

Cathodic Addition of Benzylidyne Trichloride to Ketones and Aldehydes¹⁾

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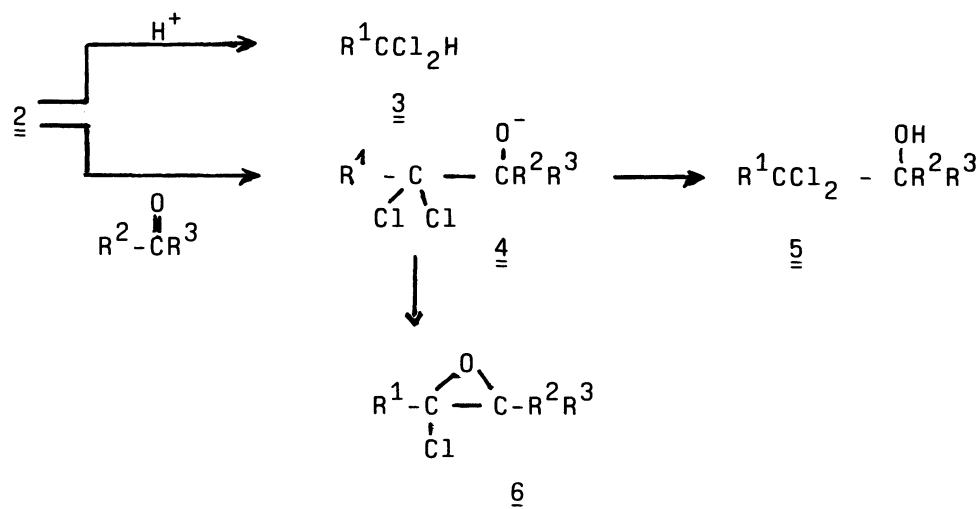
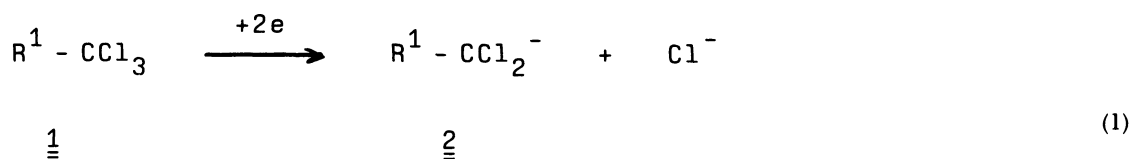
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Ketones are converted to homologated enones **7a—g** in good yields by cathodic addition of benzylidyne trichloride (**1d**). As intermediates α -chlorooxiranes **6** are assumed, which rearrange via α -keto carbenium ions **9** to enones. The intermediacy 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 compounds⁵⁾ have been used.



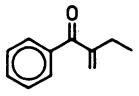
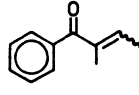
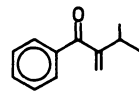
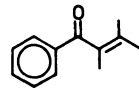
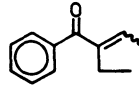
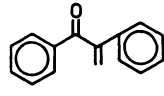
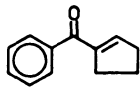
	R ¹
a	Cl
b	CH ₃
c	CO ₂ Et
d	C ₆ H ₅

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 (R¹=CO₂Et, R²=H, R³=CH(CH₃)-C₃H₇) can be isolated.⁷ These results indicate, that the further reaction of 4 depends on R¹. For R¹=Cl, CH₃, 4 is not appreciably further converted. For R¹=CO₂Et 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

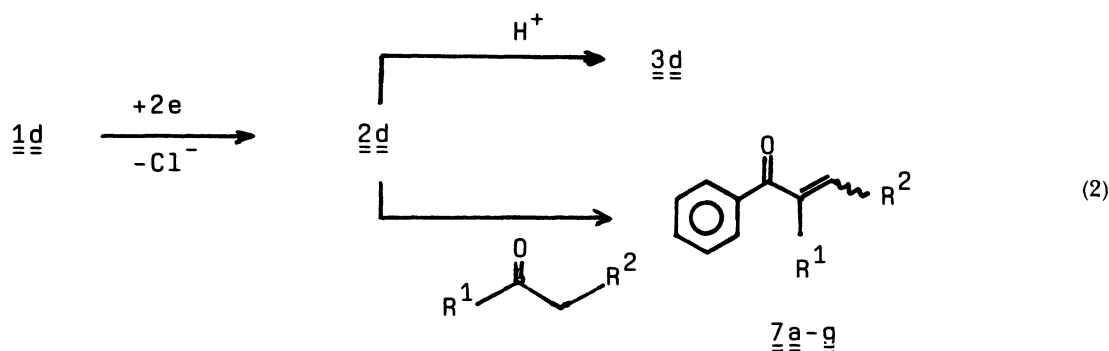
Cathodic Addition of Benzylidyne Trichloride (1d) to Ketones.⁹ The reduction potential of 1d was polarographically determined to be -0.8 V vs. Marple (-1.5 V vs. SCE). This is 0.5 V more cathodic than that of 1c, which indicates that 2d is more reactive than 2c and therefore should add also to less reactive 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

Table 1. Cathodic Addition of Benzylidyne Trichloride (1d) to Ketones^a

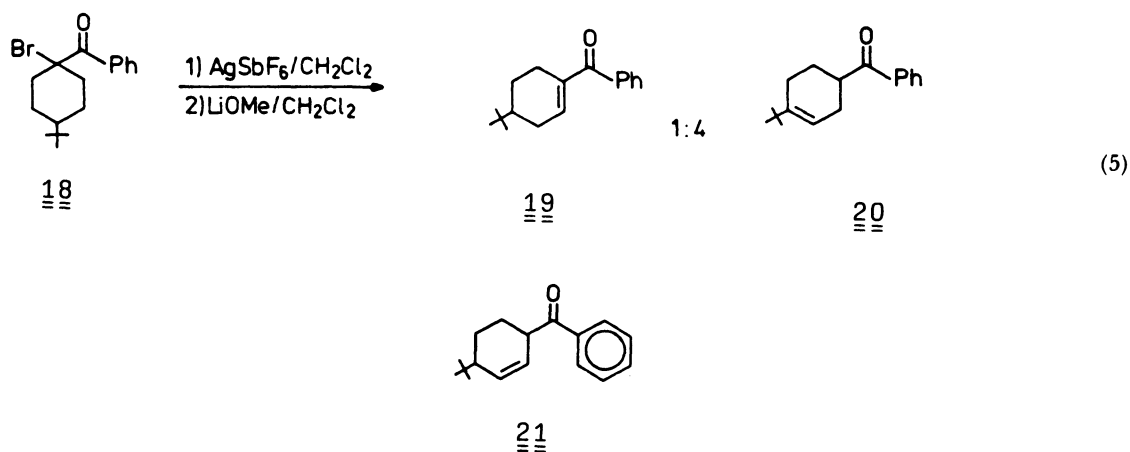
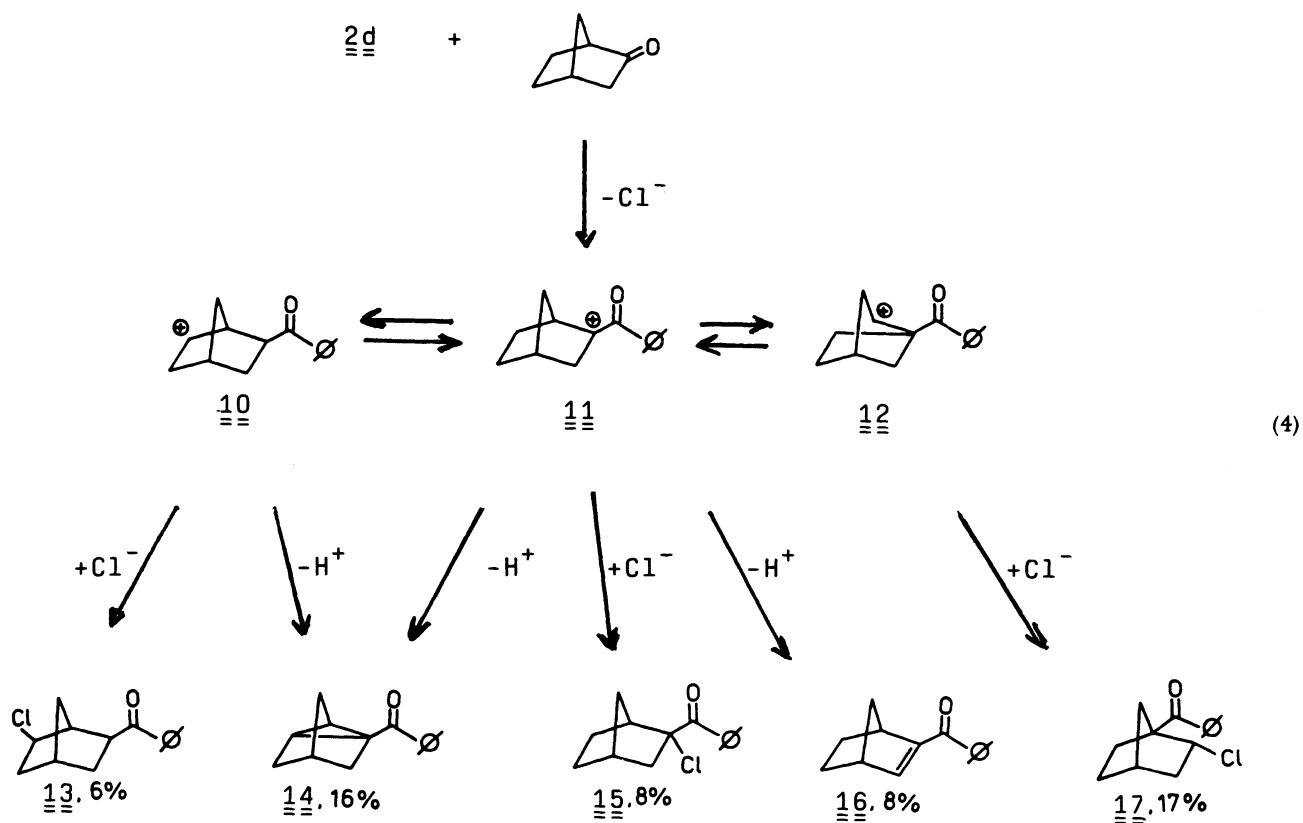
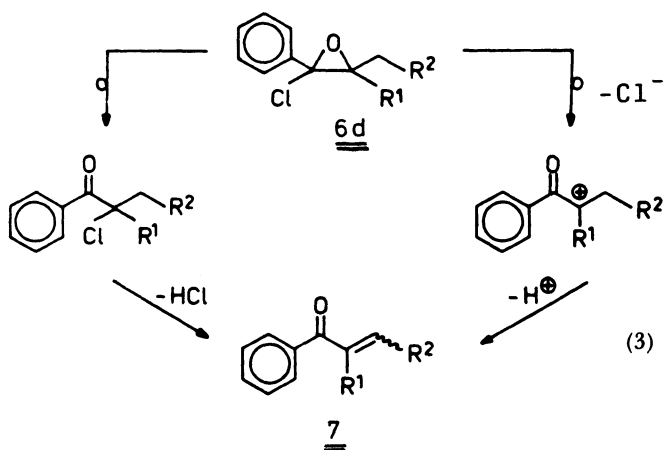
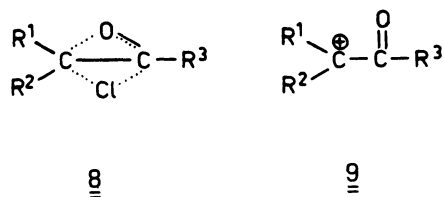
Ketone	Addition product 7		Yield/% ^b	
			7	3d
		a (40) ^c	(48)	(40)
		b (60)		
		c (70)	59	16
		d (30)		
		e	65 (34)	23 (59)
		f	58 (28)	29 (56)
		g	64 (38)	22 (58)

a) Reduction at -0.8 V vs. Marple-electrode in 0.5 mol dm⁻³ LiClO₄ in THF with addition of NaH. b) Isolated yields; numbers in parenthesis are yields without addition of NaH. c) Relative yields.

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 8¹¹ 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



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



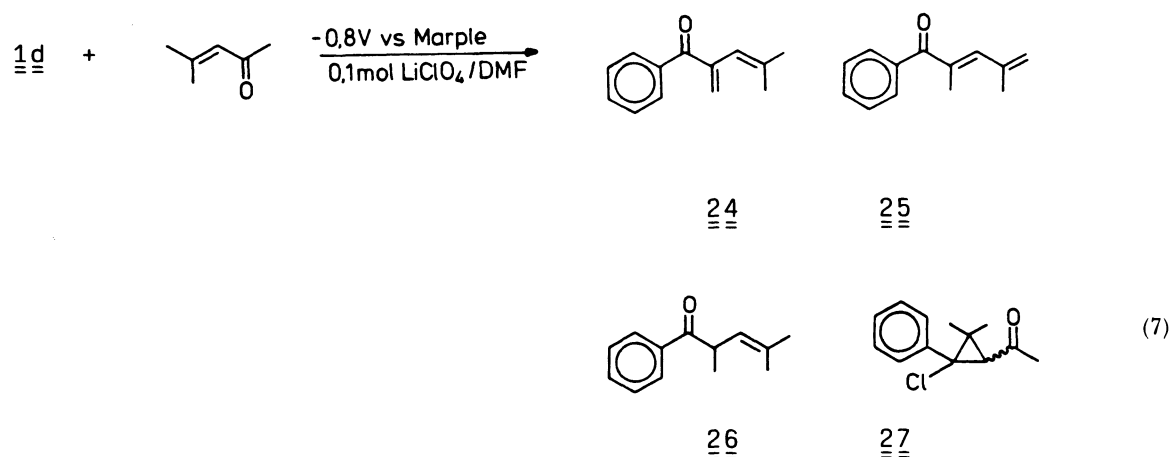
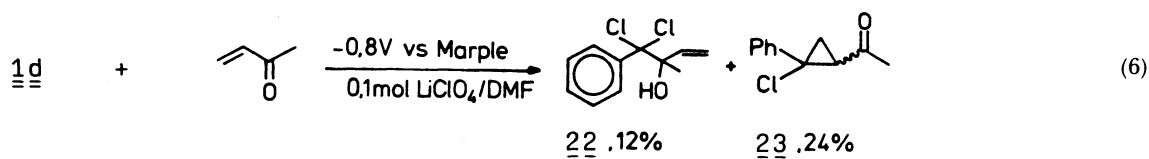
2-chlorooxirane should have led to **15** and **16** only. The intermediacy of the cations **10** to **12** is further supported by the acetolysis of *exo*-2-benzoyl-*endo*-2-norbornyl mesylate, where via an intermediate 2-benzoylnorbornyl cation acetates, corresponding to **13**, **14**, and **17**, are yielded.¹³ A α -keto carbenium ion has been generated from **18** with AgSbF₆, 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.

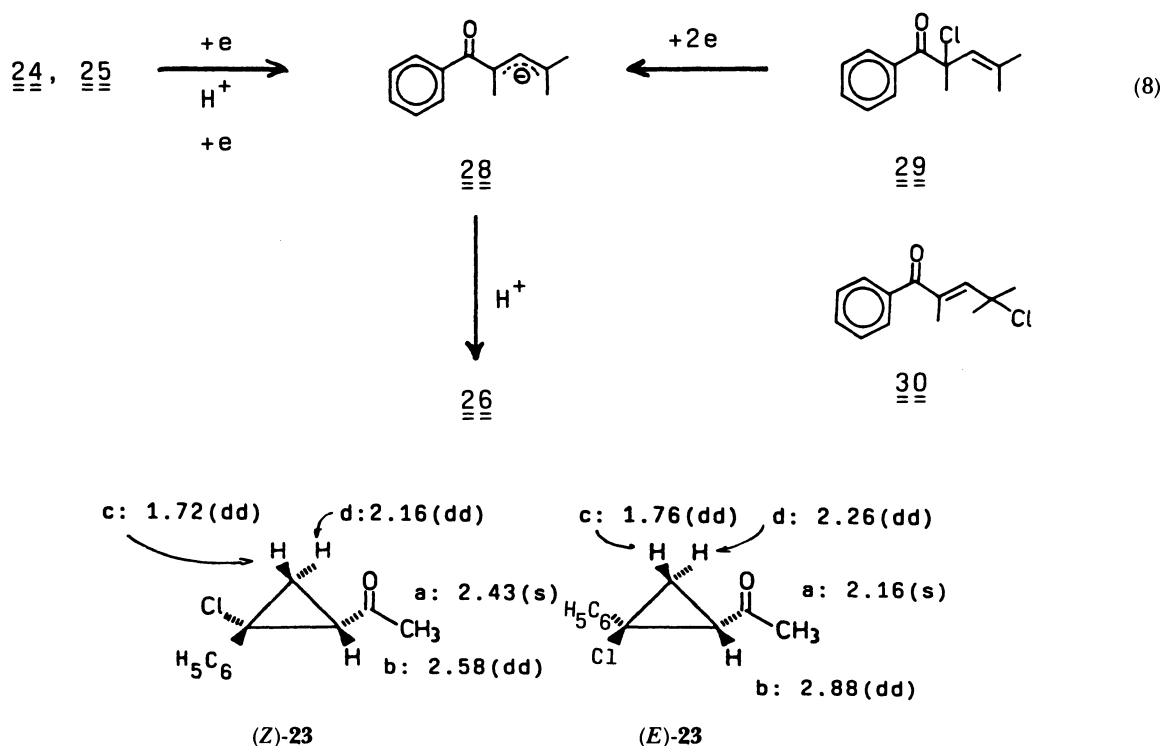
Structure Proofs: The MS spectra of all compounds exhibit besides the base peak m/z 105 (C₆H₅CO⁺) intense M⁺ ions. In the IR spectra the carbonyl group conjugated to a phenyl group and a double bond appears between 1660 and 1635 cm⁻¹. The chemical shifts of the olefinic protons in the ¹H NMR are found 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 ¹³C NMR the structure could be unambiguously 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 LiClO₄/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



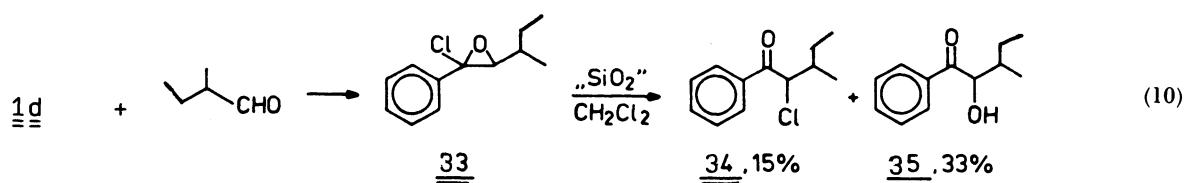
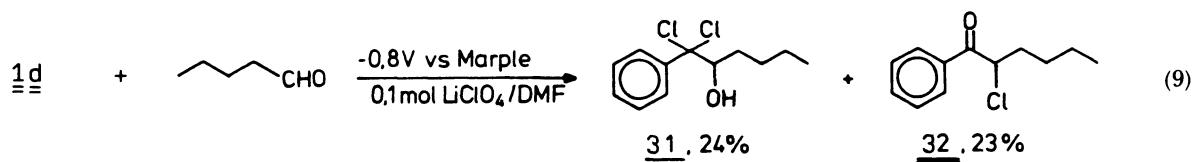


assignment was further checked by NOE. The IR spectrum of **26** with the carbonyl absorption at 1680 cm^{-1} indicates that the double bond is not conjugated with the benzoyl group. The assignment is supported by the appearance of two allylic methyl groups at δ 1.65 and 1.70 in the ^1H NMR.

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,⁹ 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-chlorooxirane **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 led 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 $m/z=105$ ($\text{C}_6\text{H}_5\text{CO}^+$) 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.



Experimental

IR spectra were obtained on Perkin-Elmer spectrometers 177 and 421. ^1H 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 LiChrosorb 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 amplitude 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} $\text{LiClO}_4/\text{DMF}$; electrolyte B, catholyte: 0.5 mol dm^{-3} $\text{LiClO}_4/\text{THF}$, 10 mg NaH, anolyte: 0.2 mol dm^{-3} $\text{LiClO}_4/\text{DMF}$, 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 $\times$ 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 Benzyldiyne 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 ^1H 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 ($\text{C}=\text{O}$) cm^{-1} ; ^1H NMR (60 MHz, CDCl_3) $\delta=1.54$ (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 ($\text{C}=\text{O}$) cm^{-1} ; ^1H NMR (CDCl_3) $\delta=1.87$ (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 ($\text{C}=\text{O}$) cm^{-1} ; ^1H NMR (60 MHz, CDCl_3) $\delta=1.15$ (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 $\text{C}_{12}\text{H}_{14}\text{O}$ (174.24): C, 82.72; H, 8.09%.

2,3-Dimethyl-1-phenyl-2-buten-1-one (7d): Oil; IR and ^1H 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 ($\text{C}=\text{O}$) cm^{-1} ; ^1H NMR (60 MHz, CDCl_3) $\delta=1.00$ (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 $\text{C}_{12}\text{H}_{14}\text{O}$ (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 ^1H 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 ^1H 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 ($\text{C}=\text{O}$) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) $\delta=0.98$ –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 $\text{C}_{14}\text{H}_{15}\text{ClO}$: 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 $\text{C}_{14}\text{H}_{14}\text{O}$ (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 $\text{C}_{14}\text{H}_{15}\text{ClO}$ (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 $\text{C}_{14}\text{H}_{14}\text{O}$: 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 $\text{C}_{14}\text{H}_{15}\text{ClO}$ (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 $\text{C}_{17}\text{H}_{22}\text{O}$ (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=CH₂) 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^+ –C₄H₇O; 8), 71 (C₄H₇O⁺; 100); Found: C, 57.31; H, 5.51; Cl, 30.13%. Calcd for $\text{C}_{11}\text{H}_{12}\text{Cl}_2\text{O}$ (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 $\text{C}_{11}\text{H}_{11}\text{ClO}$ (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 $\text{C}_{15}\text{H}_{24}\text{Cl}_2\text{OSi}$: M–CH₃ 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 $\text{C}_{12}\text{H}_{15}\text{ClO}$ (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 $\text{C}_{11}\text{H}_{13}\text{OCl}$ (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^+ –C₄H₈O; 40), 105 (100).

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References

- 1) Electroorganic synthesis, 36; Part 35: R. Michaelis, U. Müller, and H. J. Schäfer, *Angew. Chem., Int. Ed. Engl.*, **26**, 1023 (1987).
- 2) J. Casanova and L. Ebersson, "Chemistry of the Carbon–Halogen Bond," ed by S. Patai, Interscience, New York (1974), Chapt. 15.
- 3) M. Nagao, N. Sato, T. Akashi, and T. Yoshida, *J. Am. Chem. Soc.*, **88**, 3447 (1966).

- 4) M. M. Baizer and J. L. Chruma, *J. Org. Chem.*, **37**, 1951 (1972).
 - 5) a) F. Karrenbrock and H. J. Schäfer, *Tetrahedron Lett.*, **1978**, 1521; b) T. Shono, N. Kise, and T. Suzumoto, *J. Am. Chem. Soc.*, **106**, 259 (1984); T. Shono, N. Kise, M. Masuda, and T. Suzumoto, *J. Org. Chem.*, **50**, 2527 (1985). c) F. Karrenbrock, H. J. Schäfer, and I. Langer, *Tetrahedron Lett.*, **1979**, 2915; J. M. van Tilborg and C. J. Smit, *Recl. Trav. Chim. Pays-Bas*, **99**, 202 (1980).
 - 6) M. Steiniger, Masters thesis, Universität Münster 1980.
 - 7) M. Steiniger, Ph. D. Thesis, Universität Münster, 1984.
 - 8) R. W. Alder, R. Baker, and J. M. Brown, "Mechanism in Organic Chemistry," Wiley (1971), p. 198.
 - 9) Preliminary Communication: M. Steiniger and H. J. Schäfer, *Angew. Chem., Int. Ed. Engl.*, **21**, 79 (1982); *Angew. Chem. Suppl.*, **1982**, 137.
 - 10) For other procedures effecting this conversion see D. F. Taber and B. P. Gunn, *J. Org. Chem.*, **44**, 450 (1978) and there Ref. 1.
 - 11) a) A. Kirrmann, P. Duhamel, and R. Nouri-Bimorghi, *Bull. Soc. Chim. Fr.*, **1964**, 3264; *Justus Liebigs Ann. Chem.*, **691**, 33 (1966); b) A. Kirrmann and R. Nouri-Bimorghi, *Bull. Soc. Chim. Fr.*, **1968**, 3213.
 - 12) R. N. McDonald, "Mechanisms of Molecular Migrations," Wiley, New York (1971); Vol. 3, p. 67; R. N. McDonald and Th. E. Tabor, *J. Am. Chem. Soc.*, **89**, 6573 (1967); J. P. Begue and M. Charpentier-Morize, *Acc. Chem. Res.*, **13**, 207 (1980).
 - 13) X. Creary and C. C. Geiger, *J. Am. Chem. Soc.*, **104**, 4151 (1982).
 - 14) J. P. Begue, M. Charpentier-Morize, and C. Pardo, *Tetrahedron*, **31**, 1919 (1975).
 - 15) U. E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon, and S. Sternhell, *Tetrahedron*, **25**, 691 (1969).
 - 16) L. W. Marple, *Anal. Chem.*, **39**, 844 (1967).
 - 17) H. O. House, W. C. McDonald, R. F. Sieloff, and D. Vanderweer, *J. Org. Chem.*, **43**, 4316 (1978).
 - 18) G. Dana, Sa le Thi Thuan, and J. Gharbi Benarous, *Bull. Soc. Chim. Fr.*, **1974**, 2089.
 - 19) L. E. Friedrich and R. A. Fiato, *J. Am. Chem. Soc.*, **96**, 5783 (1974).
 - 20) L. E. Friedrich and R. A. Fiato, *J. Org. Chem.*, **39**, 416 (1974).
 - 21) A. B. Smith III and W. C. Ajosta, *J. Am. Chem. Soc.*, **95**, 4313 (1973).
 - 22) A. J. A. van der Weerd and H. Certontain, *J. Chem. Soc., Perkin Trans. 2*, **1980**, 592.
 - 23) G. A. Russell, B. Mudryk, M. Jawdosink, and Z. Wrobel, *J. Org. Chem.*, **47**, 1879 (1982).
 - 24) S. Hünig and G. Wehner, *Chem. Ber.*, **112**, 2062 (1979).
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