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Invited Paper

Cathodic Addition of Benzylidyne Trichloride to Ketones and Aldehydes[1)]

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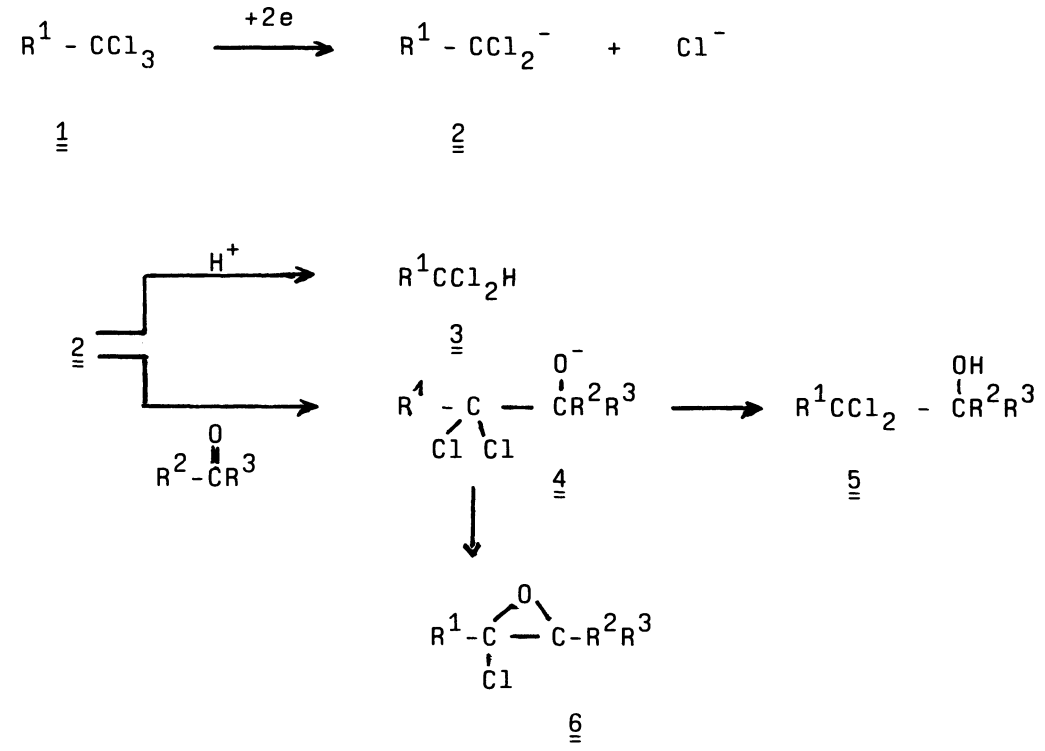
Ketones are converted to homologated enones **7a—g** in good yields by cathodic addition of benzylidyne trichloride (**1d**). As intermediates α-chlorooxiranes **6** are assumed, which rearrange via α-keto carbenium ions **9** to enones. The intermediacy of **9** is supported by the addition of **1d** to norcamphor, where the products indicate equilibrating norbornyl cations as intermediates. α,β-Unsaturated ketones lead depending on steric shielding of the double bond to the cyclopropane **23** as 1,4-adduct or the enone **26** as 1,2-adduct. With aldehydes and **1d**, α-chloro or α-hydroxy ketones, the conversion products of 2-chlorooxiranes, are obtained.

The electrochemical reduction of organic *gem*-trihalides **1** (Eq. 1) proceeds in two consecutive one-electron transfer steps and results in cleavage of the C–Halo bond to carbanions **2**,[2)] which can react with electrophiles. As electrophiles, protons,[3)] Michael acceptors,[4)] and carbonyl compounds[5)] have been used.



(1)

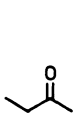
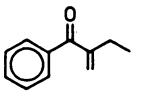
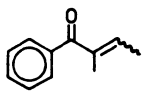
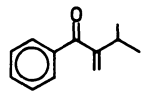
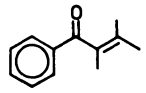
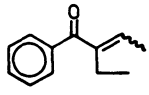
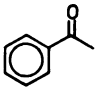
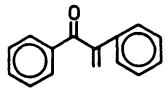
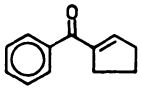
	R^1
a	Cl
b	CH_3
c	CO_2Et
d	C_6H_5

The electrochemical reduction of tetrachloromethane (**1a**) in the presence of carbonyl compounds produces trichloromethylcarbinols **5**[5a,b] and trichloroethane (**1b**) also forms analogous adducts in 19 to 34% yield.[6] The cathodic addition of ethyl trichloroacetate (**1c**) to cyclopentanone leads to a ring expansion to 2-chloro-2-(ethoxycarbonyl)cyclohexanone,[5a,6] this rearrangement points to 2-chlorooxirane **6** as intermediate. When **1c** is reduced in the presence of 2-methylpentanal 69% **6** (R^1=CO_2Et, R^2=H, R^3=$CH(CH_3)$-C_3H_7) can be isolated.[7] These results indicate, that the further reaction of **4** depends on R^1. For R^1=Cl, CH_3, **4** is not appreciably further converted. For R^1=CO_2Et an intramolecular nucleophilic substitution seems to be facilitated by the π-bond of the carbonyl group,[8] so that cyclization to **6** becomes the main reaction. To examine this assumption benzylidyne trichloride (**1d**) was reduced in the presence of carbonyl compounds. The addition of the benzyl anion **2d** should lead to **4d**, whose cyclization to **6d** should be favoured by the phenyl group.[8]

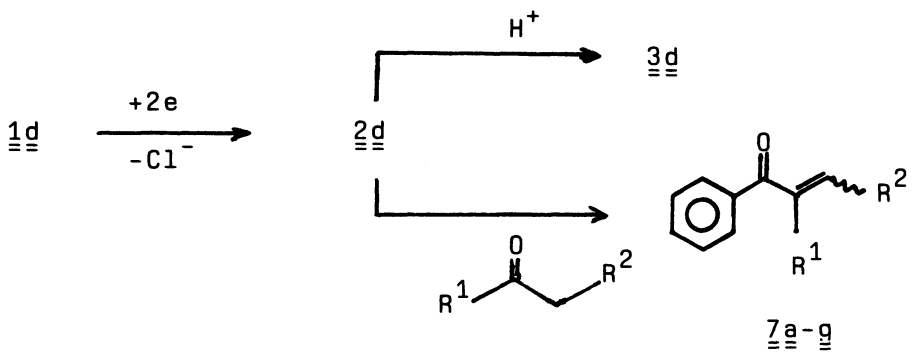
Results and Discussion

Cathodic Addition of Benzylidyne Trichloride (1d) to Ketones.[9] The reduction potential of **1d** was polarographically determined to be −0.8 V vs. Marple (−1.5 V vs. SCE). This is 0.5 V more cathodic than that of **1c**, which indicates that **2d** is more reactive than **2c** and therefore should add also to less reactive ketones. 5 to 10 mmol **1d** were electrolyzed at −0.8 V vs. Marple in the presence of 2 equiv of ketone until total conversion. After usual work up, the α,β-unsaturated ketones **7a—g** (Eq. 2) are isolated in good yields by LC (Table 1). Seen from the point of synthetic methodology, this reaction is a nucleophilic acylation with subsequent dehydration. Ketones are converted in this way to homologated enones.[10] The formation of **3d** at the expense of the wanted **7** is most probably due to protons of the anolyte passing the diaphragm. Addition of NaH to the anolyte and catholyte decreases the formation of **3d** and raises the yield to **7** significantly. The formation of the ketones **7** can be best explained with the 2-chlorooxirane **6d** as intermediate, which subsequently rearranges and eliminates HCl. The carbinol **5d** could be detected in 4% yield at the most. The exclusive cyclization of **4d** to **6d** is promoted besides by the phenyl group by the high nucleophilicity of the tertiary alcohol and the relief of its "back strain". Thermally or Lewis-acid catalyzed rearrangement of 2-halooxiranes to 2-halo ketones was accompanied mostly by migration of halogen. This can occur in a synchronous process via the transition state **8**[11] or via a α-keto carbenium ion **9**.[12] This means **6d** can be converted to **7** either via **8** or **9** and subsequent elimination of HCl (Eq. 3). A

Table 1. Cathodic Addition of Benzylidyne Trichloride (**1d**) to Ketones[a]

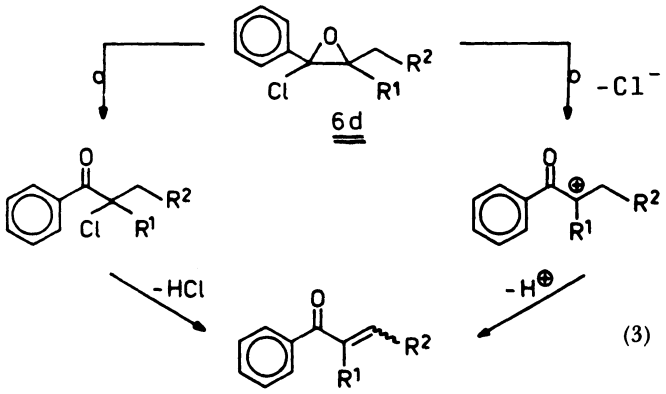
Ketone	Addition product **7**		Yield/%[b] **7**	Yield/%[b] **3d**
		**a** (40)[c]	(48)	(40)
		**b** (60)		
		**c** (70)	59	16
		**d** (30)		
		**e**	65 (34)	23 (59)
		**f**	58 (28)	29 (56)
		**g**	64 (38)	22 (58)

a) Reduction at −0.8 V vs. Marple-electrode in 0.5 mol dm^{-3} $LiClO_4$ in THF with addition of NaH. b) Isolated yields; numbers in parenthesis are yields without addition of NaH. c) Relative yields.



(2)

probe for the intermediacy of **9** should be the addition to norcamphor, where the intermediate 2-oxonorbornyl cation should lead to rearranged products. Reductive addition of **1d** to norcamphor produces the products **13**—**17**. Their formation supports the three equilibrating norbornyl cations **10**—**12** as intermediates (Eq. 4). A synchronous rearrangement of the



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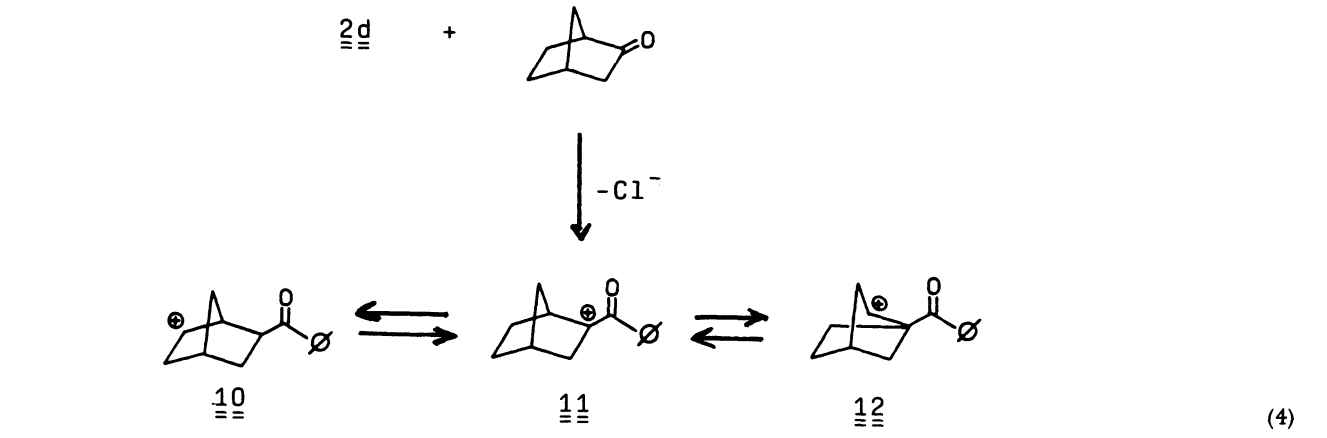

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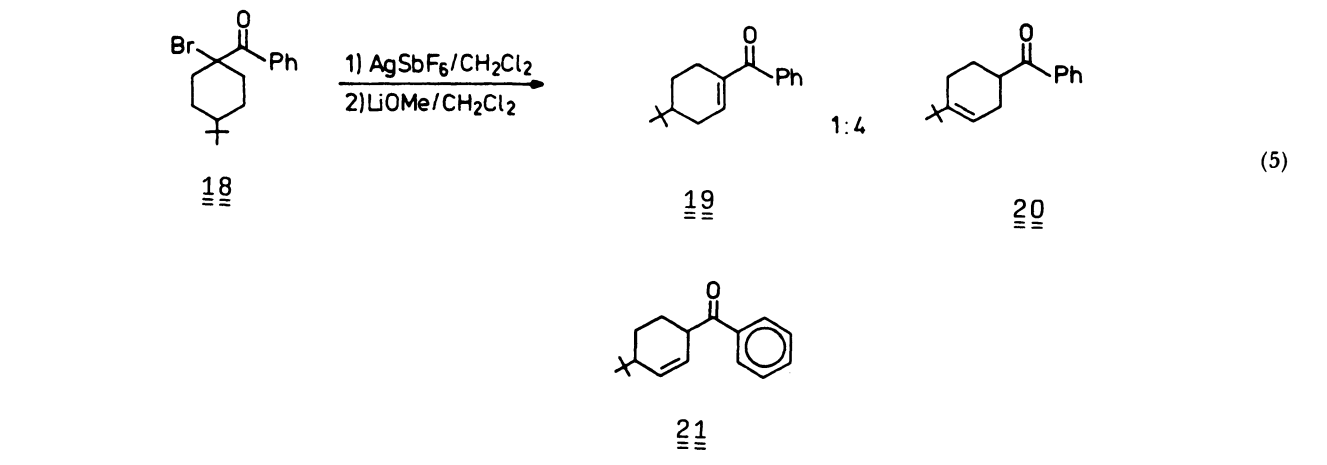


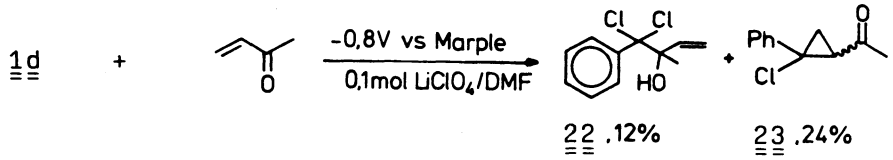
(5)

2-chlorooxirane should have led to **15** and **16** only. The intermediacy of the cations **10** to **12** is further supported by the acetolysis of *exo*-2-benzoyl-*endo*-2-norbornyl mesylate, where via an intermediate 2-benzoylnorbornyl cation acetates, corresponding to **13**, **14**, and **17**, are yielded.[13] A α-keto carbenium ion has been generated from **18** with $AgSbF_6$, its quenching with LiOMe leads to the ketones **19** and **20**.[14] The latter is formed by a transannular hydride shift, which converts the keto carbenium ion to a more stable tertiary carbocation (Eq. 5). Reductive addition of **1d** to 4-*t*-butylcyclohexanone formed, depending on the electrolyte, 21—36% **19**. Two minor products of about 5% yield were detected by GC/MS, whose structures are probably those of the isomers **20** and **21**. The different reaction behaviors could be attributed to the longer lifetime of the 2-keto carbenium ion in the first case, which favors the 1,4-hydride shift prior to deprotonation.

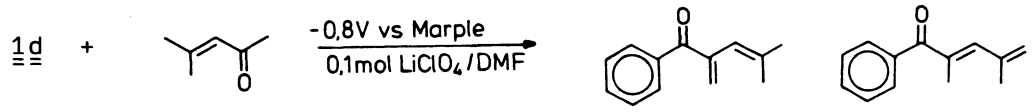
Structure Proofs: The MS spectra of all compounds exhibit besides the base peak *m/z* 105 ($C_6H_5CO^+$) intense M^+ ions. In the IR spectra the carbonyl group conjugated to a phenyl group and a double bond appears between 1660 and 1635 cm^{-1}. The chemical shifts of the olefinic protons in the ^1H NMR are found in the typical region of δ 5.45 to 6.65. The E/Z-isomers of **7b** were assigned using increments,[15] according to which the resonance of the olefinic proton in (*E*)-**7b** is found at higher δ-values. The ^1H NMR of **14** is due to the symmetry of the molecule and small coupling constants without much conclusiveness, but by its ^{13}C NMR the structure could be unambigously assigned. The chlorinated norbornyl compounds **13**, **15**, and **17** are isomers. Here the position of the chloro and the benzoyl substituent could be determined by ^1H NMR.

Cathodic Addition of 1d to α,β-Unsaturated Ketones. When **1d** is reduced as before in 0.1 mol dm^{-3} $LiClO_4$/DMF in the presence of methyl vinyl ketone, besides 8% **3d** the adducts **22** and **23** are isolated in the ratio 1:2 (Eq. 6). The low yields of adduct in spite of minor protonation of **2d** is possibly due to losses through extensive oligomer formation. **22** can be rationalized by 1,2-addition of **2d**, whilst **23** appears to be formed by 1,4-addition and subsequent cyclization. For the cathodic addition of **1c** to acrylonitrile or ethyl acrylate, the formation of analogous cyclopropane derivatives has been reported.[4] To decrease the 1,4-addition by steric shielding of the double bond **1d** was added to mesityl oxide. Although 2F(1F=96480C) mol^{-1} of charge had been passed, 20% of **1d** were recovered on work up, which indicated current consumption in a follow-up reduction of the product. The expected dienones **24**, **25** could be detected in only about 6% yield, main product with 30% was the enone **26** (44% by GLC). The 1,4-adduct **27** decreased to 6% as intended (Eq. 7). The enone **26** originates presumably from either **24**, **25**, or the chlorides **29**, **30**. They should be easily reducible at the applied potential to yield the carbanion **28**, which is protonated to **26** (Eq. 8).

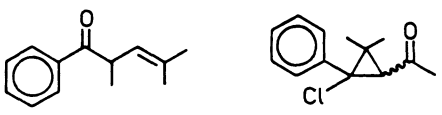
Structure Proofs: For **23** the IR absorption of the carbonyl group at 1710 cm^{-1} and the base peak *m/z*=43 in the mass spectrum indicate the acetyl group. (*Z*)- and (*E*)-**23** can be distinguished by their ^1H NMR. The characteristic changes in the shifts for the E- and Z-isomer can be rationalized by the anisotropy effect of the phenyl ring. The correct



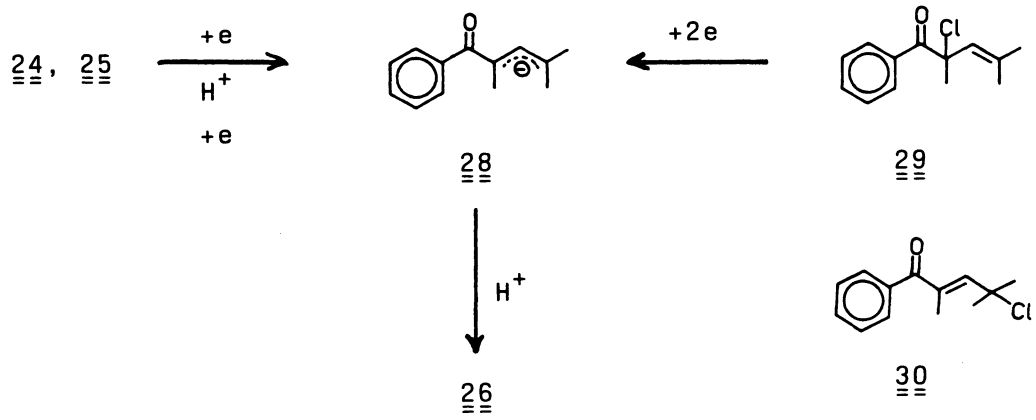
22 ,12% 23 ,24% (6)



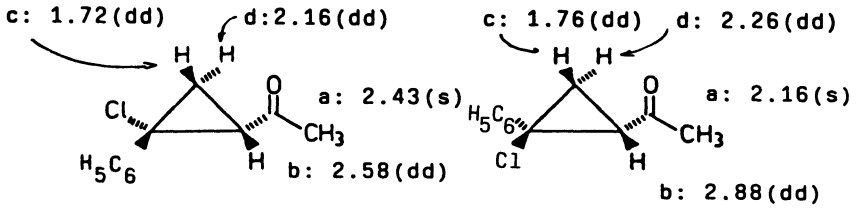
24 25



26 27 (7)



(8)



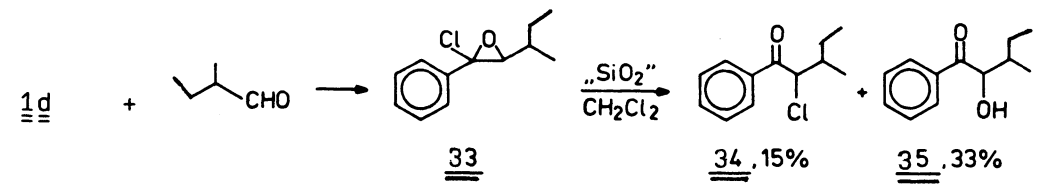
(*Z*)-**23** (*E*)-**23**

assignment was further checked by NOE. The IR spectrum of **26** with the carbonyl absorption at 1680 cm^{-1} indicates that the double bond is not conjugated with the benzoyl group. The assignment is supported by the appearance of two allylic methyl groups at δ 1.65 and 1.70 in the ^1H NMR.

Reductive Addition of 1d to Aldehydes. Reductive additions of **1d** to pentanal yielded the alcohol **31** and the chloro ketone **32** (Eq. 9). The suppressed formation of **3d** (9%) reflects the high reactivity of the aldehyde. The results further demonstrate that not only the π-system of the phenyl group,[8] but also "back strain" in **4** is necessary for the formation of the 2-chlorooxirane. It was therefore expected, that the addition to an α-branched aldehyde should lead to a higher portion of **6**. This proved indeed to be the case. Reduction of **1d** in the presence of 2-methylpentanal led besides a small amount of **3d** to the 2-chloro-oxirane **33** as a main product. Its structure was indicated by the mass spectrum and conversion to **34** and **35** (Eq. 10). Attempts to purify crude **33** by filtration over silica gel let to the α-chloro ketone **34** and the α-hydroxy ketone **35**. This conversion is not surprising, as 2-chlorooxiranes are easily hydrolyzed to mixtures of α-chloro and α-hydroxy ketones.[11b]

Structure Proofs: **31** shows in the mass spectrum the fragment ion m/z=160 from McLafferty-rearrangement. The other part of the molecule can be deduced from an α-cleavage to m/z=87. The structure of **32** is established from its carbonyl absorption at 1685 cm^{-1} in the IR, by the base peak of m/z=105 ($C_6H_5CO^+$) in the MS and the triplet for the chloromethine proton at δ 5.15 in the ^1H NMR. The ^1H NMR spectra for **34** and **35** are very similar. For **34** the chloromethine proton appears as doublet at δ 4.92, the hydroxymethine proton as multiplett between δ 4.87 and 5.16.

(9)



(10)

Experimental

IR spectra were obtained on Perkin-Elmer spectrometers 177 and 421. ^{1}H NMR spectra were recorded on a JEOL PMX 60, Varian HA 100 and Bruker WM 300. ^{13}C NMR spectra were measured on Bruker WH 90 and WM 300 spectrometers. Mass spectra were taken with the Varian instruments SM 1 and CH 7 at 70 eV ionization energy. Combined GC/MS-spectra were taken with the Varian instrument MAT 111. Elemental analyses were performed by M. Beller, Göttingen and on a Perkin-Elmer CHN-analyser. Gas chromatographic analyses were done with a Varian 1400 instrument, a Kipp & Zonen BD 7 recorder and the Minigrator Autolab of Spectra Physics. The following glass columns were used: 1.7 m, d=2 mm, 4% SE 30 on Chromosorb W, and 1.7 m, d=2 mm, 4% OV 225 on Chromosorb W. For TLC silica-gel plates 60 F 254 of Merck were used. HPLC was performed with a Waters 6000 A pump and an U6K injector together with a steel column (d=8 mm, l=50 cm) filled with LiChromosorb Si 60 (7 µm, Fa. Merck). For detection the Knauer differential refractometer type 51.78 coupled with a Abimed recorder Modell 300 was used. Eluent was in all cases CH_2Cl_2. Polarographic measurements were performed with the Bruker polarograph E 310, glass equipment and drop controller E 354 S from Metrohm and the Hewlett-Packard XY-recorder 7045 A; the following conditions were applied: drop time: 1 s, scan time: 10 mV s^{-1}, puls amphitude 50 mV. Preparative electrolyses at controlled potential were performed with the Wenking-potentiostat (3A/60 V). The electrolyses were operated in a double-walled glass cell (150 ml) with a Teflon stopper. Through this the anode compartment (glass tube with G4-frit), Luggin capillary, current feeder for the mercury pool cathode (d=4.5 cm) and nitrogen inlet were inserted. Reference electrode was the Marple electrode.[16] All electrolyses were conducted at 0 °C under nitrogen. The following electrolytes were used for polarography and preparative electrolyses: Electrolyte A: 0.2 mol dm^{-3} $LiClO_4$/DMF; electrolyte B, catholyte: 0.5 mol dm^{-3} $LiClO_4$/THF, 10 mg NaH, anolyte: 0.2 mol dm^{-3} $LiClO_4$/DMF, 10 mg NaH; electrolyte C: as B, but without NaH. For the work-up of the electrolyses, the catholyte was poured into the threefold amount of water, neutralized, extracted with ether (3×50 ml), the ether extracts were washed with water, dried ($MgSO_4$) and the ether was rotaevaporated. Benzene dried *N,N*-dimethylformamide (DMF) was stirred 24 h with P_2O_5, distilled at 18 Torr under nitrogen and stored over molecular sieve (4 Å).

Electrolysis of Benzylidyne Trichloride (1d) in Presence of 2-Butanone. 5 mmol (1.00 g) **1d** and 10 mmol (0.7 g) 2-butanone are electrolyzed in electrolyte A at −0.8 V vs. Marple until total conversion (10 mF). LC-separation of the crude product yielded 330 mg (2 mmol, 40%) **3d** and 390 mg (2.4 mmol, 48%) **7a, b**, which could be separated by analytical HPLC into **7a**, (*Z*)-**7b** and (*E*)-**7b**.

2-Ethyl-1-phenyl-2-propen-1-one (7a): Oil; IR and ^{1}H NMR spectra corresponded to those in the literature.[17]

(*Z*)-2-Methyl-1-phenyl-2-buten-1-one ((*Z*)-7b): Colorless oil; IR (neat 1655 (C=O) cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ=1.54 (d, 3H, ^4J=2 Hz), 1.95 (s, 3H, ^4J=1.5 Hz), 5.77 (q, 1H, ^4J=2 Hz), 7.15—8.05 (m, 5H); MS (70 eV) *m/z* (%) 160 (M$^+$; 32), 159 (28), 145 (38), 105 (100).

(*E*)-2-Methyl-1-phenyl-2-buten-1-one ((*E*)-7b): Oil; IR (neat) 1640 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.87 (d, 3H), 1.97 (s, 3H), 6.41 (q, 1H), 7.34—7.8 (m, 5H). **7b** is reported as E/Z-mixture in lit.[18]

Electrolysis of 1d in Presence of 3-Methyl-2-butanone. 5 mmol **1d** and 10 mmol (0.86 g) 3-methyl-2-butanone are electrolyzed in electrolyte B under efficient stirring at −0.8 V vs. Marple until 10 mF had been consumed. The catholyte is poured into ice water controlling the pH between 6—7 and worked-up. HPLC of the crude product yielded 130 mg (0.8 mmol, 16%) **3d**, 350 mg (2 mmol, 41%) **7c** and 160 mg (0.9 mmol, 18%) **7d**.

2-Isopropyl-1-phenyl-2-propen-1-one (7c): Colorless oil; IR (neat) 1655 (C=O) cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ=1.15 (d, 6H), 2.70—3.30 (m, 1H), 5.45 (s, 1H), 5.70 (s, 1H), 7.2—7.9 (m, 5H); MS (70 eV) *m/z* (%) 174 (M$^+$; 15), 173 (22), 159 (20), 105 (100); Found: C, 82.55; H, 8.15%. Calcd for $C_{12}H_{14}O$ (174.24): C, 82.72; H, 8.09%.

2,3-Dimethyl-1-phenyl-2-buten-1-one (7d): Oil; IR and ^{1}H NMR spectra agree with those in lit.[19]

Electrolysis of 1d in Presence of 3-Pentanone. 5 mmol (1.0 g) **1d** and 10 mmol (0.84 g) 3-pentanone are electrolyzed in electrolyte B or C at −0.8 V vs. Marple until 10 mF are consumed. Work-up of the crude product (1.1 g) and preparative HPLC yielded 490 mg (59%) **3d** and 300 mg (34%) **7e** (electrolyte C) or 190 mg (23%) **3d** and 580 mg (65%) **7e** (electrolyte B). **7d** was a 2:1 E/Z-mixture.

2-Ethyl-1-phenyl-2-buten-1-one (7d): Colorless oil; IR (neat) 1645 (C=O) cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ=1.00 (t, 3H), 1.80 (d, 3H), 2.45 (q, 2H), 6.25 (q, 1H), 7.25—7.75 (m, 5H); MS (70 eV) *m/z* (%) 174 (M$^+$; 20), 173 (20), 145 (81), 105 (100); Found: C, 82.64; H, 8.12%. Calcd for $C_{12}H_{14}O$ (174.24): C, 82.72; H, 8.09%.

Electrolysis of 1d in Presence of Acetophenone: As described above 5 mmol (1.0 g) **1d** were reduced in presence of 10 mmol (1.2 g) acetophenone to yield after HPLC 450 mg (56%) **3d** and 290 mg (28%) **7f** (electrolyte A) or 230 mg (29%) **3d**, 600 mg (58%) **7f** (electrolyte B). To prevent polymer formation solvents were rotaevaporated at room temp. The IR and ^{1}H NMR data of **1,2-diphenyl-2-propen-1-one (7f)**, oil, correspond to those in lit.[20]

Electrolysis of 1d in Presence of Cyclopentanone: 5 mmol (1 g) **1d** and 10 mmol (0.85 g) cyclopentanone are electrolyzed as above to afford after HPLC 450 mg (56%) **3d** and 310 mg (36%) **7g** (electrolyte A) or 170 mg (22%) **3d** and 550 mg (64%) **7g** (electrolyte B).

1-Benzoyl-1-cyclopentene (7g): Oil; IR and ^{1}H NMR spectra agree with those reported in lit.[21]

Electrolysis of 1d in Presence of Norcamphor: 10 mmol (2.0 g) **1d** and 20 mmol (2.2 g) norcamphor are electrolyzed in electrolyte B as above until 20 mF were consumed. HPLC yielded in order of elution: 500 mg (31%) **3d**, 200 mg (8%) **15**, 140 mg (6%) **13**, 400 mg (17%) **17**, 150 mg (8%) **16** and 320 mg (16%) **14**.

2-Benzoyl-6-chlorobicyclo[2.2.1]heptane (13): Oil; IR (neat) 1655 (C=O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ=0.98—1.75 (m, 4H), 2.1—2.28 (m, 2H), 2.46—2.57 (m, 1H), 2.68—2.80 (m, 1H), 3.92—4.04 (m, 1H), 4.54—4.66 (m, 1H), 7.40—7.62 (m, 3H), 7.83—8.04 (m, 2H); MS (70 eV) *m/z* (%): 234 (M$^+$; 4), 198 (17), 105 (100); Anal. by high resolution MS: Found: *m/z* 234.0811. Calcd for $C_{14}H_{15}ClO$: M, 234.0811.

1-Benzoyltricyclo[2.2.1.0^{2,6}]heptane (14): Oil; IR (neat)

1655 (C=O) cm^{-1}; ^1H and ^{13}C NMR correspond to lit;[12] MS (70 eV) *m/z* (%) 198 (M^+; 55), 105 (100); Found: C, 84.60; H, 7.10%. Calcd for $C_{14}H_{14}O$ (198.28): C, 84.81; H, 7.11%.

2-Benzoyl-2-chloro-bicyclo[2.2.1]heptane (15): Oil; IR (neat) 1675 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ=1.05—1.20 (m, 2H), 1.42—1.56 (m, 3H), 2.08—2.20 (m, 1H), 2.20—2.29 (m, 1H), 2.37—2.45 (m, 1H), 2.74—2.83 (m, 1H), 3.00—3.06 (m, 1H), 7.40—7.58 (m, 3H), 8.11—8.18 (m, 2H); MS (70 eV) *m/z* (%) 234 (M^+; 4), 105 (100); Found: C, 71.79; H, 6.68; Cl, 14.92%. Calcd for $C_{14}H_{15}ClO$ (234.7): C, 71.64; H, 6.82; Cl, 15.10%.

2-Benzoylbicyclo[2.2.1]hept-2-ene (16): Oil; IR (neat) 1635 (C=C, C=O) cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ=1.0—2.1 (m, 6H), 3.0—3.25 (m, 1H), 3.40—3.65 (m, 1H), 6.65 (d, 1H), 7.3—7.6 (m, 3H), 7.6—7.8 (m, 2H); MS (70 eV) *m/z* (%) 198 (M^+; 20), 170 (51), 105 (100); Anal. by high resolution MS: Found: *m/z* 198.1041. Calcd for $C_{14}H_{14}O$: M, 198.1044.

1-Benzoyl-2-chlorobicyclo[2.2.1]heptane (17): Oil; IR (neat) 1658 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ=1.28—1.48 (m, 1H), 1.65—2.46 (m, 8H), 4.34—4.50 (m, 1H), 7.35—7.58 (m, 3H), 7.78—7.96 (m, 2H); MS (70 eV) *m/z* (%) 234 (M^+; 7), 105 (100); Found: C, 71.70; H, 6.49; Cl, 14.88%. Calcd for $C_{14}H_{15}ClO$ (234.7): C, 71.64; H, 6.82; Cl, 15.10%.

Electrolysis of 1d in Presence of 4-*t*-Butylcyclohexanone. 5 mmol (1.0 g) **1d** and 10 mmol (1.3 g) 4-*t*-butylcyclohexanone were electrolyzed as above until total conversion in electrolyte A or B. LC (silica gel) afforded 250 mg (21%) **19** in electrolyte A or 430 mg (36%) **19** in electrolyte B. GLC shows about 5% of two double bond isomers of **19** with similar MS spectra.

1-Benzoyl-4-*t*-butyl-1-cyclohexene (19): Oil; IR (neat) 1635 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ=0.92 (s, 9H), 1.15—1.40 (m, 2H), 1.95—2.10 (m, 2H), 2.18—2.38 (m, 2H), 2.65—2.75 (m, 1H), 6.55—6.65 (m, 1H), 7.35—7.55 (m, 3H), 7.60—7.67 (m, 2H); MS (70 eV) *m/z* (%) 242 (M^+; 32), 185 (30), 105 (100); Found: C, 84.00; H, 9.27%. Calcd for $C_{17}H_{22}O$ (242.4): C, 84.25; H, 9.15%.

Electrolysis of 1d in Presence of Methyl Vinyl Ketone. 5 mmol (1.0 g) **1d** and 10 mmol (0.7 g) methyl vinyl ketone are electrolyzed in electrolyte A. Considerable loss of product (40%) during column filtration indicates polymer formation. HPLC yields 80 mg (10%) **3d**, 140 mg (12%) **22**, 80 mg (8%) (*E*)-**23** and 150 mg (16%) (*Z*)-**23**.

1,1-Dichloro-2-methyl-1-phenyl-3-buten-2-ol (22): Oil; IR (neat) 3500 (OH), 1635 (C=C), 995, 935 (C=CH_2) cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ=1.46 (s, 3H), 2.4 (s, 1H), 5.15—5.45 (m, 2H), 6.15 (dd, 1H), 7.20—7.90 (m, 5H); MS (70 eV) *m/z* (%) 159 ($M^+-C_4H_7O$; 8), 71 ($C_4H_7O^+$; 100); Found: C, 57.31; H, 5.51; Cl, 30.13%. Calcd for $C_{11}H_{12}Cl_2O$ (231.1): C, 57.17; H, 5.23; Cl, 30.68%.

1-Acetyl-2-chloro-2-phenylcyclopropane (23): Oil; IR (neat) 3060, 3030 (CH), 1710 (C=O) cm^{-1}; ^1H NMR (*E*-isomer, 300 MHz, $CDCl_3$) δ=1.76 (dd, 1H, *J*=6.3 Hz, *J*=8.5 Hz), 2.16 (s, 3H), 2.26 (dd, 1H, *J*=6.3 Hz, *J*=7.5 Hz), 2.88 (dd, 1H, *J*=7.5 Hz, 8.4 Hz), 7.24—7.40 (m, 5H); ^1H NMR (*Z*-isomer, 300 MHz, $CDCl_3$) δ=1.72 (dd, 1H, *J*=6.5 Hz, 8.6 Hz), 2.16 (dd, 1H, *J*=6.5 Hz, 7.5 Hz), 2.43 (s, 3H), 2.58 (dd, 1H, *J*=7.5 Hz, 8.6 Hz), 7.28—7.50 (m, 5H); MS (70 eV) *m/z* (%) 194 (M^+; 1), 159 (55), 43 (100); Found: C, 68.24; H, 5.76; Cl, 18.77%. Calcd for $C_{11}H_{11}ClO$ (194.7): C, 67.86; H, 5.70; Cl, 18.21%.

Electrolysis of 1d in Presence of 4-Methyl-3-penten-2-one. 7.5 mmol (1.5 g) **1d** and 15 mmol 4-methyl-3-penten-2-one are electrolyzed in electrolyte A until 15 mF are consumed. HPLC yielded 400 mg **1d** and **3d**, 528 mg (44%) **26** and 152 mg of a 1:1:1-mixture of **24**, **25**, **27**.

2,4-Dimethyl-1-phenyl-3-penten-1-one (26): Oil; IR (neat) 1680 (C=O) cm^{-1}; ^1H NMR spectrum corresponds to that reported in lit.[22]

4-Methyl-2-methylene-1-phenyl-3-penten-1-one (24): MS (70 eV) *m/z* (%) 186 (M^+; 23), 185 (20), 105 (100).

2,4-Dimethyl-1-phenyl-2,4-pentadien-1-one (25): MS (70 eV) *m/z* (%) 186 (M^+; 23), 185 (50), 171 (100), 105 (81).

1-Acetyl-2-chloro-3,3-dimethyl-2-phenylcyclopropane (27): MS (70 eV) *m/z* (%) 186 (M^+—HCl; 31), 179 (65), 43 (100).

Electrolysis of 1d in Presence of Pentanal. 10 mmol (2.0 g) **1d** are electrolyzed in presence of 20 mmol (1.72 g) pentanal. HPLC of the crude product (1.63 g) led to 140 mg (8.5%) **3d**, 480 mg (23%) **32** and 600 mg (24%) **31**.

1,1-Dichloro-1-phenyl-2-hexanol (31): Oil; IR (neat) 3400 (OH) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ=0.84 (t, 3H), 1.16—1.44 (m, 4H), 1.44—1.66 (m, 2H), 4.10 (dd, 1H), 7.32—7.80 (m, 5H); MS (70 eV) *m/z* 210 (M^+—HCl; 5); **31** (+TMS—H) MS (70 eV) *m/z* (%) 303 (M^+—15; 1); Anal. by high resolution MS, Found: *m/z* 303.0739. Calcd for $C_{15}H_{24}Cl_2OSi$: $M-CH_3$ 303.0739.

2-Chloro-1-phenyl-1-pentanone (32): Oil; IR (neat) 1685 (C=O) cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ=0.93 (t, 3H), 1.28—1.67 (m, 4H), 1.83—2.30 (m, 2H), 5.15 (t, 1H), 7.28—8.20 (m, 5H); MS (70 eV) *m/z* (%) 210 (M^+; 3), 105 (100); Found: C, 68.49; H, 7.21; Cl, 16.97%. Calcd for $C_{12}H_{15}ClO$ (210.7): C, 68.40; H, 7.18; Cl, 16.82%.

Electrolysis of 1d in Presence of 2-Methylpropanal. 10 mmol (2.0 g) **1d** and 20 mmol (1.4 g) isobutyraldehyde were electrolyzed until conversion. GLC shows besides a small amount of **3d** about 60% **33**, attempted purification of **33** by filtration over silica converts it into **34** and **35**. HPLC afforded 130 mg (8%) **3d**, 290 mg (15%) **34**, and 590 mg (33%) **35**.

2-Chloro-3-methyl-1-phenyl-1-butanone (34): Oil; IR and ^1H NMR spectra agree with those in lit.[23] Found: C, 67.31; H, 6.64; Cl, 18.18%. Calcd for $C_{11}H_{13}OCl$ (196.7): C, 67.18; H, 6.66; Cl, 18.03%.

2-Hydroxy-3-methyl-1-phenyl-1-butanone (35): Oil; IR (neat) 3450 (OH), 1675 (C=O) cm^{-1}; ^1H NMR spectrum agreed with this in lit.[24]

1-Chloro-2-isopropyl-1-phenyloxirane (33): MS (70 eV) *m/z* (%) 196 (M^+; 3), 124 ($M^+-C_4H_8O$; 40), 105 (100).

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