Reduction of Phthalyl and Succinyl Dichlorides with Tri-*n*-butyltin Hydride. Cyclization of γ-Oxoacyl Chlorides[1]

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Recently van der Kerk, Noltes, and Luijten have reported that benzaldehyde is obtained by the reduction of benzoyl chloride with triphenyltin hydride (equation 1, R = phenyl).[2]

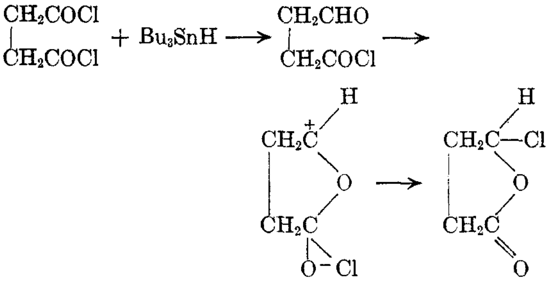
$$R_3SnH + C_6H_5COCl \longrightarrow R_3SnCl + C_6H_5CHO \quad (1)$$

We have found that a similar result is obtained with the more conveniently prepared tri-*n*-butyltin hydride. This reaction proceeds exothermically when the reactants are mixed at room temperature. Aldehydes, on the other hand, are reduced only under much more drastic conditions. Thus, a new convenient synthesis of aldehydes from acid chlorides is suggested. As part of an examination of the scope of such reductions phthalyl and succinyl chlorides have been examined as substrates.

When 1 mole of tri-*n*-butyltin hydride was added to a mole of succinyl dichloride without solvent, an exothermic reaction ensued. The reaction product, after 2 hr. at about 40°, was distilled yielding about 80% of crude product, which upon redistillation provided a product corresponding in neutral equivalent and chloride analysis to the replacement of one of the chlorines by hydrogen. The infrared spectrum showed a carbonyl band at 1810 cm.$^{-1}$, but none in the region 1635–1730 cm.$^{-1}$, nor any C—H band in the region 2700–2800 cm.$^{-1}$. The product is therefore not an aldehyde. The location of the carbonyl band is not shifted by the dilution of the chloride with 2 mol. of tri-*n*-butyltin chloride. Similar mixtures involving the tin halide and succinyl dichloride or γ-butyrolactone have carbonyl absorptions at 1785–1790 cm.$^{-1}$ or 1775 cm.$^{-1}$, respectively.

When 2 moles of hydride were used, the nature of the infrared spectrum after 2 hr. of reaction time was essentially the same as when 1 mole was used. The only difference was in broadening of the band at 1810 cm.$^{-1}$, which was due to the Sn—H band of unreacted hydride which occurs at this same frequency. Clearly the second chloride is far more difficult to reduce than the first.

The reduction product is undoubtedly γ-chloro-γ-butyrolactone, whose formation can be rationalized by the reaction sequence (2).



(2)

As there is no indication of the presence of aldehyde, the second step must be essentially irreversible. Furthermore, the cyclization must occur fairly rapidly, for the second mole of hydride does not lead to the formation of succindialdehyde, which would be expected to form fairly readily in view of the speed of reduction of the first acid chloride group.

Analogous reactions have been observed in the reaction of succinyl chloride with reagents such as diethylcadmium by Cason and Reist.[3] The products obtained are ethyl γ-ketocaproate (when diethyl ether is the solvent) and γ-ethyl-γ-caprolactone; no 3,6-octanedione is obtained. The products found can be accounted for on the basis of cyclization of initially formed γ-ketocaproyl chloride; the diketone would be formed by reaction of this (acyclic) acid chloride with another mole of diethylcadmium. An alternative mechanism proceeding through a cyclic acylonium ion can also account for the facts.[3a]

A cyclic structure has been assigned to γ-ketocaproyl chloride[3b] on the basis of the presence of a single carbonyl band at 1805 cm.$^{-1}$. Similarly,[4] four 2-benzoylbenzoyl chlorides had single carbonyl bands in the region 1790–1800 cm.$^{-1}$. These latter bands represent upward shifts of about 20 cm^{-1} from the 3-phenylphthalides. The shift from α-butyrolactone (1775 cm.$^{-1}$) to the chloro compound involves a shift of 35 cm.$^{-1}$ to a higher frequency. These examples supplement those reported earlier[5] in which electron withdrawing substituents in the γ-position cause shifts in the carbonyl bands of γ-lactones to higher frequencies.

On the basis of the examples discussed above it seems reasonable to conclude that the cyclic γ-chloro-γ-lactones are more stable thermodynamically than the acyclic tautomers, the γ-oxoacid chlorides. Furthermore the cyclization can be brought about with as weak a Lewis acid as tri-*n*-butyltin chloride, and might possibly not require a catalyst at all.

Experiments similar to those conducted with succinyl dichloride were also carried out with phthalyl dichloride. Presumably because of the

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[1] It is a pleasure to acknowledge support of this work by the Office of Ordnance Research. Thanks are also due to the Metal and Thermit Corporation for samples of tri-*n*-butyltin chloride.

[2] G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Appl. Chem.*, **7**, 356 (1957).

[3] (a) J. Cason and E. J. Reist, *J. Org. Chem.*, **23**, 1668 (1958); (b) J. Cason and E. J. Reist, *J. Org. Chem.*, **23**, 1492 (1958).

[4] W. Graf, E. Girod, E. Schmid, and W. G. Stoll, *Helv. Chim. Acta*, **42**, 1085 (1959).

[5] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley, Inc., New York, 1958, p. 187.

presence of carbonyl impurities, the spectra of the products were not amenable to reliable interpretation. However, when 2 moles of tri-*n*-butyltin hydride were allowed to react with the acid chloride, a 55% yield of phthalide crystallized from the reaction mixture. Its formation undoubtedly results from the reduction of 3-chlorophthalide formed by way of a sequence such as (2). The ready reduction of the phthalide in the second step occurs because the chlorine is now benzylic, and therefore more susceptible to reduction than that in γ-chloro-γ-butyrolactone.

EXPERIMENTAL

Reaction between succinyl dichloride and tri-n-butyltin hydride. To 2.92 g. (18.9 mmol.) of succinyl dichloride which had been freshly distilled was added 5.50 g. (18.9 mmol.) of tri-*n*-butyltin hydride.[6]

The reactants were allowed to stand, with occasional cooling to keep the temperature below about 40°, for 2 hr. Distillation from a modified Claisen flask provided two fractions: b.p. 49–62°/0.3–0.4 mm., 1.84 g. (80%) and b.p. 102–127°/0.4 mm., 6.06 g. (98% crude tri-*n*-butyltin chloride). The first fraction was redistilled yielding a main fraction b.p. 45°/0.4 mm., 1.00 g. of γ-chloro-γ-butyrolactone.

Anal. Calcd. for $C_4H_5O_2Cl$: Cl, 29.4; neut. eq., 60.3. Found: Cl, 28.1, 28.0; neut. eq., 60.5.

Reaction between phthalyl dichloride and tri-n-butyltin hydride. A mixture of 11.0 g. (37.8 mmol.) of tri-*n*-butyltin hydride and 4.54 g. (8.9 mmol.) of phthalyl dichloride was cooled in a water bath occasionally during the first hour after preparation in order to keep the temperature below 50°. It was then allowed to stand for 5 days; 0.47 g. of crystals which had appeared were filtered off and washed with 10 ml., of petroleum ether, b.p. 30–60°. The filtrate was diluted with 20 ml. more of petroleum ether, whereupon another 0.91 g. of crystals appeared. The product melted at 72–74°, undepressed upon mixture with authentic phthalide, and had an infrared spectrum identical with that of phthalide.

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(6) G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Applied Chem.*, **7**, 366 (1957).

Proton Nuclear Resonance Spectroscopy. X. Rapid Tautomerization of Formazans[1,2]

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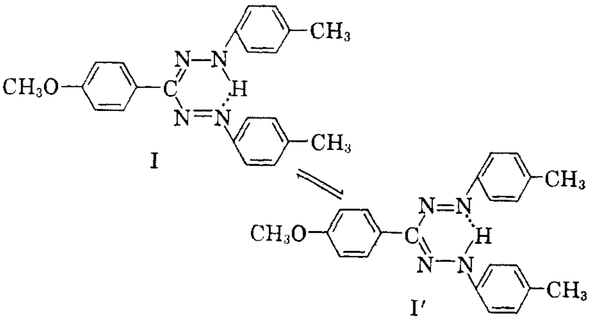
Early workers, studying the problem of tautomerism in unsymmetrically substituted formazans, reported the isolation of two tautomers[4]; however, subsequent studies[5–7] showed that only one form could be isolated. The cyclic hydrogen-bridged structure was proposed[6] in view of the chelating ability of formazans, and the failure to isolate two forms of the chelates prepared from unsymmetrical formazans. In all such studies the requirement of unsymmetrical substitution introduces the possibility of severe steric, electronic, and solvent effects upon the position of tautomeric equilibrium.

Nuclear spin resonance (NSR) spectroscopy affords a sensitive method for the detection of rapid equilibration: it is especially suitable for the study of symmetrical systems,[8] for example, 1,5-di-(4-methylphenyl)-3-(4-methoxyphenyl) formazan



I

I′

(I). For such purposes it is necessary to choose cases for which all the observed NSR peaks can be assigned with confidence; for the formazan (I) the detailed assignment is given in Table I.

TABLE I

ASSIGNMENT OF NSR SHIELDING VALUES[a] FOR FORMAZAN (I)

Proton Group	Shielding Value, τ (p.p.m.)[a]	Relative No. of Protons
For the 4-Methoxyphenyl Group:		
2-H	2.10[b] } $J =$	2
3-H	3.20[b] } 8.9*c/s*	2
4-CH_3O	6.218 ± 0.002	3
For the 4-Methylphenyl Groups:		
2-H	2.59[b] } $J =$	4
3-H	2.93[b] } 8.5*c/s*	4
4-CH_3	7.684 ± 0.002	6

[a] For the definition of τ see ref. 10; the formazan, I, concentration was 8% (wt./vol.) in CCl_4. [b] "Nonequivalent doublet" (AB-type) analyzed according to ref. 8, p. 119; the coupling constant *J* refers to spin interaction between 2- and 3-H.

Whenever NSR assignment may be desired, it is important to avoid unsubstituted phenyl groups, and to synthesize, instead, an appropriate *para*-substituted analog; it may not be widely

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(2) A portion of a dissertation submitted in partial fulfillment of the requirements for the Ph.D. degree at Kansas State University, 1959.

(3) Pan American Petroleum Foundation Fellow, 1957–58.

(4) M. Busch and R. Schmidt, *J. Prakt. Chem.*, **131**, 182 (1931).

(5) D. Jerchel and W. Woticky, *Ann.*, **605**, 191 (1957).

(6) L. Hunter and C. B. Roberts, *J. Chem. Soc.*, 820–3 (1941).

(7) R. Kuhn and D. Jerchel, *Ber.*, **74**, 941 (1941).

(8) J. A. Pople, W. G. Schneider, and H. J. Bernstein, ***High Resolution Nuclear Magnetic Resonance***, McGraw-Hill, Inc., New York, 1959, p. 438 and p. 223.