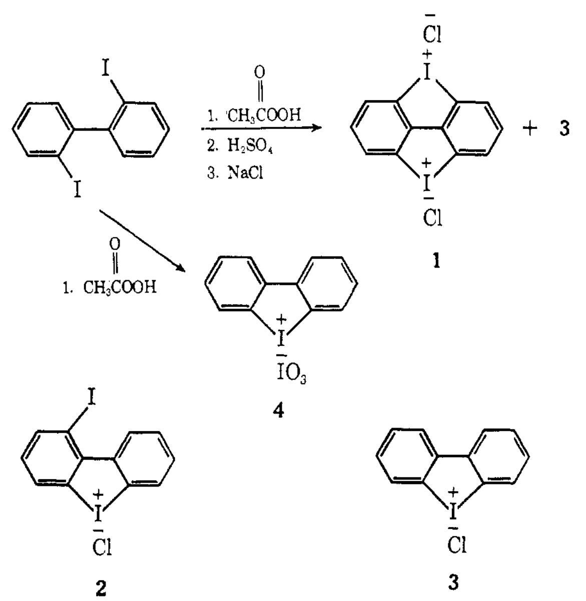
SCHEME I



mixture was allowed to stand at room temperature for 48 hr. The reaction mixture was poured into ice–water (500 ml) and the solid was collected and washed with water (1.0 l. at 70°). To the combined filtrate was added sodium chloride until precipitation was complete, which afforded III as the chloride.

Anal. Calcd for $C_{12}H_8ICl$: Cl, 11.28. Found: Cl, 10.99.

The residue was dissolved in boiling water (6.0 l.) and filtered while hot. To the hot filtrate was added sodium chloride until precipitation was complete, which afforded I as the dichloride, yield 0.5 g.

Anal. Calcd for $C_{12}H_6I_2Cl_2$ (0.0662- and 0.1310-g samples): AgI + AgCl, 0.1049, 0.2076 g. Found: AgI + AgCl, 0.1048, 0.2106 g.

When the procedure which brings about the facile ring closure of 2-iodobiphenyl[1] (5 g) was followed, the reaction mixture contained unreacted 2,2′-diiodobiphenyl, a small amount of III (0.1 g) and a relatively large amount of pale yellow II (1.1 g) which was isolated as the chloride.

Anal. Calcd for $C_{12}H_7I_2Cl$: Cl, 8.06. Found: Cl, 8.15, 8.39.

The brilliant yellow diiodide of I was prepared by the usual procedure.[1]

Anal. Calcd for $C_{12}H_6I_4$: I, 77.20. Found: I, 76.85.

The diiodide of I (1.5 g) was added to dimethyl sulfoxide (25 ml) and heated to 180° for 0.5 hr or until solution was complete. The solution was poured into 100 ml of ice–water and the solid tetraiodobiphenyl was recovered by filtration and was recrystallized from alcohol–benzene to afford brown crystals (1.0 g), mp 258°. A pale yellow-brown analytical sample melted at 262–263°.

Anal. Calcd for $C_{12}H_6I_4$: I, 77.26. Found: I, 77.22, 77.14.[4]

In a similar manner the iodide of II was prepared.

Anal. Calcd for $C_{12}H_7I_3$: I, 71.61. Found: 71.44.

The iodide was decomposed in hot dimethyl sulfoxide and afforded the triiodobiphenyl (54%). It was recrystallized three times from alcohol to give pale yellow crystals, mp 151–152°.

Anal. Calcd for $C_{12}H_7I_3$: I, 71.61. Found: I, 71.29, 71.38.[4]

A solution of 2,2′-diiodobiphenyl (2.4 g) in peracetic acid (70 ml) was allowed to stand for 1 week at room temperature (30°). White solid diphenyleniodonium iodate (1.9 g) separated and was recrystallized from water.

Anal. Calcd for $C_{12}H_8I_2O_3$: I, 55.94. Found: I, 55.57, 55.94.

An aqueous solution of the iodate was treated with sodium bisulfite and afforded pale yellow diphenyleniodonium iodide.

Anal. Calcd for $C_{12}H_8I_2$: I, 62.56. Found: I, 63.19.

The iodide was decomposed in hot dimethyl sulfoxide to produce 2,2′-diiobiphenyl, mp 109–110°. A mixture melting point with an authentic sample showed no depression.

There was also isolated from the above diphenyleniodonium iodate reaction filtrate the iodonium salt as the chloride (0.4 g).

Anal. Calcd for $C_{12}H_8ICl$: 11.28. Found: Cl, 11.22, 11.41.

Diphenyleniodonium chloride or the sulfate (3 g) was dissolved in boiling water (2 l.) and to the solution was added cuprous chloride (10 g) followed by a *very slow* and *careful* addition of concentrated ammonium hydroxide (100 ml). The mixture was refluxed for 1 hr and carbazole (65%) was recovered by filtration and extraction by the usual procedure.

Registry No.—2,2′-Diiodobiphenyl, 2236-52-4; **1** dichloride, 18399-12-7; **2** chloride, 18399-13-8; 2,2′,6,6′-tetraiodobiphenyl, 18399-10-5; **2** iodide, 18354-33-1; 2,2′,6-triiodobiphenyl, 18399-11-6; **3** chloride 4673-26-1; **3** iodide, 1010-76-0; **4** 18399-16-1.

Acknowledgments.—We are very grateful for the continued help and encouragement given to us by Professor Harry Gunning. We are also very grateful to Miss D. Roberts and Mrs. A Dunn for elemental microanalysis. We also express our thanks to the National Research Council of Canada, for financial aid.

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[4] Microanalyses by Micro-Tech Laboratories, Inc., Skokie, Ill.

Reactions of Chloroacetone in Basic Media

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In the interest of ascertaining the susceptibility of chloroacetone to function as a donor enolate at the chlorine-bearing carbon, the behavior of this ketone to various basic conditions was examined. Initial experiments revealed the essentially titrametric velocity with which chloroacetone reacts with aqueous alkali to afford quantitatively acetol as determined by the blue tetrazolium assay method.[1] Despite this extremely rapid hydrolysis of chloride, however, deuterium exchange and correspondingly formation of the pertinent anion at the chloromethylene center is a more rapid process. Thus when chloroacetone was allowed to react with 0.1 equiv of sodium deuterioxide in D_2O–CH_3OD, the nmr spectrum of the surviving chloroacetone, isolated after a 2-min reaction period, exhibited a 3:1 proton area ratio at τ 7.69 and 5.90 consistent with 1-chloro-1-monodeuterioacetone. In the absence of alkali, chloroacetone did not undergo measurable deuterium exchange after 0.5 hr.

Attempts to mediate condensations of chloroacetone *via* its pyridinium salt (**3**, NR_3 = pyridine)[2] proved ineffective apparently in virtue of the relatively stable character of the latter species. With triethylamine condensation proceeded in two independent directions according to the media employed. In aprotic media such as glyme the two components did not react in a simple manner to give the quaternary salt **3** (R = C_2H_5) but instead gave triethylamine hydrochloride

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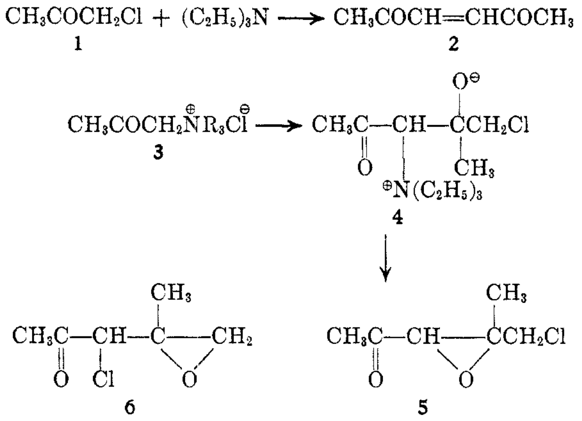
[1] See Experimental Section; also A. S. Meyer and M. C. Lindberg, *Anal. Chem.*, **27**, 813 (1955), and references therein.

[2] C. Dreser, *Arch. Pharm.*, **236**, 334 (1898).

together with *trans*-diacetylethylene (2)[3] as the major isolable product (Scheme I). When reaction, on the other hand, was effected in protic media such as methanol, a Darzens-type reaction ensued with formation of the oxido chloro ketone **5** as a mixture of diastereoisomers.

SCHEME I



Analysis of **5** by vapor phase chromatography revealed two very close-lying peaks in the ratio of 1:1 with retention times of 13 and 14 min, respectively. Each of the two corresponding substances exhibited a parent mass ion of 148/150 and the fragmentation pattern of both was essentially the same. The appearance of a mass peak at 99 (loss of CH_2Cl) supported structure **5** over **6**. Definitive for structure **5** was its zero response to alkaline tetrazolium assay, a method quantitatively applicable to α-halo ketones such as chloroacetone, 21-chloro-20-ketopregnanes, etc.[1,4] The nmr spectrum of **5** further exhibited doublet peaks at the various pertinent regions in conformity with expectations based on a mixture of diastereoisomers.

The essentially exclusive formation of **5** in the self-condensation of chloroacetone in alcoholic triethylamine is perhaps best accommodated as arising *via* an intermediate betaine **4** wherein preferred extrusion of the triethylammonium group *vis-a-vis* chlorine would be expected to be favored. Isolation, in fact, of an unstable trimethylammonium salt (**3**, R = CH_3) derived from chloroacetone at low temperature has been reported.[5] The reaction of chloroacetone with triethylamine in aprotic media probably proceeds *via* nucleophilic coupling with subsequent dehydrochlorination, a process formally indistinguishable from dimerization of an intermediate keto carbene resulting from α elimination.

The reaction of chloroacetone with methanolic triethylamine in the presence of 2 equiv of benzaldehyde yielded the Darzens product, benzalacetone oxide, also obtained previously employing the conventional strong base (CH_3ONa) technique.[6]

Experimental Section

Chloroacetone Solvolysis.—To a stirred solution of 3.0 ml of chloroacetone, 5 ml of methanol and 5 ml of water at 24° was added rapidly 4.0 ml of 1 *N* potassium hydroxide (0.1 mol/mol of chloroacetone). The rate of solvolysis was followed as a function of changed in pH with time on a recording pH meter. After an initial very steep rise, the pH value dropped rapidly and reached a value of pH 7 in 1.3 min.

Blue Tetrazolium Assay.[7]—The reagents used were (1) **tetramethylammonium hydroxide** (1 ml of a 10% aqueous solution) diluted to 100 ml with 95% ethanol, and (2) blue tetrazolium (5 mg/ml in 95% ethanol).

Sample solutions were (1) chloroacetone (105.9 μg/ml in methanol) and (2) epoxy chloro ketone **5** (78.8 μg/ml in methanol).

Procedure.—Chloroacetone was used as the standard for the color calibration curve. Aliquots of the chloroacetone solution (0.1–1.0 ml) were diluted to 1.0 ml with methanol and treated with 10 ml of tetramethylammonium hydroxide solution. After 1 min 1 ml of blue tetrazolium reagent was added and the sample was held at 24° for 45 min. The optical density at 5250 Å was determined on a Cary Model 14 recording spectrophotometer.

A plot of sample weight *vs.* optical density at 5250 Å provided a standardization curve and demonstrated the color linearity of chloroacetone. No discernible color was observed for 3,4-oxido-4-chloromethylpentanone-2 (**5**).

Chloroacetone–Deuterium Exchange.—To a vigorously stirred solution of 8.0 ml of deuterium oxide, 8.0 ml of methanol-d_1 and 5.0 g of chloroacetone was added rapidly a solution of 0.3 g of sodium methoxide in 2.0 ml of deuterium oxide. The reaction mixture was stirred for 2 min and then diluted with 100 ml of ether. The ethereal layer was separated, dried ($MgSO_4$) and the solvent removed. Distillation of the residue gave 4.4 g of chloroacetone: bp 62–63° (85 mm); nmr ($CDCl_3$) τ 5.90 (s, 1, CHDCl) and 7.69 ppm (s, 3, CH_3CO).

***trans*-1,2-Diacetylethylene (2).**—A mixture of 20 ml of chloroacetone, 32 ml of triethylamine and 50 ml of dimethoxyethane was stirred at 26° for 18 hr. At the end of this period the reaction mixture was diluted with 150 ml of ether and the ethereal solution washed with dilute hydrochloric acid, water, and dried ($MgSO_4$). The solvents were removed *in vacuo* and the dark residue was distilled, product fraction bp 100–110° (18 mm). The distilled material crystallized on standing at room temperature. Recrystallization from hexane gave 2.7 g of *trans*-1,2-diacetylethylene: mp 74–76°; uv max (CH_3OH) 228 mμ (*E* 1285); ir ($CHCl_3$) 5.95 (C=CC=O) and 6.18 μ (C=C); the mixture melting point with an authentic sample[8] was not depressed.

3,4-Oxido-4-chloromethylpentanone-2 (5).—A mixture of 100 ml of methanol, 50 ml of chloroacetone and 40 ml of triethylamine under a nitrogen atmosphere was stirred at 24° for 18 hr. The solvent was removed *in vacuo* and the residue was slurried with 400 ml of ether. Triethylamine hydrochloride was removed by filtration. The filtrate was washed with dilute hydrochloric acid, dried ($MgSO_4$), concentrated *in vacuo* and distilled to afford 18.2 g of the epoxy chloro ketone **5** as a pale yellow liquid, bp 99–108° (12 mm). Analytical material was obtained by chromatography on silica G and distillation: bp 98–100° (15 mm); ir 5.80 μ (C=O); glpc (20% SE-30/Chromosorb W, 100°) equal area peaks at 13 and 14 min; nmr ($CDCl_3$) τ 6.4 (d, 2, $\mathbf{CH_2}$Cl), 7.7 (d, 3, $\mathbf{CH_3}$CO) and 8.5 ppm (m, 4, CH_3 and **CH**).

Anal. Calcd for $C_6H_9ClO_2$: C, 48.47; H, 6.10; Cl, 23.85. Found: C, 48.73; H, 6.06; Cl, 23.56.

4-Phenyl-3,4-oxidobutanone-2.—A solution of 10 ml of chloroacetone, 16 ml of triethylamine, 27 ml of benzaldehyde and 20 ml of methanol was combined at 0° and held at 24–26° for 48 hr. At the end of this period the reaction mixture was concentrated *in vacuo* at <40°. The residue was diluted with 150 ml of ether and filtered. The ethereal solution was washed with dilute hydrochloric acid, sodium bicarbonate, dried ($MgSO_4$), concentrated *in vacuo* and distilled through a 15-cm stainless steel gauze packed column. The product fraction, bp 86–89° (1 mm), crystallized spontaneously. Recrystallization from ether–hexane gave 5.84 g of product: mp 52–53° (lit.[9] mp 52–53°); ir ($CHCl_3$)

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(3) K. F. Armstrong and R. Robinson, *J. Chem. Soc.*, 1650 (1934).

(4) Unpublished observations from these laboratories.

(5) L. Niemilowicz, *Monatsh. Chem.*, **7**, 241 (1886).

(6) (a) T. I. Temnikova and V. F. Martynov, *J. Gen. Chem. USSR*, **15**, 499 (1945); *Chem. Abstr.*, **40**, 4694 (1946); (b) H. Kwart and L. G. Kirk, *J. Org. Chem.*, **22**, 116 (1957).

(7) Based on the method of W. J. Mader and R. R. Buck, *Anal. Chem.*, **24**, 666 (1952).

(8) Prepared according to M. W. Goldberg and P. Müller, *Helv. Chim. Acta*, **21**, 1699 (1938).

(9) E. Weitz and A. Scheffer, *Ber.*, **54**, 2327 (1921).

5.85 μ (C=O); nmr ($CDCl_3$) τ 2.65 (s, 5, aromatic), 5.98 (d, 1, J = 2 Hz), 6.50 (d, 1, J = 2 Hz) and 7.83 ppm (s, 3, CH_3CO).

Registry No.—**1**, 78-95-5; **2**, 820-69-9; **5**, 18266-87-0.

Acknowledgment.—The authors wish to thank Mr. A. B. White, Physical Measurements Department, for the blue tetrazolium assay determinations.

Reactions of Group IV Organometallic Compounds. VII.[1] Ring-Opening Reactions of β-Propiolactone with Various Trimethyltin Compounds

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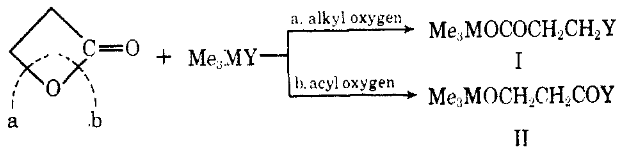
β-Propiolactone is the simplest four-membered cyclic ester among various cyclic compounds showing rather low basicity[2] associated with large ring strain. It is known to react readily with a large number of nucleophilic reagents through ring opening. Nucleophilic attack takes place either on sp^2 carbon atom which is the usual position for various open chain or higher membered cyclic esters, or on sp^3 carbon atom. The mode of the ring opening reaction was influenced by both the nature of nucleophiles and experimental conditions.

When trimethylmetal(IV) organometallic compounds are used as acceptor molecules to β-propiolactone, the following two modes of pathways are possible—(a) alkyl oxygen bond fission to give trimethylmetal(IV) β-substituted propionate (I) and (b) acyl oxygen bond fission to give β-keto-substituted ethoxytrimethylmetal(IV) (II).



In previous publications,[3-5] the mode of fission of β-propiolactone was found to depend on the central metal moiety. For the reaction with amino derivatives of trimethylmetal(IV) compounds with this substrate, the alkyl oxygen fission occurs when M = Si or Ge and the alkyl oxygen fission when M = Sn. These findings enforced us to study the effect of substituents (Y) on the mode of cleavage of β-propiolactone. Trimethyltin derivatives were chosen as suitable models since the corresponding trimethylsilyl or trimethylgermanium analogs showed only limited reactivity toward β-propiolactone on account of the considerable depression of basicity by (p–d)π interaction for some substituents with the metal.

Results

Determination of the Preferential Mode of Cleavage.—Relative amounts of products II/I were determined for the reaction of each 10.0 mmol of β-propiolactone and trimethyltin compounds in 2.00 ml of ethylene dichloride at 80°. As the reactivity of trimethyltindiethylamide was extremely high, treatment of β-propiolactone was carried out at 0° in the concentrations described above. β-Trimethylstannoxypropion-N,N-diethylamide, arising from selective acyl oxygen fission [II, Y = $N(C_2H_5)_2$], was isolated as a predominant product for the reaction of trimethyltin diethylamide with β-propiolactone. Preferential cleavage through the acyl oxygen bond was also observed for the reaction with trimethyltin methoxide, giving methyl β-trimethylstannoxypropionate (II, Y = OMe). At the same time, considerable amounts of product through alkyl oxygen fission (I, Y = OMe) were also detected by nmr and infrared spectrometry. From nmr peak areas of methoxy proton, relative amounts of II/I were estimated in the same manner as that described[1]—II/I = 7.7. Although this product ratio was found to depend on the polarity of the reaction media, the predominant mode was acyl oxygen bond fission for a variety of solvents.[1] The corresponding trimethylsilyl analog, trimethylmethoxysilane, did not react at all with β-propiolactone on account of the large stabilization due to (p–d)π overlap between silicon and oxygen.

A drastic change of mode of fission was however suggested when trimethyltin methylsulfide was utilized as an addendum toward β-propiolactone. After standing overnight, the reaction mixture was distilled under reduced pressure and the main product was isolated in 60% yield. This product showed characteristic nmr and infrared spectra for trimethyltin carboxylate[6] and was identified as trimethyltin β-methylthiopropionate (I, Y = SMe). The relative ratio of products for this system was determined in an analogous way as its oxygen analog from the relative intensity of methylthio protons in the reaction mixture—II/I = 0.15.

The preferential alkyl oxygen bond fission was also found for trimethyltin bromide and chloride. The reaction mixture of β-propiolactone and trimethyltin bromide gave an addition product which could be crystallized from acetone and was identified as trimethyltin β-bromopropionate (I, Y = Br) in 85% yield. Unfortunately, exact amounts of I and II could not be obtained because of the absence of key nmr proton signals and the low stability of the acyl halide structure in II (Y = Br). For the reaction with trimethyltin chloride, behavior was the same as the corresponding bromide, giving trimethyltin β-chloropropionate (I, Y = Cl) which arose through alkyl

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