1,2,4,6-Tetramethylpyridinium perchlorate (160 mg) was irradiated for 17 hr in 40 ml of methanol-*O-d*. Removal of the solvent and recrystallization of the residue from methanol gave 155 mg (97%) of the starting material, mp 196–202° (lit.[33] 204.5–205.5°). No detectable deuterium incorporation in the 2-, 4-, and 6-methyl groups was observed as confirmed by the integration value of the nmr spectrum using the β-aryl hydrogens and the *N*-methyl group as internal standards.

Attempted trapping of a photoenol from 31b was carried out by irradiating the salt (2.20 g, 6.0 mmol) in the presence of dimethyl acetylenedicarboxylic acid (0.63 g, 6 mmol) in 300 ml of a 1:1 mixture of *tert*-butyl alcohol and water. (This medium, in which photoinduced deuterium incorporation in the 2- and 6-methyls also occurred, was chosen expecially to prevent photoreduction.) The experiment was followed by uv and glc. Although glc analysis demonstrated that the acetylenic ester was consumed during the irradiation, no changes were observed in the uv absorptions of the solute. The residue, obtained after 24 hr of irradiation and evaporation of the solvent, showed only resonances corresponding to those of the starting material.

Acknowledgment. We express our gratitude to Mr. C. Kruk of the University of Amsterdam for carrying out many of the 100-MHz nmr experiments.

Empirical Rules for Estimating the Reduction Potential of α,β-Unsaturated Carbonyl Compounds[1]

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Abstract: The polarographic reduction potentials (*vs.* sce) for a series of α,β-unsaturated carbonyl compounds have been measured in the aprotic solvent, dimethylformamide. For a variety of cyclic or acyclic aldehydes, esters, and ketones, a simple set of empirical rules (Table I) serves to predict within ±0.1 V the reduction potentials for compounds, $R_3R_4C{=}CR_2COR_1$, as the position and nature of the substituents are varied among the series R = H, alkyl, alkoxy, or phenyl.

A knowledge of the reduction potentials of α,β-unsaturated carbonyl compounds *in aprotic media* can be of considerable value both for assessing the feasibility of performing selective reductions of these conjugated systems with dissolving metals or electrochemically[2] and for determining whether these unsaturated systems will be suitable substrates for the conjugate addition of lithium dialkylcuprates and possibly other organometallic reagents.[3] Although several compilations of polarographic reduction potentials are available,[4] most of the data pertain to reductions in protic media (typically ethanol or aqueous dioxane) where the reduction potentials of unsaturated carbonyl compounds are substantially less negative than in the aprotic media.[4c,5] However, the reduction potentials in aprotic media are the appropriate values to employ for reactions involving organometallic reactants, reductions with alkali metals, and many electrochemical reductions.

For this reason, we have measured the polarographic $E_{1/2}$ values (*vs.* sce) for *ca.* 10^{-3} *M* solutions of a number of representative α,β-unsaturated aldehydes, ketones, and esters in dimethylformamide (DMF) containing 0.5 *M* tetraalkylammonium salt (either $n\text{-}Pr_4NClO_4$ or $n\text{-}Bu_4NBF_4$) as a supporting electrolyte. Although the lifetimes of the anion radicals formed in these reductions may be markedly diminished by the presence of low concentrations (10^{-1}–10^{-3} *M*) of proton donors (t-BuOH, H_2O) or lithium salts,[5] the $E_{1/2}$ values of the unsaturated carbonyl compounds studied become only slightly (0.1 V or less) more positive under these circumstances. Thus, no serious error is being introduced in these polarographic reduction potentials even when competing protonation of the anion radicals *in the reaction solution* is preventing their formation under truly reversible conditions.[6]

The polarographic $E_{1/2}$ values obtained for α,β-unsaturated carbonyl compounds in measurements reported here and in an earlier paper[5] are summarized in Table II. As noted elsewhere,[7] these reduction potential values provide a measure of the energy difference between an anion radical **2** with an extra electron in the lowest antibonding molecular orbital (*i.e.*, the π^* orbital) and the unsaturated carbonyl system **1**.

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[1] This research has been supported by Public Health Service Grant No. 7-RO1-CA-12634 from the National Cancer Institute.

[2] For recent reviews, see (a) M. Smith in "Reduction," R. L. Augustine, Ed., Marcel Dekker, New York, N. Y., 1968, pp 95–170; (b) H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, pp 145–227.

[3] H. O. House and M. J. Umen, *J. Amer. Chem. Soc.*, **94**, 5495 (1972).

[4] (a) M. Kotake, Ed., "Constants of Organic Compounds," Asakura Publishing Co., Ltd., Tokyo, 1963, pp 680–693; (b) L. Meites, "Polarographic Techniques," 2nd ed, Wiley-Interscience, New York, N. Y., 1965, pp 671–711; (c) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York, N. Y., 1970, pp 177–189.

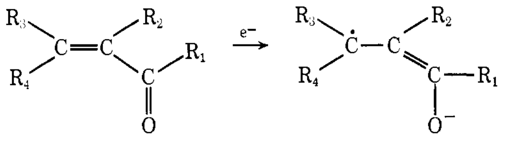
[5] K. W. Bowers, R. W. Giese, J. Grimshaw, H. O. House, N. H. Kolodny, K. Kronberger, and D. K. Roe, *J. Amer. Chem. Soc.*, **92**, 2783 (1970).

[6] This assumption is probably not valid for measurements of the $E_{1/2}$ values for certain unsubstituted vinyl and ethynyl carbonyl compounds such as acrolein ($E_{1/2}$ −1.73, αn = 0.3), 1-butyn-3-one ($E_{1/2}$ −1.79, αn = 0.6), and methyl vinyl ketone ($E_{1/2}$ = −1.97, αn = 0.5). In these cases, it seems likely that the anion radical reacts with a second molecule of the highly reactive starting unsaturated carbonyl compound before it has diffused from the electrode surface resulting in an apparent $E_{1/2}$ value which is more positive than the reversible value by 0.1–0.3 V. For recent reviews, see J. D. Anderson, J. P. Petrovich, and M. M. Baizer, *Advan. Org. Chem.*, **6**, 257 (1969); M. M. Baizer and J. P. Petrovich, *Progr. Phys. Org. Chem.*, 7, 189 (1970). Presumably, a related phenomenon, protonation of the anion radical before it diffuses from the electrode surface, accounts for the significantly less negative $E_{1/2}$ values observed when α,β-unsaturated carbonyl compounds are reduced in media containing high concentrations of proton donors.

[7] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, pp 173–185.

Just as it is possible to correlate the positions of ultraviolet maxima (corresponding to promotion of an electron from a π to a π^* molecular orbital) in α,β-unsaturated ketones with number and type of substituents present,[8] a correlation of reduction potentials (**1** → **2**) with the number and nature of R substituents was also to be expected.[9] In fact, the rather simple set of empirical rules summarized in Table I provided estimates of the reduction potentials for α,β-unsaturated aldehydes, ketones, and esters that agreed with the measured values (Table II) to within ±0.1 V. Although we found that more elaborate correlation schemes involving a larger number of numerical parameters would narrow the range of agreement between calculated and measured values to *ca.* ±0.05 V, the extra complexity involved led us to reject these more elaborate correlations in favor of the simple scheme presented in Table I.

Table I. Empirical Rules for Estimating Reduction Potentials *vs.* sce in Aprotic Media



1 **2**

base value ($R_1 = R_2 = R_3 = R_4 = H$), −1.9 V

Substituent	Increment for reduction potential, V R_1	 R_2	 R_3 or R_4
Alkyl group	−0.1	−0.1	−0.1
First alkoxy group	−0.3	0	−0.3
First phenyl group	+0.4	+0.1	+0.4

The destabilizing effect of alkyl substituents (−0.1 V) was small, additive, and appeared to be independent of the location of the alkyl group. The destabilizing effect of the more polar alkoxy substituents (−0.3 V at R_1, R_3, or R_4) was larger when these substituents were located at the carbonyl carbon or β-carbon atom; however, in the limited number of cases examined with an alkoxy substituent at the α carbon, this substituent had practically no effect on the reduction potential. This result is compatible with both the prediction from simple molecular orbital theory that the first antibonding molecular orbital of an enone will have a node located near the α carbon and with the observed epr spectra of several enone anion radicals which indicate a relatively low electron density at the α carbon.[5,10] The stabilizing effect of the first phenyl substituent was substantial (+0.4 V) and of similar magnitude at any of the locations R_1, R_3, or R_4. The presence of additional phenyl substituents at these locations had little further influence on the reduction potential even in cases where there would be no serious steric barrier to having at least two phenyl substituents coplanar with the enone system. However, as with the alkoxy substituents, the effect of a phenyl substituent at the α carbon atom (*i.e.*, R_2) was relatively small (+0.1 V). These empirical rules are apparently applicable both to α,β-unsaturated carbonyl compounds that exist in the usual transoid conformation and to compounds that for steric reasons exist principally in a cisoid conformation.

Finally, we note that from the limited number of measurements (Table III) involving α,β-unsaturated nitriles and α,β-acetylenic carbonyl compounds, a comparable correlation will probably be applicable to these materials. A base value of −1.8 V with the same incremental values listed in Table I would appear to be appropriate for the system $R_3C{\equiv}CCOR_1$; similarly, a base value of −2.3 V seems appropriate for the system $R_3(R_4)C{=}C(R_2)C{\equiv}N$.

Experimental Section[11]

Preparation of Unsaturated Carbonyl Compounds. Commercial samples of carbonyl compounds **3**, **19**, **23**, **30**, **31**, **32**, and **39** were employed. The preparation and properties of the following unsaturated compounds have been described elsewhere: **4**,[12] **5**,[12] **6**,[13] **7**,[13] **8**,[13] **9**,[14] **10**,[15] **11**,[15] **12**,[15] **13**,[16] **14**,[17] **18**,[18] **20**,[19] **24**,[20] **25**,[21] **26**,[22] **27**,[22] **28**,[22] **29**,[22,23] **33**,[24] **34**,[25] **35**,[26] **36**,[27] and **38**.[14] A sample of the lithium carboxylate **12** (R = Li) was obtained by reaction of 2.11 mmol of the acid **12** (R = H) with 2.28 mmol of LiOH in MeOH; the resulting mixture was concentrated and then dried under reduced pressure. The same procedure was followed to prepare the lithium carboxylate **15** (R = Li).

A mixture of 5.207 g (46.3 mmol) of the acid **15** (R = H), 6.6 g (46 mmol) of $BF_3 \cdot OEt_2$,[28] and 14.88 g (465 mmol) of MeOH was refluxed for 22.5 hr, concentrated, and then diluted with Et_2O and stirred with aqueous $NaHCO_3$ for 1 hr. The organic layer was washed successively with aqueous $NaHCO_3$ and aqueous NaCl and then dried and concentrated. Distillation of the residual liquid afforded 3.269 g (56%) of the ester **15** (R = CH_3) as a colorless liquid: bp 35–86° (40 mm); $n^{25}D$ 1.4389 [lit.[29] bp 65° (10 mm),

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(8) For reviews, see (a) L. F. Fieser and M. Fieser, "Steroids," Reinhold, New York, N. Y., 1959, pp 15–24; (b) D. J. Pasto and C. R. Johnson, "Organic Structure Determination," Prentice-Hall, Englewood Cliffs, N. J., 1969, pp 83–108.

(9) We have examined briefly a possible correlation between our reduction potentials (Table II) and the ultraviolet absorption maxima for these materials. No useful correlation was evident.

(10) (a) G. A. Russell and G. R. Stevenson, *J. Amer. Chem. Soc.*, **93**, 2432 (1971); (b) I. H. Elson, T. J. Kemp, and T. Stone, *ibid.*, **93**, 7091 (1971); (c) G. A. Russell and R. L. Blankespoor, *Tetrahedron Lett.*, 4573 (1971).

(11) All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated magnesium sulfate was employed as a drying agent. The infrared spectra were determined with a Perkin Elmer Model 257 infrared recording spectrophotometer fitted with a grating. The ultraviolet spectra were determined with a Perkin Elmer Model 202 recording spectrophotometer. The nmr spectra were determined at 60 mHz with a Varian Model A-60 nmr spectrometer. The chemical-shift values are expressed in δ values (ppm) relative to a tetramethylsilane internal standard. The mass spectra were obtained with an Hitachi (Perkin Elmer) or a Varian Model M-66 mass spectrometer. All reactions involving strong bases or organometallic intermediates were performed under a nitrogen atmosphere.

(12) H. O. House and W. F. Fischer, Jr., *J. Org. Chem.*, **33**, 949 (1968).

(13) H. O. House and M. J. Umen, manuscript in preparation.

(14) H. O. House and H. W. Thompson, *J. Org. Chem.*, **26**, 3729 (1961).

(15) H. O. House, W. L. Respess, and G. M. Whitesides, *ibid.*, **31**, 3128 (1966).

(16) B. B. Corson and W. L. Benson, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 273.

(17) E. L. Eliel, R. O. Hutchins, and Sr. M. Knoeber, *Org. Syn.*, **50**, 38 (1970).

(18) H. O. House, R. W. Giese, K. Kronberger, J. P. Kaplan, and J. F. Simeone, *J. Amer. Chem. Soc.*, 92, 2800 (1970).

(19) G. Wittig and A. Hesse, *Org. Syn.*, **50**, 66 (1970).

(20) H. O. House and W. F. Gilmore, *J. Amer. Chem. Soc.*, **83**, 3972 (1961).

(21) H. O. House and R. S. Ro, *ibid.*, **80**, 2428 (1958).

(22) H. O. House and D. J. Reif, *ibid.*, **77**, 6525 (1955).

(23) E. P. Kohler, *Amer. Chem. J.*, **36**, 177 (1906).

(24) The preparation and characterization of this compound, performed in our laboratories by Dr. David S. Crumrine, will be described elsewhere.

(25) H. O. House and G. H. Rasmusson, *J. Org. Chem.*, **28**, 31 (1963).

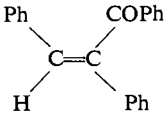
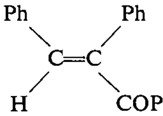
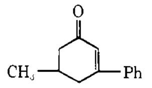
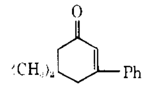
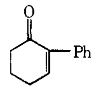
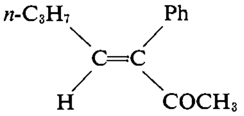
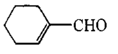
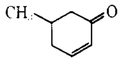
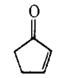
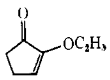
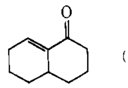
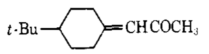
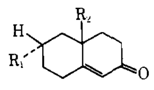
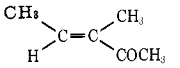
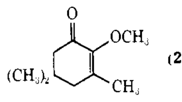
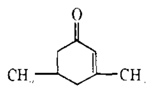
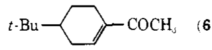
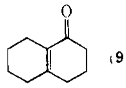
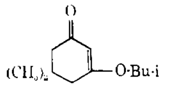
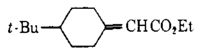
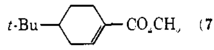
(26) H. O. House, B. M. Trost, R. W. Magin, R. G. Carlson, R. W. Franck, and G. H. Rasmusson, *ibid.*, **30**, 2513 (1965).

(27) We are indebted to Professor Drury S. Caine for supplying us with an authentic sample of this substance.

(28) The esterification procedure of P. Kadaba, *Synthesis*, 316 (1971).

(29) A. O. Zoss and G. F. Hennion, *J. Amer. Chem. Soc.*, **63**, 1151 (1941).

Table II. Comparison of Measured and Calculated Polarographic Reduction Potentials for α,β-Unsaturated Carbonyl Compounds in Dimethylformamide Solution

Compound	$E_{1/2}$ (V) *vs.* sce	
	Measd	Calcd
trans-PhCH=CHCOPh (**23**)	−1.41	−1.5
Ph_2C=CHCOPh (**26**)	−1.44	−1.5
Ph_2C=CHCHO (**20**)	−1.51	−1.5
trans-PhCH=CHCHO (**19**)	−1.53	−1.5
 (**28**)	−1.58	−1.5
 (**29**)	−1.58	−1.5
Ph_2C=C(Ph)COPh (**27**)	−1.59	−1.5
trans-PhCH=CHCOCH$_3$	−1.64^a	−1.6
trans-*t*-BuCH=CHCOPh	−1.69^a	−1.6
trans-PhCH=CHCOBu-*t* (**18**)	−1.65 (−1.70)^a	−1.6
cis-PhCH=CHCOBu-*t*	−1.71^a	−1.6
	−1.71^a	−1.7
 (**17**)	−1.71	−1.7
trans-PhCH=CHCO$_2$CH$_3$ (**32**)	−1.81	−1.8
trans-CH$_3$CH=CHCHO (**30**)	−1.91	−2.0
 (**37**)	−1.96	−2.0
 (**33**)	−2.07	−2.0
 (**21**)	−2.03	−2.1
 (**5**)	−2.07	−2.1
trans-CH$_3$CH=CHCOCH$_3$ (**10**)	−2.08	−2.1
 (**34**)	−2.16	−2.1
 (**35**)	−2.23	−2.1
trans-*t*-BuCH=CHCOBu-*t*	−2.22^a	−2.1
cis-*t*-BuCH=CHCOBu-*t*	−2.21^a	−2.1
 (**38**)	−2.11	−2.2
	−2.12^a	−2.2
		
R$_1$ = R$_2$ = H	−2.15^a	−2.2
R$_1$ = *t*-Bu; R$_2$ = H	−2.15^a	−2.2
R$_1$ = H; R$_2$ = CH$_3$	−2.10^a	−2.2
 (**25**)	−2.18	−2.2
 (**24**)	−2.20	−2.2
	−2.22^a	−2.2
 (**6**)	−2.24	−2.2
trans-CH$_3$CH=CHCO$_2$CH$_3$ (**31**)	−2.33	−2.3
 (**9**)	−2.34	−2.3
 (**4**)	−2.43	−2.4
 (**11**)	−2.45	−2.4
 (**7**)	−2.50	−2.4

^{a} Data from ref 5.

n^{20}D 1.4409]; ir (CCl$_4$) 2240 (C≡C) and 1720 cm^{-1} (ester C=O); uv$_{max}$ (95% EtOH) 207.5 mμ (ϵ 6200); nmr (CCl$_4$) δ 3.68 (3 H$_s$, OCH$_3$), 2.2–2.5 (2 H$_m$, CH$_2$C≡C), 1.3–2.0 (2 H$_m$, CH$_2$), and 0.8–1.2 (3 H$_m$, CH$_3$); mass spectrum, *m/e* (rel intensity), 126 (M$^+$, 8), 95 (100), 66 (20), 53 (23), and 41 (20).

1-Pentyne (3.09 g or 45.4 mmol) was converted to 4.041 g (69%) of the corresponding copper(I) acetylide, a yellow solid, by the general procedure of Owsley and Castro.[30] A mixture of 4.04 g (31.0 mmol) of this acetylide and 6.13 g (78.2 mmol) of acetyl chloride was allowed to stand at 25–30° for 24 hr in a closed vessel protected from light. The resulting purple suspension was diluted with 100 ml of Et$_2$O and filtered. After the filtrate had been concentrated, distillation of the residue separated 2.493 g of colorless liquid, bp 35–77° (40–43 mm), which contained (glpc) the ketone **16** and several unidentified components. An Et$_2$O solution of this material was washed with aqueous NaHCO$_3$, dried, concentrated, and distilled to give 1.623 g of liquid, bp 35–75° (60–75 mm), which contained (glpc) primarily the ketone **16** (retention time, 8.2 min) accompanied by three minor components (7.1, 13.8, and 19.6 min). A pure sample of ketone **16** was collected (glpc) as a colorless liquid: n^{25}D 1.4428 (lit.[31] n^{25}D 1.4450); ir (CCl$_4$) 2220 (C≡C) and 1680 cm^{-1} (conjugated C=O); uv$_{max}$ (95% EtOH) 215 (ϵ 7750) and 301 mμ (24); mass spectrum *m/e* (rel intensity) 110 (M$^+$, 9), 95 (100), 53 (31), and 43 (33); nmr (CCl$_4$) δ 2.1–2.5 (2 H$_m$, CH$_2$C≡C), 2.23 (3 H$_s$, OCH$_3$), 1.3–1.9 (2 H$_m$, CH$_2$), and 0.8–1.2 (3 H$_m$, CH$_3$).

Reaction of 60.0 g (0.30 mol) of the enol ether **4** with 0.45 mol of PhMgBr in 430 ml of Et$_2$O by the previously described procedure[32] yielded 25.2 g (42%) of the enone **17** as white needles from hexane: mp 51–52.5° (lit.[32] mp 54–54.5°); ir (CCl$_4$) 1668 (conjugated C=O) and 1610 cm^{-1} (C=C); uv$_{max}$ (95% EtOH) 219 (ϵ 11,100) and 285 mμ (22,000); nmr (CCl$_4$) δ 7.3 (5 H$_m$, aryl CH), 6.13 (1 H$_t$, J = 2 Hz, vinyl CH), 2.57 (1 H$_d$, J = 2 Hz, allylic CH$_2$), 2.10 (2 H$_s$, CH$_2$-CO), and 1.09 (6 H$_s$, CH$_3$); mass spectrum *m/e* (rel intensity), 200 (M$^+$, 38), 144 (100), 106 (40), 105 (35), 44 (43), and 40 (29).

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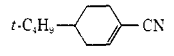
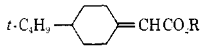
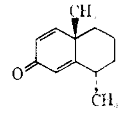
(30) (a) D. C. Owsley and C. E. Castro, *Org. Syn.*, **52**, 128 (1972); (b) C. E. Castro, R. Havlin, V. K. Honwad, A. Malte, and S. Mojé, *J. Amer. Chem. Soc.*, **91**, 6464 (1969).

(31) V. Theus, W. Surber, L. Colombi, and H. Schinz, *Helv. Chim. Acta*, **38**, 239 (1955).

(32) G. F. Woods, *J. Amer. Chem. Soc.*, **69**, 2549 (1947).

Table III. Polarographic Reduction Potentials Determined at 25° on Solutions in $(CH_3)_2NCHO$ Containing 0.50 *M* n-Bu_4NBF_4

	First wave		Second wave	
Compd (concn, *M* × 10³)	$E_{1/2}$ *vs.* sce, V	αn value	$E_{1/2}$ *vs.* sce, V	αn value
Fluorenone **3** (1.4–2.7)	−1.29	1.1	−1.95	0.6
4 (1.5–1.7)	−2.43	1.0		
5 (1.4–1.6)	−2.07	1.1		
6 (1.3–4.6)	−2.24	1.2		
7 (1.5–3.1)	−2.50	1.1		
 **8**(1.1–2.0)	−2.55	0.9		
9 (3.2–4.9)	−2.34	1.3		
10 (2.7–11.7)	−2.08	1.0		
11 (1.9–3.0)	−2.45	1.2		
 **12**, R = Li(2.6–4.4)	−2.37	0.8		
$(C_2H_5O_2C)_2C{=}C(CO_2C_2H_5)_2$ **13** (1.1–2.0)	−0.97	1.1	−1.10	1.0
$(CH_3)_2C{=}C(CO_2C_2H_5)_2$ **14** (1.4–6.1)	−2.13	1.2		
n-$C_3H_7C{\equiv}CCO_2R$				
15, R = CH_3 (2.9–6.5)	−2.26	0.7		
15, R = Li (5.0–5.1)	−2.31	0.9		
n-$C_3H_7C{\equiv}CCOCH_3$ **16** (4.9–6.4)	−1.99	0.8		
17 (1.5–2.0)	−1.71	1.2	−2.06	1.3
18 (1.0–2.0)	−1.65	1.5	−2.12	1.2
19 (2.0)	−1.53	1.2	−2.08	1.0
20 (2.0)	−1.51	1.0	−1.93	1.2
21 (2.0–5.0)	−2.03	1.0		
23 (1.9–3.2)	−1.41	1.5	*Ca.* −2.1	
24 (1.6–7.2)	−2.20	1.3		
25 (3.0–7.5)	−2.18	0.9		
26 (1.9–2.5)	−1.44	1.2	−1.82	1.4
27 (1.9–2.1)	−1.59	1.0	*Ca.* −1.7	
28 (2.4–2.5)	−1.58	1.2	−1.94	1.3
29 (2.4–2.6)	−1.58	1.3	−1.94	1.2
30 (1.4–1.7)	−1.91	0.8		
31 (8.8)	−2.33	1.2		
32 (1.6–2.7)	−1.81	1.2	−2.27	1.2
33 (1.1)	−2.07	0.9		
34 (2.2–2.6)	−2.16	0.7		
35 (2.0–2.4)	−2.23	0.8		
	−2.01	0.8		
36 (2.1–2.6)				
37 (2.0–2.2)	−1.96	1.3		
38 (1.8–3.6)	−2.11	0.7		
trans-$CH_3CH{=}CHCN$ **39** (0.7–1.5)	−2.37	0.6		

The unsaturated aldehyde **21** was prepared by the general procedure of Ireland and Schiess[33] in which a mixture of 40.9 g (0.325 mol) of 2-hydroxymethylenecyclohexanone,[34] 38.0 g (0.38 mol) of cyclohexanol, and 25 mg of *p*-toluenesulfonic acid in 300 ml of PhH was refluxed for 9 hr with continuous separation of H_2O. The resulting mixture was partitioned between Et_2O and aqueous 5% NaOH and the organic layer was dried and concentrated. Distillation of the residual liquid separated 33.26 g (50%) of crude 2-cyclohexyloxymethylenecyclohexanone (**22**) as a yellow liquid, bp 111–117° (0.10–0.15 mm), which was used without further purification. After reaction of the enol ether **22** (33.26 g or 0.160 mol) with 10.2 g (0.270 mol) of $NaBH_4$ in a mixture of 300 ml of MeOH and 50 ml of aqueous 1% NaOH for 1.8 hr, the mixture was concentrated under reduced pressure and then partitioned between Et_2O and H_2O. The Et_2O solution (200 ml) was stirred with 200 ml of aqueous 1 *M* HCl at 0° for 1 hr and at 25° for 2 hr and then the combined Et_2O layer and Et_2O extract of the aqueous phase were washed with aqueous NaCl, dried, and concentrated. Distillation of the residue afforded 20.3 g of the crude aldehyde **21** as a colorless liquid, bp 64–68° (14 mm), $n^{20}D$ 1.4792. This crude product was stirred with saturated aqueous $NaHSO_3$ and the crude bisulfite adduct (19.7 g) was collected and washed with Et_2O. The bisulfite adduct was shaken with a mixture of Et_2O and aqueous 1 *M* HCl. The Et_2O layer was dried, concentrated, and distilled to separate 4.05 g of the aldehyde **21** as a colorless liquid: bp 74–75° (11 mm); $n^{25}D$ 1.4930 [lit.[35] bp 70° (13 mm), $n^{17}D$ 1.4921]; ir (CCl_4) 2710 (aldehyde CH), 1687 (conjugated C=O), and 1644 cm^{-1} (C=C); nmr (CCl_4) δ 9.38 (1 H_s, CHO), 6.73 (1 H_m, vinyl CH), 1.9–2.3 (4 H_m, allylic CH_2), and 1.3–1.9 (4 H_m, CH_2).

A commercial sample of 2-phenylcyclohexanol was oxidized[36] with H_2CrO_4 in acetone to yield 2-phenylcyclohexanone as white

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[33] R. E. Ireland and P. W. Schiess, *J. Org. Chem.*, **28**, 6 (1963). This experiment was performed in our laboratories by Dr. C. J. Blankley.

[34] C. M. Ainsworth, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 536.

[35] I. Heilbron, E. R. H. Jones, R. W. Richardson, and F. Sondheimer, *J. Chem. Soc.*, 737 (1949).

[36] This experiment was performed in our laboratories by Dr. D. S. Crumrine. The course of the bromination and subsequent dehydrobromination of 2-phenylcyclohexanone has recently been reexamined by B. Miller and H.-S. Wong, *Tetrahedron*, **28**, 2369 (1972).

needles from hexane: mp 56–57° (lit.[37] 53-55°); ir (CCl_4) 1718 cm^{-1} (C═O); nmr (CCl_4) δ 6.9–7.5 (5 H_m, aryl CH), 3.3–3.7 (1 H_m, benzylic CH), and 1.5–2.5 (8 H_m, aliphatic CH); mass spectrum *m/e* (rel intensity) 174 (48, M^+), 130 (100), 117 (49), 104 (30), and 91 (25). After 4.00 g (23 mmol) of 2-phenylcyclohexanone in 15 ml of CCl_4 had been brominated[36] with 3.85 g (24 mmol) of Br_2, a solution of the crude product in 80 ml of 2,6-lutidine was refluxed for 1 hr. The resulting mixture was concentrated under reduced pressure and then partitioned with Et_2O and aqueous HCl. The neutral ethereal layer was dried and concentrated and the residual brown oil (3.75 g) was chromatographed on SiO_2. From fractions eluted with 20% Et_2O in hexane was isolated 1.910 g (48%) of the crude unsaturated ketone **37**, mp 86–90°. Recrystallization from an Et_2O–hexane mixture afforded 692 mg (17.5%) of the pure enone **37** as white needles: mp 93–95° (lit. 95–96°,[38] 96–97°[39]); ir (CCl_4) 1685 cm^{-1} (conjugated C═O); uv_{max} (95% EtOH) 221 (ϵ 12,500) and 262 mμ (2700); nmr (CCl_4) δ 7.2–7.5 (5 H_m, aryl CH), 6.92 (1 H_t, J = 4.4 Hz, vinyl CH), and 1.8–2.7 (6 H_m, aliphatic CH); mass spectrum *m/e* (rel intensity) 172 (100, M^+), 144 (53), 116 (39), and 115 (38).

Polarographic Measurements. The previously described[5,18,40] procedures were followed with a Heath polarograph (Model EU-402V) and a Leeds and Northrup Speedomax G recorder. The electrodes were a dropping Hg cathode, a Pt wire anode, and a saturated calomel reference electrode with intermediate salt bridges containing aqueous 1 M $NaNO_3$ and 0.5 M $Et_4N^+BF_4^-$ or $(n\text{-}C_4H_9)_4N^+BF_4^-$ in $(CH_3)_2NCHO$. The solvent and supporting electrolyte were purified[41] in $(CH_3)_2NCHO$ containing 0.50 M $(n\text{-}C_4H_9)_4N^+BF_4^-$.[42]

The $E_{1/2}$ values (*vs.* sce) and the αn values, obtained from plots of E *vs.* $\log [i/(i_d - i)]$, are listed in Table III. These are average values from two or more separate runs.

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(37) M. S. Newman and M. D. Farbman, *J. Amer. Chem. Soc.*, **66**, 1550 (1944).

(38) W. E. Bachmann and L. B. Wick, *ibid.*, **72**, 3388 (1950).

(39) D. Ginsburg and R. Pappo, *J. Chem. Soc.*, 516 (1951).

(40) H. O. House, D. G. Koepsell, and W. J. Campbell, *J. Org. Chem.*, **37**, 1003 (1972).

(41) The solvent was purified by drying over molecular sieves, type 4A, followed by distillation under reduced pressure (bp 50° (14 mm)).

(42) H. O. House, E. Feng, and N. P. Peet, *J. Org. Chem.*, **36**, 2371 (1971).

Electrochemical Reduction of Stereoisomeric Geminal Dihalonorbornanes[1,2]

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Abstract: The electrochemical reduction of 2,2-dichloronorbornane, 2-*exo*-bromo,2-*endo*-chloronorbornane, 2,-*exo*-chloro,2-*endo*-bromonorbornane, and 2,2-dichloronorbornane-2-*exo*-^{36}Cl was investigated in dimethylformamide under a wide variety of conditions. All dihalides gave the same mixture of *endo*-norbornyl chloride and nortricyclene when reduced under identical conditions. The fact that methanol and water appear to be much better proton donors than phenols or acetic acid toward an intermediate carbanion in the reduction is interpreted as a surface phenomenon. Analyses of the relative rates of heterogeneous electron transfer to the two bromo chlorides and of the isotopic label retained after reduction of the labeled dichloride indicate stereochemically preferred attack by the electrode upon the norbornane nucleus from the exo direction. Alkylmercury intermediates were shown not to be required to explain the unusual effects of proton donors. Finally, electrochemical reduction of a 2,2-dihalonorbornane in the presence of a dialkyl sulfide and phenol was found to produce norbornane, and a path to account for production of the latter hydrocarbon is proposed.

The stereochemistry of electrochemical reduction of alkyl halides has received a great deal of attention recently.[3–5] Most such studies have involved reduction of cyclopropyl halides.[4,5] It appears that the predominant stereochemical pattern in such systems is reduction with (partial) retention of configuration, although (partial) inversion has also been observed during reduction of 2,2-diphenyl-1-bromocyclopropanecarboxylic acid and its methyl ester.[5b] Reduction with a high degree of stereochemical inversion was reported for the electrochemical reduction of α-chloro-α-phenylpropionic acid.[5d,6] Since the studies upon cyclopropyl halides must proceed through cyclopropyl anions, which are known to possess considerable configurational stability,[7] stereochemical patterns observed with these compounds cannot be taken as representative of alkyl halides in general. Likewise, the fact that the presence of a carboxyl group can substantially affect the overall stereochemistry of reduction[5b] indicates that the high degree of stereochemical inversion reported[5d] for the electrochemical reduction of α-chloro-α-phenylpropionic acid, even if correct,[6] might not be typical of other alkyl halides. The present study was initiated to obtain information concerning

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(1) This research constituted part of the Ph.D. Thesis of R. G. R., Wesleyan University, 1971.

(2) Portions of these results have been described in preliminary form: (a) papers presented at the 21st Meeting of the International Society of Electrochemistry, Prague, Czechoslovakia, Sept 1970, and at the 139th National Meeting of the Electrochemical Society, Washington, D. C., May 1971; (b) A. J. Fry and R. G. Reed, *J. Amer. Chem. Soc.*, **93**, 553 (1971).

(3) A. J. Fry and M. A. Mitnick, *ibid.*, **91**, 6207 (1969).

(4) J. L. Webb, C. K. Mann, and H. M. Walborsky, *ibid.*, **92**, 2042 (1970).

(5) (a) R. E. Erickson, R. Annino, M. D. Scanlon, and G. Zon, *ibid.*, **91**, 1767 (1969); (b) R. Annino, R. E. Erickson, J. Michalovic, and B. McKay, *ibid.*, **88**, 4424 (1966); (c) A. J. Fry and R. H. Moore, *J. Org. Chem.*, **33**, 1283 (1968); (d) B. Czochralska, *Chem. Phys. Lett.*, **1**, 239 (1967); (e) A. J. Fry and W. E. Britton, *Tetrahedron Lett.*, 4363 (1971).

(6) A reinvestigation of this report has, however, shown that the phenylpropionic acid formed in this reaction is essentially completely racemic: Professor R. E. Erickson and C. Fischer, private communication, Aug 4, 1971.

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