Reduction with Trichlorosilane. III. Cyclic Ether from Lactone

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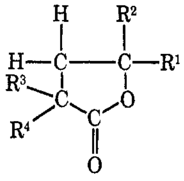
The reduction of γ, δ, and ε lactones to the corresponding cyclic ethers by means of trichlorosilane is described. The reaction was initiated by γ and uv irradiations and photoinduced decomposition of *tert*-butyl peroxide. This method yielded cyclic ethers in comparatively high yields except for the β lactone which was found to suffer ring opening.

Recently we reported that aliphatic esters were reduced to dialkyl ethers by trichlorosilane under free-radical conditions.[1] The present paper reports the extension of this reduction to lactones, which are expected to give the corresponding cyclic ethers. Although reductions of lactones are well known to give diols, some literature reports of successful hydrogenation of lactones to cyclic ethers have been made. Pettit, *et al.*,[2] reported that boron trifluoride–lithium aluminum hydride or boron trifluoride–sodium borohydride can reduce some lactones occurring in natural products to cyclic ethers, but reduce lactones prepared from primary alcohols to glycols. Edward and Ferland,[3] found that Adams catalyst in acetic acid can reduce δ lactones to the corresponding cyclic ethers, but cannot reduce γ and ε lactones to ethers. From the viewpoints mentioned above, β, γ, δ, and ε lactones and several γ lactones such as **1–5** were subjected to the reduction with trichlorosilane. Since the reduction to cyclic ethers succeeded in all lactones except β lactone, this method will provide a new synthetic route to cyclic ethers.



1, $R^1 = CH_3$; $R^2 = R^3 = R^4 = H$
2, $R^1 = C_2H_5$; $R^2 = R^3 = R^4 = H$
3, $R^1 = R^2 = CH_3$; $R^3 = R^4 = H$
4, $R^1 = R^2 = R^3 = H$; $R^4 = CH_3$
5, $R^1 = R^2 = H$; $R^3 = R^4 = CH_3$

The reduction with trichlorosilane was initiated by three methods, γ and uv irradiation and photoinduced decomposition of di-*tert*-butyl peroxide. A degassed mixture of γ-butyrolactone and trichlorosilane was irradiated with γ rays in a glass tube, and with uv rays in a quartz tube. The same mixture in the absence or presence of di-*tert*-butyl peroxide in a Pyrex tube was also irradiated similarly with uv. Comparison of run 4 with 3, and further comparison of run 4 with 5 and 6 in Table I allow us to realize that photoinduced decomposition of the peroxide can initiate the reaction as γ and uv irradiations can. The *G* value (number of molecules formed per 100 eV of energy absorbed) calculated from run 1 is about 600. These results clearly indicate a free-radical chain mechanism for this reduction.

TABLE I

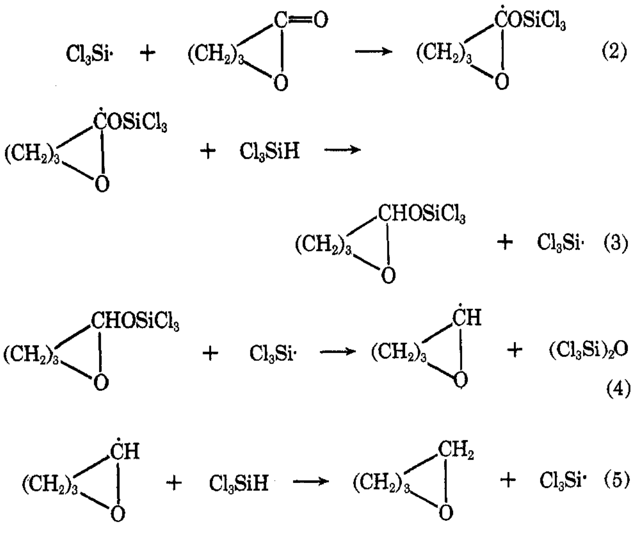
REDUCTION OF γ-BUTYROLACTONE TO TETRAHYDROFURAN WITH TRICHLOROSILANE

Run	Starting molar ratio: Silane/lactone	Starting molar ratio: Peroxide/lactone	Irradiation time, hr: γ^a	Irradiation time, hr: Uv	Yield, %, based on lactone
1	2		8		33
2	2		40		81
3	4			1 (quartz)	37
4	4	0		2 (Pyrex)	0
5^b	4	0.02		2 (Pyrex)	66
6^b	4	0.05		2 (Pyrex)	94

[a] Dose rate = 0.185 Mrad/hr. [b] Initiated by photoinduced decomposition of the peroxide, because run 4 shows that in the absence of the peroxide the reduction does not proceed by light filtered by Pyrex.

The high yield (81%) of run 2 (2:1 molar ratio of silane/lactone) supports that a 2 *M* amount of trichlorosilane is sufficient to reduce the lactone as in our previous communication.[1] Our detailed kinetic study on the reduction of methyl acetate to ethyl methyl ether[4] revealed that the reduction proceeds *via* a free-radical chain mechanism, *i.e.*, addition of trichlorosilane to the carbonyl group of methyl acetate followed by further attack of the silane to the resulting acetal-type intermediate. By the analogy with the reduction of methyl acetate, we can write the sequence of the present reaction as eq 1–5.

$$Cl_3SiH \xrightarrow[\textit{tert}\text{-butoxy radical}]{\gamma,\ \text{uv or}} Cl_3Si\cdot \qquad (1)$$



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[2] (a) G. R. Pettit, B. Green, T. R. Kasturi, and U. R. Ghatak, *Tetrahedron*, **18**, 953 (1962); (b) G. R. Pettit, U. R. Ghatak, B. Green, T. R. Kasturi, and D. M. Piatak, *J. Org. Chem.*, **26**, 1685 (1961).

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[4] Y. Nagata, T. Dohmaru, and J. Tsurugi, submitted for publication. This paper also reports that benzene acts as a scavenger of trichlorosilyl radical. Therefore, carboxylic esters containing a benzene ring could not be reduced by this method. In the present paper lactones containing no benzene ring were used as starting materials, and di-*tert*-butyl peroxide was utilized as an initiator.

TABLE II

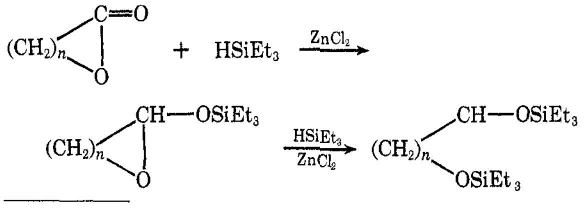
SCOPE OF THE REDUCTION OF LACTONES TO CYCLIC ETHERS (LACTONE/SILANE = 1:4)

Lactone	Registry no.	Product	Registry no.	Yield, %	
				γ^a	Photoinduced decompn of peroxide^b
β-Propio-	57-57-8	Trimethylene oxide		0	0
γ-Butyro-	96-48-0	Tetrahydrofuran		82	94
δ-Valero-	542-28-9	Tetrahydropyran		68	93
ε-Capro-	502-44-3	Hexamethylene oxide		86	96
γ-Valero- (**1**)	108-29-2	2-Methyltetrahydrofuran		62	88
γ-Capro- (**2**)	695-06-7	2-Ethyltetrahydrofuran		89	37
γ-Isocapro- (**3**)	3125-97-5	2,2-Dimethyltetrahydrofuran	1003-17-4	~100^c	~80^d
α-Methyl-γ-Butyro- (**4**)	1679-47-6	3-Methyltetrahydrofuran	13423-15-9	~80^c	~70^d
α,α-Dimethyl-γ-Butyro- (**5**)	3709-08-8	3,3-Dimethyltetrahydrofuran	15833-75-7	~90^c	~70^d

^{a} Dose rate = 0.3 Mrad/hr, total dose = 7.2 Mrad. ^{b} Peroxide/lactone = 0.05, uv irradiation time = 2 hr. ^{c} Identified and estimated by nmr. (See Experimental Section.) ^{d} Estimated by glpc using the corresponding ether which was identified by footnote *c* as the standard.

For synthetic purposes, the scope of this reduction is summarized in Table II, where only γ irradiation and photoinduced decomposition are utilized for the initiation. Table II indicates that the reaction product of β-propiolactone was not trimethylene oxide, but a complex mixture, judging from the glpc chart. This may be ascribed to ring opening, probably because of the greater strain of the four-membered ring. Shostakovskii and Lavrov reported that ethylene oxide[5] and propylene oxide[6] underwent ring opening by simple mixing or mild warming with alkylchlorosilane. Here we attempted to mix trimethylchlorosilane with trimethylene oxide, which was the expected product from β-propiolactone. The product was identified as 3-chloropropoxytrimethylsilane, $ClCH_2CH_2CH_2OSiMe_3$, by glpc. Nmr study suggests that trichlorosilane reacts similarly with trimethylene oxide to give 3-chloropropoxydichlorosilane, $ClCH_2CH_2CH_2OSiCl_2H$. Therefore, even if trimethylene oxide would be produced, it would undergo ring opening with trichlorosilane. The complexity of the glpc chart of the product from β-propiolactone suggests that ring opening really occurs.

Calas, *et al.*,[7] reported that γ-butyro-, γ-valero- and δ-valerolactones, when heated at 120–130° with triethylsilane in the presence of a catalytic amount of zinc chloride, gave disiloxy derivatives *via* intermediates similar to the one assumed in eq 3 and 4. In contrast to Calas' results, higher yields of cyclic ethers shown in Table II support that C–O bond fission of the –C(O)O– group did not occur in the free-radical reduction with trichlorosilane.



(6)

The results in Table II indicate that this reduction is applicable to γ, δ, and ε lactones and several alkyl-substituted γ lactones to yield the corresponding cyclic ethers in comparatively high yields, and may be presumed to be applicable also to alkyl-substituted δ and ε lactones. In this respect, this method has the advantage over other methods using lithium aluminum hydride and Adams catalyst, and will provide a new synthetic route to cyclic ethers from lactones.

Experimental Section

All boiling points are uncorrected. Ir spectra were taken with a Perkin-Elmer Model 221, and nmr spectra on a JNM 3H-60 with tetramethylsilane as an external standard. Gas chromatography was performed with a Yanagimoto GCG-5DH using a 2.5-m column containing 25% Silicone DC-200 on Celite 545.

Lactones.—δ-Valerolactone was prepared from 1,5-pentanediol in the presence of copper chromite as a catalyst similar to the literature[8] for β-methyl-δ-valerolactone: bp 112–113° (13 mm) [lit.[9] bp 113–114° (13–14 mm)]; ir 1735 cm^{-1} (δ-lactone C=O). γ-Isocaprolactone (**3**) was synthesized by the method of Stevens and Tarbell[10] *via* diethyl β-methylallylmalonate starting from diethyl malonate and β-methylallyl chloride: bp 68–70° (4 mm); $n^{25}D$ 1.4320 [lit.[10] bp 74–76° (5–6 mm); $n^{25}D$ 1.4315]; ir 1770 cm^{-1} (γ-lactone C=O); nmr (neat) δ 1.57 [s, 6, $C(CH_3)_2$], 2.25 (m, 2, $-CH_2C(O)-$), 2.75 (m, 2, CCH_2C). The $CCH_2CH_2C(O)$ group constitutes an A_2B_2 system ($\Delta\nu_{AB}$ = *ca.* 30 Hz, J_{AB} = *ca.* 10 Hz). α-Methyl-γ-butyrolactone (**4**) was prepared from diethyl methyl-β-hydroxyethylmalonate by the method of Meincke and McElvain[11] for α-ethyl-γ-butyrolactone. Diethyl methyl-β-hydroxyethylmalonate was prepared from diethyl methylmalonate and ethylene chlorohydrin by the conventional method: bp 77° (10 mm) [lit.[12] bp 81° (11 mm)]; ir 1770 cm^{-1} (γ-lactone C=O); nmr (neat) δ 1.42 (d, 3, CH_3), 1.90–3.2 (m, 3, $>CHCH_2-C$), 4.45 (m, 2, CCH_2O). α,α-Dimethyl-γ-butyrolactone (**5**) was prepared by the method of Baas, *et al.*,[13] from γ-butyrolactone and methyl iodide using sodium hydride: bp 69° (10 mm)

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(5) M. F. Shostakovskii and S. P. Lavrov, *Dokl. Akad. Nauk SSSR*, **114**, 128 (1957); *Chem. Abstr.*, **52**, 1056*h* (1958).

(6) M. F. Shostakovskii, M. S. Malinovskii, M. K. Romantsevich, and D. A. Kochkin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 632 (1956); *Chem. Abstr.*, **51**, 1026*i* (1957).

(7) E. Frainnet, R. Calas, and A. Berthault, *C. R. Acad. Sci.*, **258**, 613 (1964). Yields of disiloxy derivatives were 76, 51, and 47% for γ-butyro-, γ-valero-, and δ-valerolactones, respectively. Yields of cyclic ethers could be read as a trace in all cases. When disiloxy derivatives were heated with 7 mol % of zinc chloride at 200°, they gave the corresponding cyclic ethers in *ca.* 80% yields.

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(9) Beilstein's "Handbuch der Organischen Chemie," Vol. 17, 1933, p 235.

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[lit.[13] bp 74° (10 mm)]; ir 1765 cm^{-1} (γ-lactone C=O); nmr (neat) δ 1.43 [s, 6, $(CH_3)_2$], 2.37 (t, 2, CCH_2C), 4.48 (t, 2, CCH_2O).

Other lactones, commercial materials, were distilled and each stored in an ampoule.

Procedure for Irradiation.—A given amount of lactone or mixture with di-*tert*-butyl peroxide was degassed by three thawings and freezings at −190° in a glass tube or nmr sample tube, to which degassed trichlorosilane was transferred by a vacuum line. The tube, after being fused, was irradiated by γ rays from a ^{60}Co source or uv rays from a medium-pressure mercury lamp at room temperature.

Identification and estimation of cyclic ethers was performed by glpc, except for those described in footnote *c* in Table II. Commercial cyclic ethers purified by the conventional method were used as the standards, with the exception of 2-ethyl tetrahydrofuran and hexamethylene oxide. These were prepared by γ-induced reduction of 25 g of γ- and ϵ-caprolactones with trichlorosilane, respectively. To the irradiated mixture was added water for decomposition of chlorosilanes and siloxanes. After neutralization with aqueous sodium hydroxide solution, the cyclic ethers produced were extracted with diethyl ether. Two distillations gave 2-ethyltetrahydrofuran and hexamethylene oxide, respectively, which were identified by the coincidence of physical constants cited in the literatures: 2-ethyltetrahydrofuran, bp 106–108° (lit.[14] bp 108.5°), $n^{20}D$ 1.4159 (lit.[15] 1.4170); hexamethylene oxide, bp 117–118° [lit.[16] bp 121° (741 mm)], $n^{20}D$ 1.4369 [lit.[17] 1.4361].

Identification and Estimation of Cyclic Ether by Nmr.—The cyclic ethers which were footnoted by *c* in Table II were identified by nmr. The nmr spectrum of α,α-dimethyl-γ-butyrolactone (**5**) in trichlorosilane follows: δ 1.54 [s, 6, $(CH_3)_2$], 2.42 (t, 2, $>CCH_2C$), 4.53 (t, 2, CCH_2O). The γ irradiation of the mixture in the same nmr tube as used for nmr determination of **5** in trichlorosilane gave the following spectrum: δ 1.45 [s, 6, $(CH_3)_2$], 1.57 (s, 0.7), 2.01 (t, 2, $>CCH_2C$), 3.72 (s, 2, $>CCH_2O$), 4.17 (t, 2, $CH_2C\mathbf{H}_2O$). Among these, the singlet at δ 1.57 was regarded as the methyl signal of the unchanged lactone, and the others were assigned to protons of 3,3-dimethyltetrahydrofuran produced. The amount of the ether produced was estimated by comparison of the intensity of the methyl signal which appeared newly at δ 3.72 with the sum of methyl absorptions of unchanged lactone (at δ 1.57) and the ether (at δ 1.45). The same procedure was applied for 2,2-dimethyl- and 3-methyltetrahydrofurans. In the case of 2,2-dimethyltetrahydrofuran, methyl absorption (δ 1.72) of the starting γ-isocaprolactone (**3**) was not observed among the absorptions of the irradiated mixture: δ 1.58 [s, 6, $(CH_3)_2$], 2.11 (m, 4, CCH_2CH_2C), 4.15 (t, 2, CCH_2O). Nmr spectrum of the irradiated mixture of α-methyl-γ-butyrolactone (**4**) with trichlorosilane was δ 1.43 (d, 3, CH_3), 1.62 (d, 0.7), 1.70–3.00 (m, 3, CCH_2C and $>CH$), 3.60 (m, 1, one proton of $>CHC\mathbf{H}_2O$), 4.12 (m, 3, $CH_2C\mathbf{H}_2O$ and one proton of $>CHC\mathbf{H}_2O$), where the doublet at δ 1.62 is regarded as the methyl signal of the unchanged **4**. The $>CHCH_2O$ group constitutes an ABX system; the multiplet at δ 3.60 is the B part; and the A and X parts may be contained in multiplets at δ 4.12 and 1.70–3.00, respectively. 3-Methyltetrahydrofuran produced was estimated by comparing the intensity of the methylene signal which appeared newly at δ 3.60 with the sum of methyl absorptions at δ 1.43 (ether) and 1.62 (**4**).

3-Chloropropoxytrimethylsilane.—The titled compound as standard was prepared by the procedure of Speier[18] using pyridine as an acceptor for hydrogen chloride.

3-Chloropropoxydichlorosilane.—Degassed trichlorosilane was transferred by a vacuum line into a nmr tube, which in advance contained degassed trimethylene oxide. Nmr spectrum of the mixture after γ irradiation: δ 2.45 (m, 2, CCH_2C), 4.02 (t, 2, $ClCH_2C$ or CCH_2O), 4.51 (t, 2, CCH_2O or $ClCH_2C$), 6.00 (s, 1, SiH).

Registry No.—Trichlorosilane, 10025-78-2.

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Acid-Catalyzed Rearrangements and Additions of β,γ-Unsaturated Ketones[1]

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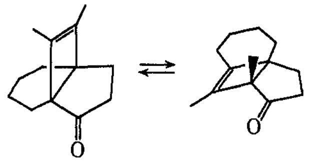
The acid-catalyzed isomerization of 10,11-dimethyltricyclo[4.3.2.$0^{1,6}$]undec-10-en-7-one (**1**) to 7,8-dimethyltricyclo[5.2.2.$0^{1,6}$]undec-5-en-9-one (**3**) and 1,11-dimethyltricyclo[6.2.1.$0^{3,8}$]undec-3-en-2-one (**4**) is described. Chemical and X-ray diffraction analyses provided evidence for structures **3** and **4**. The mechanism of the isomerization is discussed and a new interpretation of the addition of hydrogen halide to 7-ketonorbornene is presented.

We have previously described acid-catalyzed addition and isomerization reactions of β,γ-unsaturated ketones in which the double bond is contained in a four-membered ring.[2,3] Similar studies have also been reported from other laboratories.[3] We report here our study of the acid-catalyzed isomerizations of tricyclic ketones **1** and **2**.

Ketones **1** and **2** have already been shown to undergo light-induced as well as acid-catalyzed interconversion.[4]



1 **2**

The equilibrium concentrations of **1** and **2** indicate that **1** is the more stable isomer by *ca.* 1.5 kcal/mol.[4] In our investigation of the acid-catalyzed equilibration of **1** and **2** we found that vigorous or prolonged treatment of either **1** or **2** with *p*-toluenesulfonic acid in benzene led to disappearance of both **1** and **2** and formation of two new ketones which are assigned structures **3** and

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[1] We thank the National Science Foundation for generous support of this research.

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