3.86 (d, 2H, J=6.6 Hz), 6.31 (t, 1H, J=6.6 Hz), 7.63 (d, 2H, J=8.6 Hz), 7.83 (d, 2H, J=8.6 Hz); ^{13}C NMR δ ($CDCl_3$, 100.8 MHz): 39.20 (CH_2), 122.18 (CH), 123.04 (CCl_2), 128.98 (C), 129.71 (CH), 132.18 (CH), 134.73 (CH), 193.98 (CO); MS, m/z (%): 183 (100), 185 (98), 157 (28), 155 (27), 76 (20), 76 (17); FAB$^+$: 293 (M+H$^+$); IR (Nujol): 1684, 1628, 1583, 1339, 1241, 1087, 1073, 988, 904, 792, 613 cm^{-1}. Anal. Calcd for $C_{10}H_7BrCl_2O$: C, 40.86; H, 2.40. Found: C, 40.59; H, 2.32.

3.3.5. 4,4-Dichloro-1-(4-tolyl)but-3-en-1-one (5e). Yield 98%. White plates, mp 76–77 °C (petroleum ether). ^{1}H NMR δ ($CDCl_3$, 200 MHz): 2.42 (s, 3H), 3.85 (d, 2H, J=6.0 Hz), 6.33 (t, 1H, J=6.0 Hz), 7.27 (d, 2H, J=8.0 Hz), 7.86 (d, 2H, J=8.0 Hz); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 21.73 (CH_3), 39.13 (CH_2), 122.47 (CCl_2), 122.83 (CH), 128.32 (CH), 129.50 (CH), 133.59 (C), 144.60 (C), 194.59 (CO); FAB$^+$: 229 (M+H$^+$); IR (Nujol): 1679, 1607, 1347, 1243, 1201, 1184, 1088, 996, 991, 905, 793, 770, 638 cm^{-1}. Anal. Calcd for $C_{11}H_{10}Cl_2O$: C, 57.67; H, 4.40. Found: C, 57.38; H, 4.41.

3.3.6. 4,4-Dichloro-1-(4-methoxyphenyl)but-3-en-1-one (5f). Yield 96%. White plates, mp 72–73 °C (petroleum

ether). ^{1}H NMR δ ($CDCl_3$, 300 MHz): 3.83 (d, 2H, J=6.6 Hz), 3.87 (s, 3H), 6.33 (t, 1H, J=6.6 Hz), 6.95 (d, 2H, J=8.7 Hz), 7.94 (d, 2H, J=8.7 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 38.91 (CH_2), 55.54 (CH_3), 113.94 (CH), 122.38 (CCl_2), 123.00 (CH), 139.06 (C), 130.51 (CH), 163.91 (C), 193.51 (CO); FAB$^+$: 245 (M+H$^+$); IR (Nujol): 1677, 1601, 1511, 1354, 1261, 1247, 1174, 1030, 993, 904, 833, 802 cm^{-1}. Anal. Calcd for $C_{11}H_{10}Cl_2O_2$: C, 53.90; H, 4.11. Found: C, 53.69; H, 4.02.

Crystal data: $C_{11}H_{10}Cl_2O_2$, M=245.09, $P2_1/c$, a=14.0637(9) Å, b=13.7598(9) Å, c=5.6360(4) Å, α=90°, β=97.9751(11)°, γ=90°, V=1080.10(13) Å^3, Z=4, d_{calcd}=1.507 Mg/m^3, μ=0.575 mm^{-1}, T=100(2) K. Colourless block-like crystals were grown by evaporation of a solution of **5f**; 6232 reflections were measured ($2\theta_{max}$ 52.7°) using monochromated Mo Kα radiation on a Bruker Smart Apex CCD machine, of which 2196 were unique and used for all calculations (program ShelXL-97, G. M. Sheldrick, University of Göttingen). The structure was solved by direct methods, and was refined anisotropically on F^2. Hydrogen atoms were included using a riding model or rigid methyl group. The final $wR(F^2)$ was 0.0812 with conventional $R(F)$ 0.0324, for 137 parameters and 3 restraints; highest peak 0.00239, hole −0.00325 e/pm.

Tables of fractional atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Center (CCDC 607589).

3.3.7. 4,4-Dichloro-1-(4-nitrophenyl)but-3-en-1-one (5g). Yield 72%. Yellow needles, mp 103–105 °C (cyclohexane). ^{1}H NMR δ ($CDCl_3$, 400 MHz): 3.96 (d, 2H, J=6.6 Hz), 6.32 (t, 1H, J=6.6 Hz), 8.14 (d, 2H, J=8.9 Hz), 8.35 (d, 2H, J=8.9 Hz); ^{13}C NMR δ ($CDCl_3$, 100.8 MHz): 39.73 (CH_2), 121.44 (CH), 123.76 (CCl_2), 124.11 (CH), 129.30 (CH), 140.41 (C), 150.69 (C), 193.52 (CO); FAB$^+$: 260 (M+H$^+$); IR (Nujol): 1697, 1606, 1520, 1245, 1199, 996, 904 cm^{-1}. Anal. Calcd for $C_{10}H_7Cl_2NO_3$: C, 46.18; H, 2.71; N, 5.39. Found: C, 45.85; H, 2.66; N, 5.57.

3.3.8. 4,4-Dichloro-1-(2,4-dimethylphenyl)but-3-en-1-one (5h). Yield 97%. Chromatography (silica gel/ethyl acetate–hexane, ratio 1:2) gave yellow oil. ^{1}H NMR δ ($CDCl_3$, 400 MHz): 2.35 (s, 3H), 2.50 (s, 3H), 3.80 (d, 2H, J=6.8 Hz), 6.29 (t, 1H, J=6.8 Hz), 7.07 (s, 1H), 7.09 (s, 1H), 7.61 (d, 1H, J=8.4 Hz); ^{13}C NMR δ ($CDCl_3$, 100.8 MHz): 21.43 (CH_3), 21.78 (CH_3), 41.47 (CH_2), 122.38 (CCl_2), 123.13 (CH), 126.52 (CH), 129.29 (CH), 133.21 (CH), 133.21 (CH), 133.46 (C), 139.48 (C), 142.80 (C), 197.58 (CO); IR (film): 3351, 3239, 3057, 3020, 2965, 2923, 1685, 1612, 1566, 1452, 1334, 1205, 985, 882, 803, 725, 633 cm^{-1}. Anal. Calcd for $C_{12}H_{12}Cl_2O$: C, 59.28; H, 4.97. Found: C, 59.23; H, 5.17.

3.3.9. 1-(4-Biphenylyl)-4,4-dichlorobut-3-en-1-one (5i). Yield 95%. Pale yellow needles, mp 113–114 °C (petroleum ether). ^{1}H NMR δ ($CDCl_3$, 200 MHz): 3.91 (d, 2H, J=6.6 Hz), 6.36 (t, 1H, J=6.6 Hz), 7.52–7.40 (m, 3H), 7.62 (dd, 2H, J=8.4 Hz, J=1.5 Hz), 7.69 (d, 2H, J=8.4 Hz), 8.03 (d, 2H, J=8.4 Hz); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 39.31 (CH_2), 122.67 (CCl_2), 127.33 (CH), 127.49 (CH), 128.46 (CH), 128.83 (CH), 128.83 (CH), 129.06 (CH), 134.72 (C), 139.68 (C), 146.36 (C), 194.57 (CO); FAB$^+$: 291 (M+H$^+$); IR (Nujol): 1678, 1628, 1605, 1342, 1249, 1201, 1089, 989, 906, 804, 759, 691 cm^{-1}. Anal. Calcd for $C_{16}H_{12}Cl_2O$: C, 66.00; H, 4.15. Found: C, 65.88; H, 4.10.

3.3.10. 4,4-Dichloro-1-(naphthalen-2-yl)but-3-en-1-one (5j). Yield 96%. Pale yellow needles, mp 80–81 °C (petroleum ether). ^{1}H NMR δ ($CDCl_3$, 400 MHz): 4.02 (d, 2H, J=6.6 Hz), 6.39 (t, 1H, J=6.6 Hz), 7.54–7.63 (m, 2H), 7.87 (s ancho, 1H), 7.90 (d, 1H, J=8.7 Hz), 7.97 (d, 1H, J=8.0 Hz), 8.01 (dd, 1H, J=8.7 Hz, J=1.8 Hz), 8.47 (br s, 1H); ^{13}C NMR δ ($CDCl_3$, 100.8 MHz): 39.34 (CH_2), 112.74 (CH), 123.73 (CH), 127.73 (CH), 127.89 (CH), 128.89 (CH), 129.68 (CH), 130.06 (CH), 132.49 (C), 133.37 (C), 135.83 (C), 194.95 (CO); FAB$^+$: 265 (M+H$^+$); IR (Nujol): 1679, 1624, 1360, 1336, 1172, 1126, 964, 944, 911, 804, 769, 745 cm^{-1}. Anal. Calcd for $C_{14}H_{10}Cl_2O$: C, 63.42; H, 3.80. Found: C, 62.92; H, 3.75.

3.4. Isomerization of 5e to 6e

A mixture of 4,4-dichloro-1-(4-tolyl)but-3-en-1-one **5e** (1.8 mmol), pyridine (3.9 mmol) and ethanol (15 mL) was refluxed for 5 h. Evaporation to dryness under reduced pressure yielded a crude material that was stirred in cold water (25 mL) and extracted with ether (2×25 mL). The combined extracts were washed with hydrochloric acid (5%; 25 mL), water (2×20 mL) and dried with anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure leaving a mixture exclusively formed by the starting material and 4,4-dichloro-1-(4-tolyl)-2-buten-1-one **6e** (ratio 1:1), which was isolated by column chromatography (silica gel/*tert*-butyl methyl ether–hexane, ratio 1:19).

3.4.1. 4,4-Dichloro-1-(4-tolyl)but-2-en-1-one (6e). Yield 45%. White needles, mp 34–35 °C (petroleum ether). ^{1}H NMR δ ($CDCl_3$, 400 MHz): 2.44 (s, 3H), 6.37 (d, 1H, J=6.5 Hz), 7.06 (dd, 1H, J=15.0 Hz, J=6.5 Hz), 7.19 (d, 1H, J=15.0 Hz), 7.30 (d, 1H, J=8.2 Hz), 7.87 (d, 1H, J=8.2 Hz); ^{13}C NMR δ ($CDCl_3$, 100.8 MHz): 21.75 (CH_3), 68.82 ($CHCl_2$), 126.06 (CH), 128.85 (CH), 129.54 (CH), 134.33 (C), 141.56 (CH), 144.71 (C), 188.72 (CO); MS, m/z (%): 230 (M$^+$+2, 4), 228 (M$^+$, 6), 158 (10), 145 (5), 119 (100), 91 (40), 69 (17), 65 (14); IR (Nujol): 1666, 1627, 1602, 1342, 1306, 1251, 1239, 1182, 1108, 1012, 967, 745, 700 cm^{-1}. Anal. Calcd for $C_{11}H_{10}Cl_2O$: C, 57.67; H, 4.40. Found: C, 57.31; H, 4.37.

3.5. Preparation of 1-(4-bromophenyl)-4,4-dichloro-1,3-butadien-1-yl benzoate (7d)

1-(4-Bromophenyl)-4,4,4-trichlorobut-2-en-1-one **3d** (5 mmol) was electrolyzed operating as described to generate compounds **5** but with the experiment being carried out in the presence of benzoyl chloride (30 mmol) instead of acetic acid. The cathodic potential was −0.30 V versus SCE and the electricity consumption was 2 F/mol. The catholyte solution was dropped onto concentrated ammonium hydroxide (50 mL)–ice (200 g) and the mixture was extracted with ether. The ether layers were collected and dried over anhydrous magnesium sulfate, concentrated to 20 mL and cooled to −20 °C for 2 h. The solid precipitate (benzamide) was

removed by filtration. The filtrate was concentrated to dryness under reduced pressure and the residual material was crystallized from cool methanol.

Yield 72%. Pale yellow needles, mp 113–114 °C (petroleum ether). ^{1}H NMR δ ($CDCl_3$, 400 MHz): 6.62 (d, 1H, J=10.8 Hz), 6.68 (d, 1H, J=10.8 Hz), 7.39 (d, 2H, J=7.1 Hz), 7.47 (d, 2H, J=7.1 Hz), 7.55 (t, 2H, J=7.6 Hz), 7.69 (t, 1H, J=7.6 Hz), 8.21 (d, 2H, J=7.6 Hz); ^{13}C NMR δ ($CDCl_3$, 100.8 MHz): 112.06 (CH), 122.58 (CH), 123.67 (C), 124.26 (C), 126.44 (CH), 128.34 (C), 128.98 (CH), 130.42 (CH), 132.09 (CH), 132.95 (C), 134.34 (CH), 147.76 (C), 164.14 (CO); MS, *m/z* (%): 183 (2), 149 (8), 105 (100), 77 (73); FAB$^+$: 397 (M+H$^+$); IR (Nujol): 1734, 1585, 1253, 1240, 1172, 1082, 1064, 1005, 914, 831, 810, 713, 689 cm^{-1}. Anal. Calcd for $C_{17}H_{11}BrCl_2O_2$: C, 51.26; H, 2.84. Found: C, 51.29; H, 2.79.

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Supplementary data

X-ray structural data of compound **5f**, ^{1}H NMR and ^{13}C NMR spectra of compounds **2**–**5**, **6e** and **7d**, preparative procedure for compounds **2**, optimized geometries and energies. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.11.054.

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19. Electrolysis of **3g** requires a rigorous control of cathodic potential to avoid the reduction of the nitro group, which was found to be electroactive at potentials higher than −0.45 V (Hg) and −0.60 V (C) versus SCE.
20. Caution must be exercised when handling perchlorates in order to exclude explosion risk. Evaporation of organic solutions containing perchlorates requires to be carried out in vacuo and at moderate temperature. Contact with strong acids must be avoided.