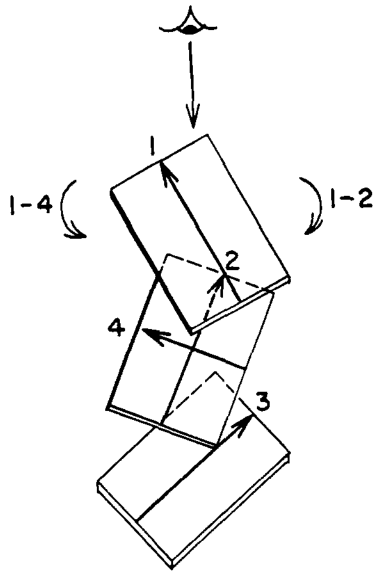
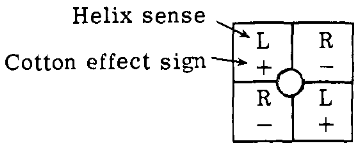
Cotton effect (CE) is found for the first electronic transition ($^1L_b \leftarrow {}^1A$) in compounds I–III and negative CE's for all other bands >220 nm. The relative intensities of the LCICD bands in compounds I–III follow the ordinary absorption except for the $^1L_b \leftarrow {}^1A$ transition which has mixed polarization character resulting in a reduction of CD band intensity due to overlapping positive and negative transitions within the CD bands.[6,7]

LCICD appears to arise from (a) the solute being exposed to a helical arrangement of solvent molecules, as well as (b) a helicoidal arrangement of solute molecules. The relative importance of the above two mechanisms seems to vary with solute concentration and symmetry, as well as the characteristics of the liquid-crystalline solvent. The details of the physical origin of LCICD will be the subject of a future publication.[8]

Since the organizations of planar solute molecules in liquid-crystalline mesophases are known to orient their long axis parallel to the alignment of the liquid-crystal molecules,[9] an attempt was made to rationalize the change in LCICD sign with the solute transition moment polarization. The following diagram describes the situation for dilute solutions of solutes in cholesteric mesophase (mechanism a) where each block represents a single isolated molecule (arrows indicate molecular axes) in three nematic-like layers in the cholesteric helix. If the molecule in the center, for example, is a solute with perpendicular electronic transition moments, as in compounds I–III, one can readily see that the longitudinally polarized transition moment is in an environment of opposite chirality (right-handed helix) from that seen by the transversely polarized moment (left-handed helix). With the above experimental observations in mind a general rule for relating the sign of solute LCICD bands to the polarization of their electronic transition moments is proposed. Looking down the transition moment axis of the chromophore of interest (normal to the cholesteric helical axis), the chirality of the perturbing helical environment (*vide infra*) is noted.





If the transition moment is exposed to a right-handed helical disposition of molecules in the cholesteric helix (upper right and lower left quadrants), a negative LCICD band is observed. Conversely, a positive LCICD band is observed when the transition moment is exposed to a left-handed helical structure (upper left and lower right quadrants). The above rule is designed for solutes in cholesteric mesophases composed of cholesteryl derivatives and may change as the components of the cholesteric mesophase are varied (*e.g.*, from steroidal to nonsteroidal).

In summary, LCICD is a novel technique for investigating the circular dichroism of achiral and chiral molecules. The sign of the LCICD bands has been found to provide spectroscopic information about solutes in cholesteric mesophases, and a quadrant rule for predicting electronic transition polarizations from the sign of the LCICD band has been formulated. More detailed studies attempting to compare LCICD to natural and MCD are currently underway.

Acknowledgment. Stimulating discussions with J. J. Wysocki and Drs. W. H. H. Gunther and G. Johnson as well as the provision of *N*-ethylcarbazole by Dr. G. Johnson are gratefully acknowledged.

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Photocyclizations of Pharmacodynamic Amines. VII. Photorearrangements and Roentgen-Ray Analyses of Novel Tyramine Dimers[1]

Sir:

When *N*-chloroacetyltyrosine was irradiated by uv light the phenolic chromophore disappeared rapidly.[2] Previous attempts to isolate the photocyclization products were unsuccessful.[3] We have now been able to isolate dimers from the photolysis of six homologous *N*-chloroacetyltyramines (Ia–e) and to elucidate the structure of these novel cage compounds by Roentgen-ray analysis. These dimers are remarkable because they result from ortho and para ring closures of reactive dienones (or exciplexes) which, rather than adding solvent, undergo a series of $[{}_\pi 4 + {}_\pi 2]$ and $[{}_\pi 2 + {}_\pi 2]$ cycloadditions and, in the end, an unexpected bond switching process or possibly a cycloreversion $({}_\sigma 2_a + {}_\sigma 2_a)$.[4]

When a 10 m*M* solution of Ia in 10% aqueous ethanol was irradiated for 1.5 hr with a 100-W high-pressure

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(6) O. E. Weigang, Jr., *J. Chem. Phys.*, **43**, 3609 (1965).

(7) J. Horwitz, F. H. Strickland, and C. Billups, *J. Amer. Chem. Soc.*, **91**, 184 (1969).

(8) F. D. Saeva, to be submitted for publication.

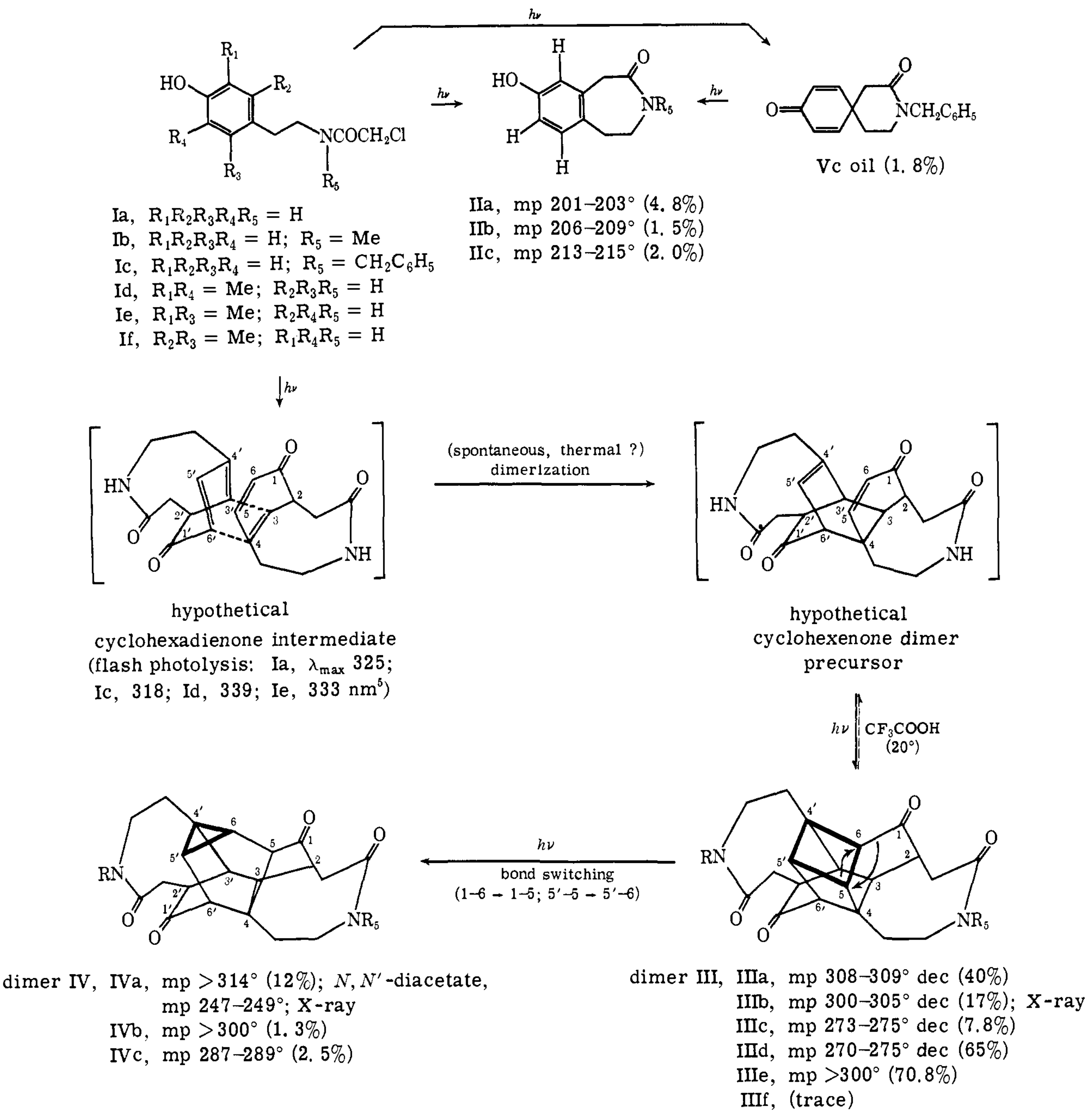
(9) G. P. Ceasar and H. B. Gray, *J. Amer. Chem. Soc.*, **91**, 191 (1969), and reference cited therein.

(1) Preceding paper in this series: O. Yonemitsu, H. Nakai, Y. Okuno, S. Naruto, K. Hemmi, and B. Witkop, *Photochem. Photobiol.*, **15**, 509 (1972).

(2) O. Yonemitsu, B. Witkop, and I. L. Karle, *J. Amer. Chem. Soc.*, **89**, 1039 (1967).

(3) O. Yonemitsu, T. Tokuyama, M. Chaykovsky, and B. Witkop, *ibid.*, **90**, 776 (1968).

(4) R. B. Woodward and R. Hoffmann, The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1971, pp 65–100.



Ia, $R_1R_2R_3R_4R_5 = H$
Ib, $R_1R_2R_3R_4 = H$; $R_5 = Me$
Ic, $R_1R_2R_3R_4 = H$; $R_5 = CH_2C_6H_5$
Id, $R_1R_4 = Me$; $R_2R_3R_5 = H$
Ie, $R_1R_3 = Me$; $R_2R_4R_5 = H$
If, $R_2R_3 = Me$; $R_1R_4R_5 = H$

IIa, mp 201–203° (4. 8%)
IIb, mp 206–209° (1. 5%)
IIc, mp 213–215° (2. 0%)

Vc oil (1. 8%)

hypothetical
cyclohexadienone intermediate
(flash photolysis: Ia, λ_{max} 325;
Ic, 318; Id, 339; Ie, 333 nm[5])

hypothetical
cyclohexenone dimer
precursor

dimer IV, IVa, mp >314° (12%); *N,N′*-diacetate, mp 247–249°; X-ray
IVb, mp >300° (1. 3%)
IVc, mp 287–289° (2. 5%)

dimer III, IIIa, mp 308–309° dec (40%)
IIIb, mp 300–305° dec (17%); X-ray
IIIc, mp 273–275° dec (7.8%)
IIId, mp 270–275° dec (65%)
IIIe, mp >300° (70.8%)
IIIf, (trace)

mercury lamp, the benzazepinone (IIa) was isolated from the fraction soluble in ethyl acetate. From the aqueous layer the dimeric cage compounds IIIa and IVa were isolated in yields of 40 and 12%, respectively. Further irradiation in neutral or acidic medium converted IIIa to IVa in over 90% yield. Both IIIa and IVa have the composition $C_{20}H_{22}N_2O_4$ on the basis of high-resolution mass spectra and, surprisingly, in the nmr spectrum no signals due to vinyl protons. On the basis of the molar extinction coefficients $n \rightarrow \pi^*$ $\lambda_{max}^{H_2O}$ 300 nm (ϵ 102.5) and its *p*-bromophenylhydrazone, mp 300°, λ_{max}^{EtOH} 292.5 nm (ϵ 60,340), IIIa has two ketonic groups. Reduction of IIIa by sodium borohydride or by catalytic hydrogenation (PtO_2) gave a diol, mp 270° (60 or 70% yield) (*N,N,O,O*-tetraacetate, mp 256–258° dec).

The homologs Ib, Ic, Id, Ie, and If were also photolyzed to dimers of type III in yields reflecting the steric or electronic effects of the various methyl substituents. A detailed report on the preparation and flash photolysis of these homologs will be presented separately.[5]

The N-substituted homologs Ib and Ic, in addition to dimers, furnished the 2,5-cyclohexadienone (Vc) which, on further irradiations afforded the benzazepinone (IIc), but no dimer. These data suggest that a (conjugated) 2,4-cyclohexadienone[6] must be the precursor for dimers III and IV, whose complete structures were determined by Roentgen-ray analysis of single crystals of IIIb and of the *N,N*-diacetate of the rearranged dimer IVa.

An automated four-circle diffractometer with Cu Kα radiation was used to collect 3132 independent intensities for IIIb. This material crystallized in the

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(5) N. Kanamaru, K. Kimura, and O. Yonemitsu, manuscript in preparation.

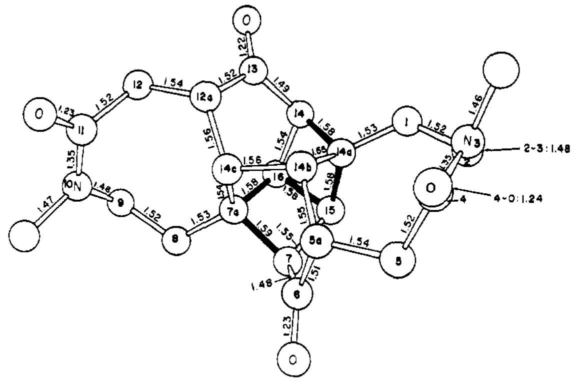


Figure 1. Correct name, numbering, and bond lengths of dimer IIIb, *i.e.*, decahydro-7,14a,7a,14-ethanediylidenenaphtho[1,8-*de*:4,5-*d*′*e*′]bisazocine-4,6,11,13(1*H*,7*H*,8*H*,14*H*)-tetrone. The solid bonds of the two cyclobutane rings are unexpectedly long and undergo significant contraction on rearrangement to IV when bonds 6–7 and 16–15 switch to 6–5a and 16–7, respectively.

monoclinic space group $P2_1/c$, with four molecules per unit cell and cell parameters $a = 12.79 \pm 0.01$, $b = 12.88 \pm 0.01$, and $c = 13.82 \pm 0.01$ Å, and $\beta = 59.97 \pm 0.05°$. Phases for the strong and moderately strong reflections were determined directly from the measured intensities by the *symbolic addition procedure* for centrosymmetric crystals.[7] The initial density map revealed the molecular structure and also showed that the unit cell contained eight water molecules. A difference map clearly defined the locations of all hydrogen atoms except those on the methyl groups and on the water molecules. The least-squares refinement of coordinates and thermal parameters has reached an agreement factor of 8.9%.

Figure 1 shows a drawing of molecule IIIb made by computer from the experimentally determined coordinates of the atoms.

Hydrogen bonding between the water molecules and the carbonyl groups on the eight-membered rings leads to an infinite-sheet structure perpendicular to the unique axis of the cell, with two water molecules between each molecular unit.

For dimer IVa, 3206 independent intensities were measured. The space group is *Pbca*, with eight molecules per unit cell and cell parameters $a = 24.93 \pm 0.01$, $b = 12.971 \pm 0.005$, and $c = 12.437 \pm 0.005$ Å.

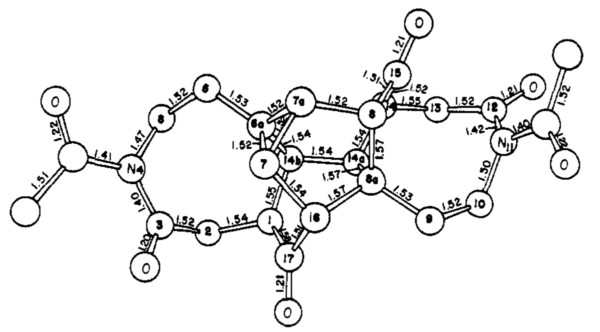
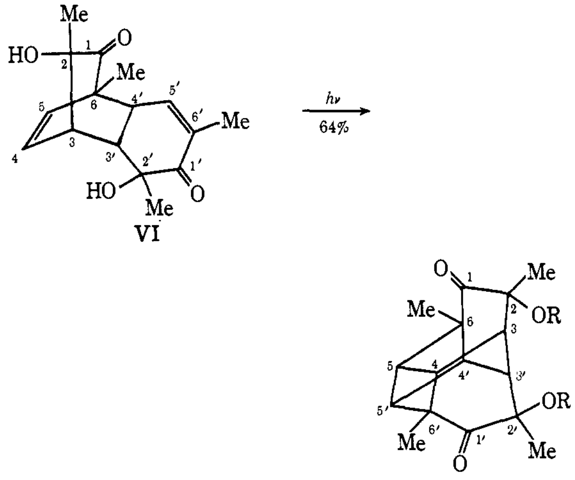


Figure 2. Correct name, numbering, and bond lengths of the *N*,*N*′-diacetate of dimer IVa: 4,11-diacetyldodecahydro-7*H*-1,7,-8a-ethanylylidene-8,14-methanocyclopropa[1,6]benzo[1,2-*d*:4,3-*d*′]-bisazocine-3,12,15,17(4*H*,9*H*)-tetrone.

The initial density map revealed the locations of the 32 nonhydrogen atoms in the molecule, and all hydrogen atoms were later located in a difference map. Least-squares refinement of the coordinates and thermal parameters has reached an agreement factor of 7.7%.

As Figure 2 shows, IVa contains a more complex, partially open cage consisting of one three-, two five-, two six-, and one seven-membered rings. The six-membered rings are in the boat conformation.

In analogy to the postulated conversion of the cyclohexenone precursor to dimer III the 2,4-cyclohexadienone dimer VI,[8] on irradiation in ethyl aceate, formed

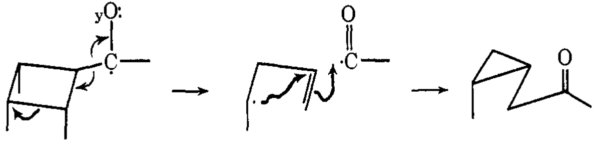


VI

VII, R = H; mp >300°
VIII, R = Ac; mp 226–229°

the cage compound VII, characterized by a diacetate, VIII.

The rearrangement of dimer III to the more stable dimer IV is brought about neither by heat nor acid, but only by uv light. The rearrangement may occur



either by a concerted $_\sigma 2_a + _\sigma 2_a$ cycloreversion[4] or may involve a Norrish type I cleavage of the 1,6 bond

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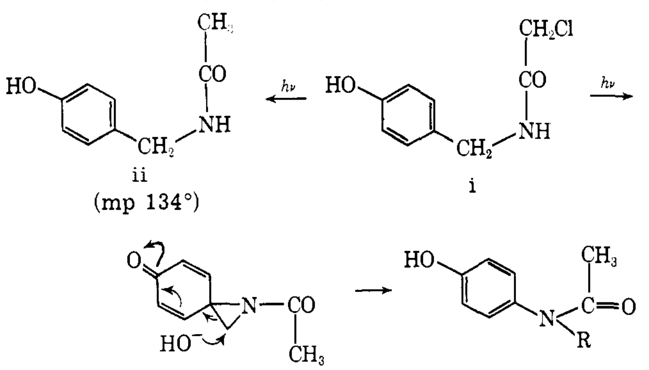
(6) S. Naruto, O. Yonemitsu, N. Kanamaru, and K. Kimura J. *Amer. Chem. Soc.*, 93, 4053 (1971). Irradiation of the benzylamine i



ii (mp 134°)

i

iii

iv, R = CH_2OH
v, R = H (mp 168°)

in dilute alkali gave ii and the aniline v (yield 10%) presumably *via* iii and iv.

(7) J. Karle and I. L. Karle, *Acta Crystallogr.*, 21, 849 (1966).

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followed by rearrangement of the [4.4] to the [3.5] bicycles.[9]

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(9) *Cf.* calathene ("basketene") to rhynchene ("snoutene"): W. G. Dauben, M. G. Buzzolini, C. H. Schallhorn, D. L. Whalen, and K. J. Palmer, *Tetrahedron Lett.*, 787 (1970).

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Selective Removal of Protecting Groups Using Controlled Potential Electrolysis

Sir:

The 2,2,2-trichloroethoxy moiety has been used recently to modify the reactivity of carboxylic acids,[1] and, similarly, the 2,2,2-trichloroethoxycarbonyl group has been shown to be useful for protection of hydroxy and amino units.[2] The unique feature of the 2,2,2-trichloroethoxy derivatives is easy disassembling *via* reduction with zinc metal in acetic acid or hot ethyl alcohol.[1,2]

We wish to report that controlled potential electrolysis in conjunction with a variety of 2-haloethyl moieties expands the versatility of and introduces selectivity into this technique. Controlled potential electrolysis at a mercury electrode allows removal of 2-haloethoxy groups in neutral media (protic or aprotic) at temperatures ranging from ambient or higher to well below 0°. Most importantly, the electrolytic technique makes possible selective removal of very similar protecting groups by careful choice of electrode potential.

A central feature of this method is the availability of 2-iodoethyl,[3] 2,2,2-tribromoethyl,[4] and 2,2-dichloroethyl chloroformates[5] in addition to the commercially available 2,2,2-trichloroethyl chloroformate. The chloroformates interact with amino,[2a,b] hydroxyl,[2a,c] and thiol groups to afford the 2-haloethoxycarbonyl derivatives (*e.g.*, Table II).

Polarographic studies (Table I) indicate that the ease of reduction of 2-haloethoxy esters is very sensitive to the identity of the halogen atom and nearby substituents. Commercially available potentiostats[6] are capable of controlling the reduction potential to ±0.01 V, which, in practical terms, allows quantitative reduction of one compound in a mixture where the components differ in $E_{1/2}$ by 0.3 V. Thus reduction of a particular 2-haloethoxy group in the presence of a less easily reduced analog from Table I is simple and efficient.

Table I

Ester	$E_{1/2}{}^a$
$PhCO_2CH_2CH_2I$	$> -2.20^b$
$PhCO_2CH_2CHCl_2$	-1.91
$PhCO_2CH_2CCl_3$	-1.28
$PhCO_2CH_2CBr_3$	-0.60^c

[a] Half-wave potentials are in volts relative to the saturated calomel electrode. The polarographic studies were done in methyl alcohol containing 0.1 *M* lithium perchlorate. [b] A discrete wave was not observed for this derivative; at −2.2 V, the medium begins to show significant reduction. [c] The half-wave is partially obscured by a maximum which could not be suppressed.

Representative results of the electrolytic removal of 2-haloethoxy units from simple monofunctional compounds are displayed in Table II. The general experimental procedure involves a cylindrical vessel fitted with two side arms which are separated from the main compartment with coarse grade glass frits. A mercury pool electrode in the main compartment serves as the cathode (working electrode) while a saturated calomel reference electrode is placed in one side arm and a platinum sheet in the other side arm (anode, counter electrode). The cylinder is capped with a large ground-glass joint bearing a gas inlet tube and an exit stopcock; the lower portion of the apparatus is encased in a water jacket for cooling. The electrolyte solution (0.1 *M* lithium perchlorate in methyl alcohol) is added to the cell and the side arms. To the solution in the main compartment (*ca.* 20 ml)

Table II

Substrate	Product	V	Yield, %
1. $PhCO_2CH_2CCl_3$	$PhCO_2H$	−1.65	87 (91[a])
2. $PhCO_2CH_2CHCl_2$	$PhCO_2H$	−1.85	78
3. $PhCO_2CH_2CBr_3$	$PhCO_2H$	−0.70	85
4. *p*-$CH_3C_6H_4NHCO_2$-CH_2CCl_3	*p*-$CH_3C_6H_4NH_2$	−1.70	88
5. *p*-$CH_3C_6H_4NHCO_2$-CH_2CHCl_2	*p*-$CH_3C_6H_4NH_2$	−2.15	47
6. $PhCH_2OCO_2CH_2CCl_3$	$PhCH_2OH$	−1.50	70
7. $PhCH_2SCO_2CH_2CCl_3$	$PhCH_2SH$	−1.50	90[b]
8. $PhCH_2SCO_2CH_2CCl_3$	$PhCH_2SSCH_2Ph$	−1.50	90[c]
9. Cholesteryl 2,2,2-trichloroethyl carbonate	Cholesterol	−1.65	80
10. *N*-Acetyl-*S*-(2,2,2-trichloroethoxycarbonyl)-cysteine	*N*-Acetylcysteine	−1.60	100[d]
11. *N*-Acetyl-*S*-(2,2,2-trichloroethoxycarbonyl)-cysteine methyl ester	*N*-Acetylcysteine methyl ester	−1.50	88[b]

[a] This is the result of an experiment with a platinum gauze electrode in place of the mercury pool, and dimethylformamide in place of methyl alcohol. [b] The isolation procedure involved addition of a small molar excess of acetic acid immediately after electrolysis. [c] This experiment was done without purging with inert gas. [d] The crude product had mp 93–104° [mp 109–110° reported by T. A. Martin, J. R. Corrigan, and E. W. Waller, *J. Org. Chem.*, **30**, 2839 (1965)], and no impurities detectable by ^1H nmr. Purification by recrystallization was not efficient.

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(1) (a) R. B. Woodward, K. Heusler, J. Gosteli, P. Naegeli, W. Oppolzer, R. Ramage, S. Ranganathan, and H. Vorbrüggen, *J. Amer. Chem. Soc.*, **88**, 852 (1966); (b) J. E. Pike, F. H. Lincoln, and W. P. Schneider, *J. Org. Chem.*, **34**, 3552 (1969); (c) R. D. G. Cooper and F. L. José, *J. Amer. Chem. Soc.*, **94**, 1022 (1972), and references therein.

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(3) J. Grimshaw, *J. Chem. Soc.*, 7136 (1965).

(4) A. F. Cook, *J. Org. Chem.*, **33**, 3589 (1968).

(5) Conversion of 2,2-dichloroethyl alcohol to the corresponding chloroformate has been achieved in 58% yield (bp 30–32° (0.10 Torr)) using pyridine and phosgene in benzene.

(6) The present work was done on a Wenking Model 68FR0.5 Potentiostat from Brinkman Instruments Inc.