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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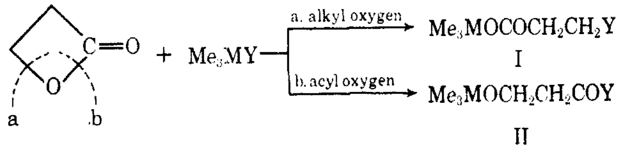
β-Propiolactone is the simplest four-membered cyclic ester among various cyclic compounds showing rather low basicity[2] associated with large ring strain. It is known to react readily with a large number of nucleophilic reagents through ring opening. Nucleophilic attack takes place either on sp^2 carbon 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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[1] Part VI: K. Itoh, S. Kobayashi, S. Sakai, and Y. Ishii, *J. Organometal. Chem.*, **10**, 451 (1967).

[2] Y. Yamashita, T. Tsuda, M. Okada, and S. Iwatsuki, *J. Polym. Sci.*, Part *A-1*, **4**, 2121 (1966).

[3] K. Itoh, S. Sakai, and Y. Ishii, *J. Org. Chem.*, **31**, 3948 (1966).

[4] K. Itoh, S. Sakai, and Y. Ishii, *Tetrahedron Lett.*, 4941 (1966).

[5] K. Itoh, Y. Kato, S. Sakai, and Y. Ishii, *Kogyo Kagaku Zasshi*, **70**, 935 (1967); *Chem. Commun.*, 36 (1967).

[6] R. Okawara and M. Wada, *Advan. Organometal. Chem.*, **5**, 137 (1967).

oxygen cleavage of β-propiolactone. All results we have obtained in this series of study are summarized in Table I.

Table I

Reaction of β-Propiolactone with Various Group IV Organometallic Compounds

Compound	Predominant mode of fission	Difference in electronegativity	Second order rate constant,[a] l./mol sec k_{AL}	k_{AC}
$Me_3SnN(C_2H_5)_2$	Acyl oxygen	1.2		$>10^{-1}$
$Me_3GeN(C_2H_5)_2$	Alkyl oxygen[b]	1.2	4.9×10^{-3}	
$Me_3SiN(C_2H_5)_2$	Alkyl oxygen[b]	1.2	6.1×10^{-4}	
Me_3SnOMe	Acyl oxygen	1.7	2.1×10^{-4}	1.8×10^{-3}
Me_3SnSMe	Alkyl oxygen	0.7	2.1×10^{-5}	3.1×10^{-6}
Me_3SnBr	Alkyl oxygen	1.0	3.0×10^{-6}	
Me_3SnCl	Alkyl oxygen	1.2	7.9×10^{-7}	
$Me_3SiSC_2H_5$	Alkyl oxygen	0.7	7.2×10^{-7}	

[a] Temperature 65.0° in ethylene dichloride. [b] See ref 3-5. [c] K. Itoh, K. Matsuzaki, and Y. Ishii, *J. Chem. Soc. C*, in press.

Study on the Reactivity of Various Trimethylmetal(IV) Compounds.—For comparing the reactivity between various group IV organometallic compounds toward ring-opening reaction of β-propiolactone, kinetic studies were performed. All reaction was found to fit well to secord-order kinetics and the second-order rate constants for alkyl oxygen bond fission (k_{AL}) and those for acyl oxygen bond fission (k_{AC}) were determined. Results are included in Table I. As trimethyltin methoxide and trimethyltin methylsulfide showed dual behavior for the reaction, second-order rate constants for each cleavage were calculated as $k_{AL} = k_{obsd}(I/I + II)$ and $k_{AC} = k_{obsd}(II/I + II)$.

Discussion

In order to explain the preferential mode of fission of β-propiolactone, the principle of hard and soft acid and bases (HSAB)[7,8] attracted our attention, because β-propiolactone owns both "hard" sp^2 carbonyl carbon atom and "soft" sp^3 carbon atom in the same molecule. Nucleophilic reagents such as nitrogen or oxygen are known to behave as "hard bases," whereas sulfur or bromine are considered as "soft bases," when they react as free anions. However, the HSAB principle is not simply applicable to explain the reaction behavior of group IV organometallic compounds, because their bonds are essentially covalent.

Degree of ionization which is influenced by (1) difference in electronegativity and (2) contribution of $(p-d)\pi$ bonding between metal(IV) and heteroatom(Y) is important in determining both the mode of fission of β-propiolactone and the reactivity of group IV organometallic compounds. The latter effect diminishes in the order as Si > Ge > Sn when these atoms form chemical bonds with nitrogen or oxygen atom.[9] Consequently, bonds such as Sn–N or Sn–O are considered to have high polar character and trimethyltin diethylamide and trimethyltin methoxide act as "hard" nucleophiles, giving the adduct through acyl oxygen cleavage. In other words, the ring-opening reaction of β-propiolactone is charge controlled.[8] The fact that the alkyl oxygen bond fission becomes prevalent for trimethylsilyl- and trimethylgermylamines is ascribed to a change of the reaction from charge controlled to frontier controlled due to the increase of $(p-d)\pi$ interaction between the metal and nitrogen atoms. The reactivity difference between trimethyltin bromide and chloride (Br > Cl) is compatible with the HSAB principle. However, the reactivity difference between trimethyltin methoxide and methyl sulfide in acyl oxygen cleavage is not consistent with HSAB predictions. This difference might be ascribed to the smaller polar character of Sn–S bond.

It was pointed out that the second-order rate constant for the reaction of β-propiolactone with trimethyltin methoxide was smaller in ethylene dichloride than carbon tetrachloride[1] ($k_2 = 4.8 \times 10^{-3}$ l./mol sec). This trend was quite reversed in the case of alkyl oxygen fission for trimethylsilyl- and trimethylgermylamines.[5] The transition state for the acyl oxygen fission would not be dipolar.

Experimental Section

General Remarks.—Infrared and nmr spectra were recorded with Nippon Bunko IR-S type and a Japan Electron Optics C-60 spectrometer, respectively. All reactions were performed under the atmosphere of argon. Trimethyltin halides were prepared by the well-known disproportionation reactions. Trimethyltin diethylamide,[10] methoxide,[11] and methyl sulfide[12] were obtained as cited and purified by distillation. β-Propiolactone was supplied by Dicel Co. Ltd., and purified by distillation.

Reaction of Trimethyltin Compound with β-Propiolactone.—Trimethyltin compounds (10 mmol) were dissolved in 2.00 ml of ethylene dichloride and were added dropwise to equimolar amounts of β-propiolactone. The reaction mixture was kept at 80° (for Y = $N(C_2H_5)_2$ at 0°). Determination of the relative amounts of I and II was performed by measuring the relative intensities of the corresponding peaks in the nmr chemical shifts which were in the case of trimethyltin methoxide, τ 6.77 for I, and τ 6.42 for II and in the case of trimethyltin methyl sulfide, τ 7.84 for I and τ 6.42 for II.

β-Trimethylstannoxypropion-N,N-diethylamide [II, Y = N(C_2H_5)$_2$].—The reaction was performed by mixing β-propiolactone with an ethylene dichloride solution of trimethyltin diethylamide in the general condition at 0°. After the removal of solvent, the product was obtained as distillation residue (yield 92%): ir (CCl_4), 1641 cm^{-1} (C=O); nmr (CCl_4) τ 9.69 with satellites (s, 9 H, CH_3Sn), 8.93 and 8.82 (two t, 6 H, CH_3CH_2), 7.68 (t, 2 H, CH_2CO-), 6.72 (q, 4 H, CH_2N), and 6.21 (q, 4 H, CH_2O). *Anal.* Calcd for $C_{10}H_{23}NO_2Sn$: C, 39.00; H, 7.54; Sn, 38.54. Found: C, 38.97; H, 7.42; Sn, 38.67.

Trimethyltin β-Methylthiopropionate (I, Y = SMe).—The reaction mixture obtained under the general reaction conditions for 10 hr was distilled under reduced pressure at 110° (0.8 mm). The product was isolated in 60% yield as a colorless waxy material. Recrystallization was accomplished with acetone and white crystals were obtained: mp 107°; ir ($CHCl_3$) 1657 cm^{-1} (C=O); nmr ($CHCl_3$) τ 9.42 (s, 9 H, with two satellites; $J_{Sn^{117}-H}$ = 54.7 and $J_{Sn^{119}-H}$ = 56.8 Hz, CH_3Sn), 7.84 (s, 3 H, CH_3S), 7.30 (m of Ab type, 4 H, two methylenes). *Anal.* Calcd for $C_7H_{16}O_2Sn$: C, 29.71; H, 5.71; Sn, 41.98. Found: C, 29.86; H, 5.89; Sn; 42.06.

Trimethyltin β-Bromopropionate (I, Y = Br).—After reaction under the standard condition, the product was isolated by crystallization with *n*-hexane in 85% yield and recrystallization from *n*-hexane: mp 114.0–114.5°; ir ($CHCl_3$) 1657 cm^{-1} (C=O); nmr ($CHCl_3$) τ 9.41 (s, with two satellites; $J_{Sn^{117}-H}$ = 56.3 and $J_{Sn^{119}-H}$ = 58.4 Hz, 9 H, CH_3Sn), 7.16 (t, 2 H, CH_2CO), and 6.44 (t, 2 H, CH_2Br). *Anal.* Calcd for $C_6H_{13}BrO_2Sn$: C, 22.82; H, 4.15. Found: C, 22.98; H, 4.20.

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(7) R. G. Pearson and J. Songstad, *J. Amer. Chem. Soc.*, **89**, 1827 (1967).

(8) G. Klopman, *ibid.*, **90**, 223 (1968).

(9) E. W. Abel, D. A. Armitage, and D. B. Brady, *Trans. Faraday Soc.*, **62**, 3459 (1966).

(10) K. Jones and M. F. Lappert, *J. Chem. Soc.*, 1944 (1965).

(11) J. Lorberth and M.-R. Kula, *Chem. Ber.*, **97**, 3444 (1964).

(12) E. W. Abel and D. B. Brady, *J. Chem. Soc.*, 1192 (1965).

Trimethyltin β-Chloropropionate (I, Y = Cl).—The reaction conditions were the same as the corresponding bromide. Purification of the adduct was made by sublimation of the reaction mixture under reduced pressure. Product was isolated as a white needles in 75% yield: mp 88.5–89.4°; ir ($CHCl_3$) 1662 cm^{-1} (C═O); nmr ($CHCl_3$) τ 9.45 (s, with two satellites; $J_{Sn^{117}-H}$ = 60.2 and $J_{Sn^{119}-H}$ = 62.4 Hz, 9 H, CH_3Sn), 7.36 (t, 2 H, CH_2CO) and 6.36 (t, 2 H, CH_2Cl). *Anal.* Calcd for $C_6H_{13}ClO_2Sn$: C, 26.56; H, 4.84; Cl, 43.30. Found: C, 26.75; H, 4.97, Cl; 43.34.

Kinetic Study.—Trimethylmetal(IV) compounds (1 mmol) were dissolved in 9.00-ml samples of ethylene dichloride and kept at 65 ± 0.5°. β-Propiolactone (1 mmol) was added by means of a syringe and the solution was diluted to 10.00 ml. At a suitable time, a sample was withdrawn by syringe and the remaining amounts of β-propiolactone were determined with the characteristic infrared absorption at 1835 cm^{-1}. Second-order rate constants were calculated from the slope of the plot $1/(\beta - PL)$ *vs.* time. On account of the low reactivity of trimethyltin bromide, chloride, and trimethylsilyl ethyl sulfide, the following method was performed. Metal compound (20 mmol) was dissolved in 4.0 ml of ethylene dichloride and 0.5 mmol of β-propiolactone was added by microsyringe. The total volume was diluted to 5.00 ml and the following measurements were the same as above. The second-order rate constants were estimated from $k_2 = (2.303/t) \log [b(a - x)/a(b - x)]$.

Registry No.—β-Propiolactone, 57-57-8; I (Y = SMe), 18386-59-9; I (Y = Br), 18386-60-2; I (Y = Cl), 18386-61-3; II [Y = $N(C_2H_5)_2$], 13340-30-2.

1,1,2-Triphenylbenzocyclobutene

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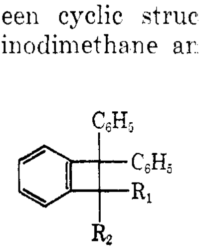
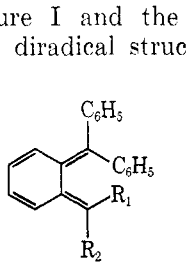
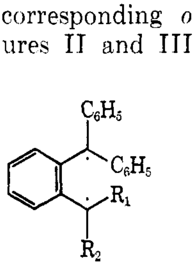
Following the demonstration[1] of the intermediacy of *o*-quinodimethanes in the reactions of benzocyclobutenes, a reexamination of the synthesis of one of the *gem*-diphenylbenzocyclobutenes was considered of interest in connection with the question, first raised many years ago by Wittig and Leo,[2] of the relationship between cyclic structure I and the corresponding *o*-quinodimethane and diradical structures II and III.



I

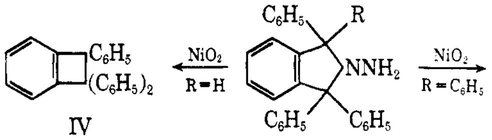


II



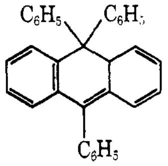
III

Applying a method which had proved successful in the synthesis of the *cis*- and *trans*-1,2-diphenyl derivatives, namely, oxidation of the corresponding N-aminodihydroisoindoles,[3-5] we examined the synthesis of 1,1,2-triphenyl- and 1,1,2,2-tetraphenylbenzocyclobutene. During the course of these studies, Quinkert[6] and coworkers described a method for the generation of the tetraphenyl derivative (I, $R_1 = R_2 = C_6H_5$) and, in fact, settled the question of the relationship between this labile hydrocarbon and its various isomers. It was demonstrated that I ($R_1 = R_2 = C_6H_5$) is stable at low temperatures but above 0° undergoes isomerization to VI. We also observed the formation of the same yellow hydrocarbon VI on oxidation of V (R = C_6H_5) by means of activated manganese dioxide or nickel peroxide.[7] On the other hand, the corresponding triphenylbenzocyclobutene (IV), obtained similarly from V (R = H), proved to be sufficiently stable to be isolated without difficulty. In reactions involving prior valence isomerization to II (R_1 = H; $R_2 = C_6H_5$) such as addition to tetracyanoethylene, IV proved to be more reactive than *trans*-1,2-diphenylbenzocyclobutene which, in turn, as shown earlier,[8] is more reactive than the corresponding *cis* isomer. The steric interaction which inhibits valence isomerization of the latter is also operative in the case of IV but is presumably outweighed by the additional conjugative stabilization due to the third phenyl group.



IV

V



VI

Experimental Section[9]

1,3,3-Triphenylisoindole.—Since the previous description[10] of the synthesis of this compound was unsatisfactory in our hands, the procedure was modified as described below. To a suspension of 205 g of anhydrous aluminum chloride in 380 ml of thiophene-free benzene there was added dropwise over 5 hr with stirring at room temperature a solution of 101 g of crude 1,3,3-trichloroisoindole[10] in 460 ml of benzene. The mixture was stirred for an additional 5 hr and poured into a mixture of 206 ml of concentrated hydrochloric acid and 800 g of chipped ice. The mixture, from which a viscous material had separated, was warmed on a hot plate with stirring until the benzene just began to boil. The mixture was removed from the hot plate and stirring continued at room temperature for 10–12 hr. The green-black solid was filtered and suspended in 880 ml of water and the mixture boiled for 10 min and filtered while hot. After air-drying

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[1] For a review, see G. Quinkert, K. Opitz, W-W. Wiersdorf, and M. Finke, *Ann.*, **693**, 44 (1966).

[2] G. Wittig and M. Leo, *Ber.*, **64**, 2395 (1931).

[3] L. A. Carpino, *J. Amer. Chem. Soc.*, **84**, 2196 (1962).

[4] W. Baker, J. F. McOmie, and D. R. Preston, *J. Chem. Soc.*, 2971 (1961).

[5] L. A. Carpino, *Chem. Commun.*, 494 (1966).

[6] G. Quinkert, W-W. Wiersdorff, M. Finke, and K. Opitz, *Tetrahedron Lett.*, 2193 (1966).

[7] K. Nakagawa, R. Konaka, and T. Nakata, *J. Org. Chem.*, **27**, 1597 (1962).

[8] R. Huisgen and H. Seidl, *Tetrahedron Lett.*, 3381 (1964).

[9] Melting and boiling points are uncorrected. Elemental analyses were by Dr. A. Bernhardt, Muhleim (Germany), and Galbraith Laboratories, Knoxville, Tenn. Nmr spectra were taken in deuteriochloroform solution on a Varian A-60 instrument using tetramethylsilane as internal standard. Infrared and ultraviolet spectra were recorded on Perkin-Elmer 237 and 202 instruments, respectively.

[10] W. Theilacker, H. J. Bluhm, W. Heitmann, H. Kalenda, and H. J. Meyer, *Ann.*, **673**, 96 (1964).