Experimental Section[6]

The general telescoped procedure is illustrated with biphenylcarbonyl chloride as substrate as follows. To a stirred solution of 2 g (0.009 mol) of the acid chloride (G & C Chemical Co., Belleville, N. J.) and 1.7 g (0.01 mol) of bistrimethylsilylacetylene[3] in 25 ml of methylene chloride (dried by storing over molecular sieves) cooled in ice–water was added 1.4 g (0.01 mol) of anhydrous aluminum chloride. After stirring for *ca.* 3 min, the cooling bath was removed. The reaction mixture was stirred at room temperature for 2 hr and then was poured into ice–water and the organic product was extracted into ether. Drying and evaporating the ether left the trimethylsilylacetylenic ketone **2** (R = biphenyl) which was treated with 20 ml of cold 0.1 *M* methanolic sodium methoxide. The cooling bath (ice–water) was removed after *ca.* 1 min and the mixture was stirred for 10 min to effect conversion to **3** (R = biphenyl). The resulting solution of **3** was cooled (ice–water), 1.2 g (0.031 mol) of solid sodium borohydride was added, the cooling bath was removed, the mixture was stirred for 20 min and poured into ice–water, and the β-hydroxy dimethyl acetal **4** (R = biphenyl) was isolated by extracting with ether and drying and evaporating the ethereal solution. Crude **4** was dissolved in 40 ml of dioxane, 20 ml of 4 *N* aqueous hydrochloric acid was added, and the mixture was heated on the steam bath at 80–85° (internal temperature) for 5 min and then allowed to cool for another 5 min. The reaction mixture was poured into ice–water to give the α,β-unsaturated aldehyde **6** (R = biphenyl) as an off-white solid, yield 1.55 g (84% from the acid chloride), mp 106–115°. Uv comparison with an analytical sample indicated it to be 81% pure. [Analytically pure aldehyde could be obtained by thick layer chromatography on 2-mm silica gel using *n*-hexane–EtOAc (4:1) for development; R_f *ca* 0.8.] It melted at 119–121° (lit.[7] mp 120–121°), λ_{max}^{MeOH} 318 nm (ε 33,300).

Liquid aldehydes (*e.g.*, cinnamaldehyde) were isolated from the hydrolysis mixture by extraction into ether.

With the biphenylchlorocarbonyl substrate the various intermediates involved in the conversion (eq 1) were isolated (by quenching in ice–water and extracting with ether after the appropriate time interval indicated in the telescoped procedure) and characterized.

p-$C_6H_5C_6H_4C(=O)C\equiv CSiMe_3$.—The analytical sample melted at 71–73° (from petroleum ether, bp 30–60°): R_f on tlc (*n*-hexane–EtOAc) *ca.* 0.9; λ_{max}^{KBr} 4.7 (C≡C, v weak), 6.13 (acetylenic ketone), and 6.25 μ (aromatic).

Anal. Calcd for $C_{18}H_{18}OSi$ (278.41): C, 77.65; H, 6.52. Found: C, 77.74; H, 6.47.

p-$C_6H_5C_6H_4C(=O)CH_2CH(OMe)_2$.—The analytical sample obtained by thick layer chromatography using *n*-hexane–EtOAc (4:1) for development melted at 35–38°: R_f *ca.* 0.3; λ_{max}^{KBr} 5.95 μ; mass spectrum *m/e* 270 (M^+), 75 [$CH(OMe)_2$].

Anal. Calcd for $C_{17}H_{18}O_3$ (270.31): C, 75.53; H, 6.71. Found: C, 75.23; H, 6.57.

p-$C_6H_5C_6H_4CHOHCH_2CH(OMe)_2$.—The analytical sample obtained by thick layer chromatography (C_6H_6–EtOAc 4:1) melted at 57–59°, λ_{max}^{KBr} 3.0 μ (OH), R_f (C_6H_6–EtOAc 4:1) *ca.* 0.35.

Anal. Calcd for $C_{17}H_{20}O_3$ (272.33): C, 74.97; H, 7.40. Found: C, 74.92; H, 7.45.

p-$C_6H_5C_6H_4CHOHCH_2CH(OH)_2$.—Treating **4** (R = biphenyl) dissolved in a small amount of ether with 6 *N* aqueous hydrochloric acid at room temperature for 15 min gave the hydrated aldehyde as a colorless solid, mp 135–140°, as indicated by ir, nmr, and mass spectral analysis. Treatment of the hydrated aldehyde with 4 *N* HCl–dioxane as described above gave the unsaturated aldehyde **6** (R = biphenyl) in 92% yield.

Cyclohexyl-COCl → Cyclohexyl-CH=CHCHO.—Using the telescoped procedure described above, cyclohexylcarbonyl chloride (Eastman) was converted to β-cyclohexylacrolein[8] in 40–45% yield. (The crude aldehyde was converted directly to its semicarbazone[8] by the usual method.[9] The yield of aldehyde indicated is based on the amount of semicarbazone obtained.)

Benzoyl Chloride → Cinnamaldehyde.—Using the telescoped procedure, benzoyl chloride was converted to cinnamaldehyde in 78% yield. (Here too, as in the previous experiment, the yield was established by conversion to its semicarbazone derivative.)

Registry No.—**1**, 14630-40-1; **2** (R = biphenylyl), 39703-85-0; **3** (R = biphenylyl), 39703-86-1; **4** (R = biphenylyl), 39703-87-2; **5** (R = biphenylyl) hydrated aldehyde, 39703-88-3; **6** (R = biphenylyl), 39703-89-4; biphenylcarbonyl chloride, 14002-51-8; cyclohexylcarbonyl chloride, 2719-27-9; β-cyclohexylacrolein, 935-03-5; benzoyl chloride, 98-88-4; cinnamaldehyde, 104-55-2.

Acknowledgments.—I thank Mr. L. Brancone and staff for the analysis, Mr. W. Fulmor and staff for the uv spectra, and Dr. G. Van Lear for the mass spectra.

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[6] Melting points are uncorrected. The thin layer and thick layer (2 mm) plates used were obtained from Analtech Inc., Newark, Del. Uv light was used for spot visualization. Mass spectra were determined on an AEI MS-9 spectrometer at 70 eV.

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Photoinduced Reduction of Polyhalogenomethyl Groups

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Studies on the stereoselective synthesis of carbohydrates by telomerization of vinylene carbonate with polyhalogenomethanes[1] have shown the need for the mild and selective reduction of tri- or dihalogenomethyl groups to di- or monohalogenomethyls, and, among the reductive agents previously reported,[2] only $Ni(CO)_4$ is satisfactorily effective for the present purpose.[3] The reduction of polyhalide is important as the preparative method for synthetically difficult lower halides.

In this paper we describe the smooth and mild conversion of polyhalogenomethyl groups to di- or monohalogenomethyls by simple irradiation with an ultraviolet lamp in tetrahydrofuran (THF). The solutions of tri- or dihalogenomethyl compounds (*ca.* 1×10^{-1} *M*) were irradiated either with a high- or low-pressure mercury lamp at room temperature and reduction is usually completed within several hours. This reaction does not proceed in the dark. The results are summarized in Table I.

Polyhalides such as 1,1,1,3-tetrabromononane, 1,1,1,3-tetrachlorooctane, and telomers of vinylene carbonate with CCl_4 (**1a** and **2a**)[1,4] could be reduced exclusively to dihalogenomethyl compounds without any detectable amount of monohalogenomethyls, while the benzylic trichloromethyl compound underwent a smooth reductive dimerization to 1,1,2,2-tetrachloro-1,2-diphenylethane in analogy with the case by

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[1] T. Tamura, T. Kunieda, and T. Takizawa, *Tetrahedron Lett.*, 2219 (1972).

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[3] T. Kunieda, T. Tamura, and T. Takizawa, *Chem. Commun.*, 885 (1972).

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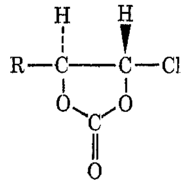
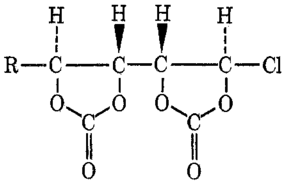
TABLE I

Compd	Registry no.	Concn, mol/l.	Irradiation time, hr	Product	Registry no.	Yield,[a] %
1,1,1,3-Tetrabromononane	1070-25-3	0.11	8	1,1,3-Tribromononane	1071-51-8	69 (0)[c]
1,1,1,3-Tetrachlorooctane	18088-13-6	0.12	11	1,1,3-Trichlorooctane	4905-80-0	78 (0)
1a		0.20	3	**1b**		76 (4)
2a		0.04	0.5	**2b**		74 (0)
Carbon tetrabromide	558-13-4	0.20	0.1	Bromoform	75-25-2	78[b] (10)
7,7-Dibromonorcarane	2415-79-4	0.02	6	7-Bromonorcarane	1121-40-0 (endo) 1121-41-1 (exo)	24 (13)
Benzotrichloride	98-07-7	0.12	4	1,1,2,2-Tetrachloro-1,2-diphenylethane	13700-81-7	40 (7)

[a] Isolated yields. [b] Determination by glc. [c] Recovery of starting material in parentheses (%).



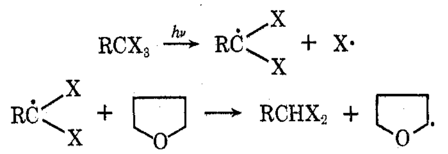
1a, R = CCl_3
b, R = $CHCl_2$



2a, R = CCl_3
b, R = $CHCl_2$

$Ni(CO)_4$.[3] 7,7-Dibromonorcarane[5] gave a mixture of *cis*- and *trans*-7-bromonorcarane in a ratio of 2.2:1, which is similar to that in the reduction *via* radical intermediates by tri-*n*-butyltin hydride[6] or methylmagnesium bromide,[7a] while 1,1-dibromocyclohexane did not give 1-bromocyclohexane under the same conditions.

This reaction would involve the initial formation of dihalomethyl radicals as important intermediates by action of uv light followed by hydrogen abstraction from tetrahydrofuran.[7b] The more stable intermediate, dichlorobenzyl radical, would couple more rapidly than abstract hydrogen from the solvent.



This mild and selective reduction is a feasible method as a general route to dihalogenomethyl compounds.

Experimental Section

The melting and boiling points are uncorrected. The nmr spectral data ($CDCl_3$, TMS internal standard, J in hertz) were obtained using a JEOL PS-100 nmr spectrometer, the glc data using a YANACO G-800 gas chromatograph (SE-30 column). Irradiations were carried out either with a HALōS PIL-60 (low pressure) or a HALōS PIH-500 (high pressure) at room temperature and the average distance of the irradiated solution from the light source was 4 cm.

1,1,3-Tribromononane.—1,1,1,3-Tetrabromononane was prepared by the addition of carbon tetrabromide to 1-octene according to the reported method.[8] 1,1,1,3-Tetrabromononane (5.0 g, 11.3 mmol) was dissolved in THF (100 ml) and irradiated in a Pyrex vessel with a high-pressure mercury lamp for 8 hr. The solvent was removed *in vacuo* and chromatography of the residue on silica gel (*n*-hexane) followed by distillation under diminished pressure gave 1,1,3-tribromononane (2.8 g, 69%) as a colorless liquid: bp 126–127° (5 mm); nmr δ 1.30 (m, 13 H), 2.70 (d d, $J_1 = 10$, $J_2 = 7$ Hz, 1 H), 2.80 (d d, $J_1 = 10$, $J_2 = 7$ Hz, 1 H), 4.10 (t t, $J = 7$ Hz, 1 H), 5.90 (t, $J = 7$ Hz, 1 H). *Anal.* Calcd for $C_9H_{17}Br_3$: C, 29.62; H, 4.97. Found: C, 29.56; H, 4.71.

1,1,1,3-Tetrachlorooctane.—1-Heptene (19.6 g) and carbon tetrachloride (92.4 g) were heated under a nitrogen atmosphere for 9 hr, and benzoyl peroxide (1.45 g) was added every 3 hr. The solvent was removed *in vacuo* and the product was purified by distillation to give 1,1,1,3-tetrachlorooctane: bp 98–99° (2.5 mm); nmr δ 1.30 (m, 11 H), 3.00 (d d, $J_1 = 16$, $J_2 = 5$ Hz, 1 H), 3.30 (d d, $J_1 = 16$, $J_2 = 5$ Hz, 1 H), 4.20 (m, 1 H). *Anal.* Calcd for $C_8H_{14}Cl_4$: C, 38.12; H, 5.60. Found: C, 38.36; H, 5.50.

1,1,3-Trichlorooctane.—1,1,1,3-Tetrachlorooctane (3.0 g, 12 mmol) was dissolved in THF (100 ml) and irradiated in a quartz vessel with a low-pressure mercury lamp for 11 hr. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel (*n*-hexene) to give 1,1,3-trichlorooctane (2.8 g, 78%) as a colorless liquid: bp 98–99° (10 mm); nmr δ 1.35 (m, 11 H), 2.50 (d d, $J_1 = 9$, $J_2 = 6$ Hz, 1 H), 2.60 (d d, $J_1 = 9$, $J_2 = 6$ Hz, 1 H), 4.10 (t t, $J = 6$ Hz, 1 H), 6.00 (d d, $J_1 = 7$, $J_2 = 5$ Hz, 1 H). *Anal.* Calcd for $C_8H_{15}Cl_3$: C, 44.17; H, 6.95. Found: C, 44.46; H, 6.92.

Irradiation with a high-pressure mercury lamp gave a similar result.

4-Chloro-5-dichloromethyl-1,3-dioxolan-2-one (1b).—4-Chloro-5-trichloromethyl-1,3-dioxolan-2-one (**1a**), mp 53–54° (4.8 g, 20 mmol), was dissolved in THF (100 ml) and irradiated in a quartz vessel without filter with a high-pressure mercury lamp for 3 hr. The solvent was removed *in vacuo* and purification by chromatography on silica gel gave 4-chloro-5-dichloromethyl-1,3-dioxolan-2-one (**1b**) (3.1 g, 76%) in addition to the unchanged material (0.2 g). Recrystallization from *n*-hexane gave an analytical sample of **1b** as colorless prisms: mp 31–33°; ir (neat) 1830 cm^{-1} ($\nu_{C=O}$); nmr δ 5.05 (d d, $J_1 = 4$, $J_2 = 2.5$ Hz, 1 H), 5.95 (d, $J = 4$ Hz, 1 H), 6.20 (d, $J = 2.5$ Hz, 1 H). *Anal.* Calcd for $C_4H_3O_3Cl_3$: C, 23.39; H, 1.47. Found: C, 23.33; H, 1.39.

5-Chloro-5′-dichloromethyl[4,4′-bi-1,3-dioxolane]-2,2′-dione (2b).—5-Chloro-5′-trichloromethyl[4,4′-bi-1,3-dioxolane]-2,2′-dione (**2a**)[1] (mp 185–186°, 1.3 g, 4 mmol), prepared by telomerization of vinylene carbonate with carbon tetrachloride, was dissolved in THF (100 ml) and similarly irradiated with a high-pressure mercury lamp for 0.5 hr. After removal of the solvent the product was purified by chromatography on silica gel and recrystallized from carbon tetrachloride to give dichloromethyl compound **2b** (864 mg, 74%) as colorless prisms: mp 115–116°; ir (Nujol) 1830 cm^{-1} ($\nu_{C=O}$); nmr (CH_3CN) δ 5.15 (m, 3 H),

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6.20 (d, J = 3 Hz, 1 H), 6.60 (d, J = 2 Hz, 1 H). *Anal.* Calcd for $C_7H_5O_6Cl_3$: C, 28.85; H, 1.73. Found: C, 29.01; H, 1.69.

Bromoform.—Carbon tetrabromide (0.65 g, 1.95 mmol) was dissolved in THF (10 ml) and irradiated through a Pyrex filter with a high-pressure mercury lamp for 6 min. The major product (78% yield by glc analysis) was identified as bromoform by direct comparison.

7-Bromonorcarane.—7,7-Dibromonorcarane[5] (4.9 g, 19.1 mmol) was dissolved in THF (1000 ml) and irradiated with a low-pressure mercury lamp under an argon atmosphere for 6 hr. Removal of the solvent followed by chromatography on silica gel (n-hexane) gave a mixture of *cis*- and *trans*-7-bromonorcarane in a ratio of 2.2:1 (0.8 g, 24%) as a colorless liquid in addition to the starting material (0.66 g): bp 78° (16 mm); nmr δ 1.35 (m, 10 H), 2.55 (t, J = 3 Hz, 0.3 H, trans isomer), 3.25 (t, J = 8 Hz, 0.7 H, cis isomer); glc retention time (120°), trans isomer 5.1 min, cis isomer 6.2 min. The nmr and glc data were identical with those of the authentic sample prepared by the literature method.[7]

1,1,2,2-Tetrachloro-1,2-diphenylethane.—A solution of benzotrichloride (2.35 g, 12 mmol) in THF (100 ml) was irradiated in a Pyrex vessel with a high-pressure mercury lamp for 4 hr. Purification of the product by chromatography on silica gel gave dimeric compound, 1,1,2,2-tetrachloro-1,2-diphenylethane (0.77 g, 40%), together with a trace of benzal chloride and the unchanged material (156 mg). The dimer was recrystallized from n-hexane to give colorless prisms, mp 163°, whose ir spectrum was identical with that of the authentic sample.[9]

Registry No.—**1a**, 39010-29-2; **1b**, 39010-30-5; **2a**, 39010-31-6; **2b**, 39010-32-7; 1-heptene, 592-76-7; carbon tetrachloride, 56-23-5.

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Photolysis of Sultones. Conversion to Butenolides and to Dimeric Sultones

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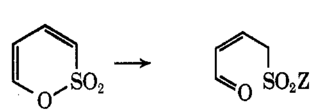
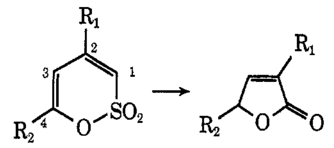
Photolysis of unsaturated sultones of general structure **1**, when carried out in methanol solution or in ether solutions containing benzylamine, has been shown to give ketosulfonic acid derivatives (**2**).[2,3]



1 **2**

Z = Me, NHCH$_2$Ph

We have found that when photolysis is carried out in the absence of a nucleophile the product is a butenolide. Thus, irradiation of 4-hydroxy-2-methyl-1,3-pentadiene-1-sulfonic acid sultone (**3a**)[4] in ether solution employing a medium-pressure mercury lamp yielded 2-methyl-4-hydroxy-2-pentenoic acid lactone (**4a**)[5] in 65% yield. Similarly irradiation of the sultone **3b**[4] gave the butenolide **4b**[6] in 53% yield. The loss of sulfur monoxide in these reactions is evidenced by the formation of both sulfur dioxide and monoclinic sulfur.[7,8]

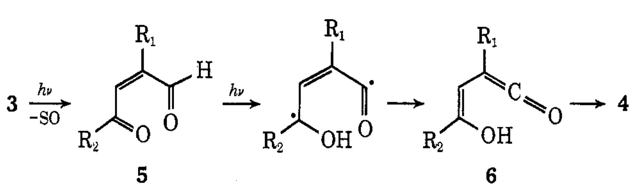


3 **4**

a, R$_1$ = R$_2$ = Me

b, R$_1$ = Me; R$_2$ = Ph

Although the detailed mechanism of this transformation has not been defined, initial formation of a dicarbonyl intermediate **5** through photochemically induced loss of sulfur monoxide from **3** seems likely.[9] Further transformation of the unsaturated keto aldehyde through photochemical γ-hydrogen abstraction, decay to the ground state, and cyclization of the ketene **6** has a close parallel in the photochemical conversion of 2-formylbenzophenone,[13] 2-formylacetophenone,[14] and phthalaldehyde[15,16] to the corresponding pthalides. In these reactions clear evidence has been adduced for γ-hydrogen abstraction in the keto aldehyde and for the intermediary of an enol ketene.[15,16]



5 **6**

Sensitized photolysis of these sultones, carried out in the presence of benzophenone, leads to the formation of dimeric products. The infrared spectra of these dimers preserved the moderately intense band near 1680 cm^{-1}, present in the starting material, which is assigned to the enol sulfonate grouping.[17] However, a second moderately intense absorption band in the starting material near 1580 cm^{-1}, assigned to the remaining double bond, is uniformly absent from the dimers.[18] These observations eliminate all possible

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[9] Sulfenes may be intermediates in this reaction. The photochemical rearrangement of the closely related sulfines to carbonyl compounds through an excited singlet state[10] has been reported for a number of such compounds.[10,11] Although the corresponding photochemical rearrangement of a sulfene has hitherto not been observed, high-temperature thermolysis of thiete 1,1-dioxides is reported to give α,β-unsaturated ketones or aldehydes formed apparently through initial cycloreversion to a vinyl sulfene followed by loss of SO.[12]

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[18] Divinyl sulfone exhibits absorption at 1613 cm^{-1} (Satler ir no. 13512).