ric hindrance at the imine carbon in **5** vs. **2** also makes ring closure to the β-lactam **4** more difficult from **9**. In contrast to **5a**, the usual oxazinone[3,10-13] adduct B from ketene additions to imines is not formed from the azetine **5b**. This again is probably because steric hindrance at the imine carbon in **8b** makes C–C bond closure to an oxazinone less favorable than in **8a**, which lacks the 3,3-dimethyl substitution.

Experimental Section

All melting points are uncorrected. Ir spectra were obtained in solution with a matched reference cell on a Perkin-Elmer 337 grating infrared spectrometer. NMR spectra were obtained on a 60-MHz Varian Associates T-60 spectrometer and a CFT-20 spectrometer. Mass spectra were obtained on a MS-902 spectrometer, and uv spectra were obtained on a Cary 15 spectrophotometer.

Materials. The 2,5-diazido-3,6-di-*tert*-butylquinone and imino ethers were made according to published procedures.[1,32]

1,3-Di-*tert*-butyl-3-cyano-4-methoxy-2-azetidinone (3). A solution of 153 mg (0.51 mmol) of 2,5-diazido-3,6-di-*tert*-butylquinone[31] dissolved in 10 ml of benzene was heated to 70°. The initially orange solution turns yellow after 1 hr indicating conversion to the cyano-*tert*-butylketene **1**. With the solution at room temperature, a solution of 100 mg (0.87 mmol) of methyl *N*-*tert*-butylformimidate (**2**) in 1.5 ml of benzene was added. The solution was heated at 70° overnight. The reaction was quantitative by NMR and ir analysis. Removal of volatiles left 186 mg (90%) of β-lactam **3**. Recrystallization from hexanes and ether gave 86 mg of **3**: mp 104–106°; ir (CCl_4) 2230 w, 1780 s, 1370, 1345, 1100 cm^{-1}; ^1H NMR (CCl_4) δ 1.12 (s, 9 H), 1.33 (s, 9 H), 3.40 (s, 3 H), 4.65 (s, 1 H); mass spectrum (70 eV) *m/e* 238.1708 (calcd for $C_{13}H_{22}N_2O_2$, 238.1681); *m/e* (rel intensity) 238 (M^+, 0.2), 223 (0.2), 208 (0.4), 185 (0.5), 184 (4), 169 (1), 168 (12), 140 (9), 139 (36), 125 (7), 124 (100), 115 (1), 110 (1), 108 (4), 100 (7), 96 (2), 86 (2), 84 (7), 68 (2), 67 (1), 66 (1), 60 (4), 58 (3), 57 (27), 56 (7), 55 (4), 53 (4), 44 (2), 43 (2), 42 (5), 41 (22), 40 (2), 39 (6).

Reaction of Azetine 5a with Ketene 1. Adding 142 mg (1.26 mmol) of 2-methoxy-4,4-dimethylazetine (**5a**) in 5 ml of benzene to a solution of ketene **1** (2.54 mmol) generated from 382 mg (1.27 mmol) of azidoquinone[31] gave immediately at 25° a mixture of products. Isolation of 39 mg (10%) of white solid **6** was achieved by column chromatography on alumina using ether–hexane (10:90) elution: mp 155–157° dec (with C_4H_8 evolution by mass spectral analysis); uv (EtOH) end absorption λ 220 nm (ε 2900); ir (CCl_4) 2960 (m), 2230 (w), 1755 (m), 1700 (s), 1470, 1460, 1262, 1247, 1233, 1198, 1189, 1142, 1112, 1060, 1049, 861 cm^{-1}; ^1H NMR (CCl_4) δ 1.26 (s, 9 H), 1.36 (s, 9 H), 1.67 (s, 3 H), 1.83 (s, 3 H), 2.53 and 2.80 (AB, J = 13.5 Hz), 3.56 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ_{Me_4Si} 187.4 (C=O), 160.7 [=C(–N–)O–], 116.2 (CN), 115.3 (CN), 92.9, 65.3, 62.9, 61.9, 52.3, 40.7, 39.7, 39.3, 28.3 (*t*-Bu), 26.5, 23.7; mass spectrum (70 eV) *m/e* 359.2216 (calcd for $C_{20}H_{29}N_3O_3$, 359.2209); *m/e* (rel intensity) 359 (M^+, 0.23), 344 (0.55), 328 (0.15), 316 (1.1), 304 (3), 303 (34), 288 (9), 272 (3), 271 (6), 256 (5), 247 (5), 216 (12), 192 (12), 178 (6], 163 (5), 153 (12), 152 (9), 151 (100), 140 (3), 139 (3), 138 (6), 124 (9), 114 (6), 108 (12), 94 (6), 84 (28), 83 (5), 82 (6), 73 (19), 68 (5), 67 (5), 58 (12), 57 (47), 56 (19), 55 (9), 53 (9), 43 (6), 42 (8), 41 (41), 39 (8). Some methyl 2-cyano-3,3-dimethylbutanoate [ir (CH_2Cl_2) 2950, 2240 (w) 1750 cm^{-1}; ^1H NMR (CH_2Cl_2) δ 1.17 (s, 9 H), 2.84 (s, 1 H), 3.76 (s, 3 H)][31] was formed in the reaction mixture and found in early chromatography fractions, but no other pure substances could be isolated from the chromatography.

Reaction of Azetine 5b with Ketene 1. Addition of 282 mg (2.00 mmol) of 2-methoxy-3,3,4,4-tetramethylazetine (**5b**) in 5 ml of benzene to a solution of ketene **1** (4.00 mmol) generated from 604 mg (2.00 mmol) of azidoquinone in 10 ml of benzene at 25° resulted in an oil after removal of the volatiles. Upon addition of ether, a white solid **7** precipitated, mp 122–126°. Recrystallization from benzene–hexanes gave 326 mg (42%): mp 131–133°; uv (EtOH) λ_{max} 232 nm (ε 8850), 275 (sh, ε 550); ir (CCl_4) 2950 (s), 2230 (vw), 2200 (w), 1925 (vw), 1870 (vw), 1705 (s), 1625 (w), 1400, 1380, 1370, 1230, 1125, 1032, 891 cm^{-1}; ^1H NMR (CCl_4) δ 1.08 (s, 3 H), 1.19 (s, 3 H), 1.38 (s, 18 H), 1.44 (s, 3 H), 1.46 (s, 3 H), 3.61 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ_{Me_4Si} no C=O, 159.3 [=C(–N–)O–], 155.5 [=C(–O–)$_2$], 117.3, 116.5, 115.2, 108.2, 71.8, 55.2, 54.3, 51.5, 45.6, 36.9, 36.2, 30.2 (*t*-Bu), 28.3 (*t*-Bu), 24.2, 20.4, 19.1, 17.3; mass spectrum (70 eV) *m/e* 387.2511 (calcd for $C_{22}H_{33}N_3O_3$, 387.2522); *m/e* (rel intensity) 387 (M^+, 0.33), 333 (0.9), 318 (1.3), 304 (0.9), 303 (5), 264 (0.8), 249 (4), 248 (23), 246 (5), 236 (1.2), 221 (3), 192 (5), 190 (1.7), 186 (1.3), 181 (3), 180 (3), 175 (3), 165 (5), 144 (2), 143 (7), 142 (2), 141 (15), 140 (4), 127 (2), 126 (10), 124 (5), 123 (15), 111 (5), 109 (4), 108 (45), 98 (3), 96 (4), 94 (2), 85 (5), 84 (24), 83 (9), 82 (3), 80 (3), 73 (16), 70 (13), 69 (23), 68 (5), 67 (3), 59 (3), 58 (45), 57 (100), 56 (8), 55 (12), 54 (4), 53 (20), 52 (3), 43 (9), 42 (16), 41 (53), 39 (17).

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Registry No.—**1**, 29342-22-1; **2**, 49680-36-6; **3**, 55712-07-7; **5a**, 23974-38-1; **5b**, 49680-46-8; **6**, 55712-08-8; **7**, 55712-09-9; 2,5-diazido-3,6-di-*tert*-butylquinone, 29342-21-0; methyl 2-cyano-3,3-dimethylbutanoate, 55712-10-2.

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A Method for Catalytic Dehalogenations via Trialkyltin Hydrides[7]

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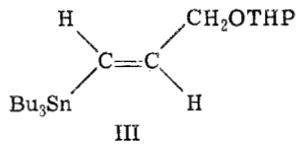
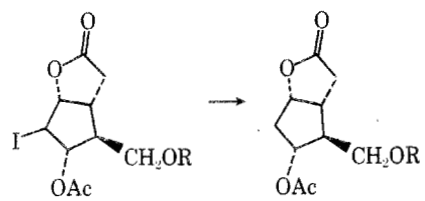
This note describes a method for the catalytic dehalogenation of organic halides with trialkyltin hydrides. The chief impetus for the development of a catalytic process was our interest in devising a simpler and more convenient procedure for the generation of the valuable prostaglandin intermediate II from the halolactone precursor I. Previous-

Table I

Substrate (mmol)	Product	Mmol of $NaBH_4$	R, R_3SnCl (mmol)	Conditions	Yield, %
$PhCH_2CH_2CH_2Br$ (1)	$PhCH_2CH_2CH_3$	2	Bu (0.1)	2.5 hr, 25°	86[b]
$PhCH_2CH_2CH_2Br$ (1)	$PhCH_2CH_2CH_3$	2	Bu (0.1)	0.5 hr, 25°, $h\nu$	88[b]
Ia (0.27)	IIa	0.41	Bu (0.027)	20 min, 10°, $h\nu$	93[a]
Ia (0.156)	IIa	0.195	Me (0.032)	20 min, 15°, $h\nu$	94[a]
n-$C_{14}H_{29}Br$ (0.35)	n-$C_{14}H_{30}$	0.56	Bu (0.035)	0.5 hr, 25°, $h\nu$	100[b]
Ib (0.078)	IIb	0.117	Me (0.026)	15 min, 15°, $h\nu$	88[a]
p-BrC_6H_4NHAc (0.08)	C_6H_5NHAc	0.1	Bu (0.008)	3 hr, 25°, $h\nu$	96[a]
$HC{\equiv}CCH_2OTHP$ (5.64)	 III	6.1	Bu (6.1)	3 hr, reflux	73.5[a]

[a] Isolated yields. [b] Yields determined by VPC.



Ia, R = CH_3; b, R = $CH_2C_6H_5$ — IIa, R = CH_3; b, R = $CH_2C_6H_5$

ly tin hydrides have usually been employed in stoichiometric amounts (either preformed or generated in situ from the nonvolatile polymethylhydrosiloxane and trialkyltin oxides).[1,2] The product, once formed by these procedures, must be separated from a full 1 equiv of trialkyltin halide. A catalytic method has been described using stoichiometric amounts of lithium aluminum hydride;[1] however, the reactivity of lithium aluminum hydride greatly limits the method's usefulness.

In our procedure the organic halide and 0.1–0.3 equiv of the trialkyltin chloride are dissolved in absolute ethanol and a solution of sodium borohydride in ethanol is added rapidly. In most experiments the reaction was carried out in Pyrex with irradiation by a 100-W mercury floodlamp so that reaction occurred rapidly at or below room temperature. The catalytic cycle is given in eq 1 and 2.

$$2R_3SnX + 2NaBH_4 \longrightarrow 2R_3SnH + 2NaCl + B_2H_6 \quad (1)$$

$$R_3SnH + R'X \longrightarrow R_3SnX + R'H \quad (2)$$

Ethanol is used as the solvent in order to trap the resulting diborane.[3]

Our results are summarized in Table I. As can be seen, ester and lactone functions do not interfere with this procedure.[4] The ethanolic solution of tributyltin hydride produced by our method also can be used in the hydrostannation reaction, illustrated by the preparation of the synthetically useful[5] *trans*-1-tri-*n*-butylstannyl-1-propene-3-tetrahydropyranyl ether (III).

Experimental Section

All reactions were performed under argon with carefully degassed solvents.

2-Oxa-3-oxo-6-*syn*-methoxymethyl-7-*anti*-acetoxy-*cis*-bicyclo[3.3.0]octane (IIa). To the iodide Ia (0.0553 g, 0.156 mmol) and trimethyltin chloride (0.0063 g, 0.0316 mmol) in 3 ml of air-free absolute ethanol cooled to 15° was rapidly added via syringe sodium borohydride (0.0076 g, 0.195 mmol) dissolved in 1.5 ml of ethanol. The solution was irradiated with a 100-W mercury floodlamp. Initially gas was rapidly evolved. After 20 min no starting material remained. Oxalic acid (0.0010 g) was added (to convert any trimethyltin hydride to the tin ester) followed 5 min later by 20 ml of CH_2Cl_2. The solution was washed once with saturated sodium bicarbonate and dried over anhydrous magnesium sulfate and the solvent was evaporated to give as a slightly yellow oil a mixture of hexamethylditin and IIa. Chromatographic separation on silica gel (eluent 1:1 benzene–ether) gave 0.0336 g (94%) of IIa, the spectral data for which were identical with those for authentic material.[6]

***trans*-1-Tri-*n*-butylstannyl-1-propene-3-tetrahydropyranyl Ether (III).** To tri-*n*-butyltin chloride (2.00 g, 6.1 mmol) in 5 ml of absolute ethanol was added dropwise sodium borohydride (0.23 g, 6.1 mmol) in 10 ml of ethanol. The solution became warm, gas was vigorously evolved, and sodium chloride precipitated. After stirring at 25° for 10 min, propargyl tetrahydropyranyl ether (0.790 g, 5.46 mmol) was added and the solution was refluxed for 3.5 hr, cooled, treated with 30 ml of pentane, and filtered. Evaporation of the solvent gave a clear oil containing (by ir and NMR) only III and tri-*n*-butyltin hydride. Distillation gave 1.78 g (73.5%) of III, bp 140–150° (0.1 mm), identical with material prepared by the direct reaction of isolated tri-*n*-butyltin hydride with propargyl tetrahydropyranyl ether.

Registry No.—Ia, 55721-21-6; Ib, 55721-22-7; IIa, 37745-51-0; IIb, 52689-80-2; III, 55723-10-9; $PhCH_2CH_2CH_2Br$, 637-59-2; n-$C_{14}H_{29}Br$, 112-71-0; p-BrC_6H_4NHAc, 103-88-8; $HC{\equiv}CCH_2OTHP$, 6089-04-9; $PhCH_2CH_2CH_3$, 103-65-1; n-$C_{14}H_{30}$, 629-59-4; C_6H_5HNAc, 103-84-4; $NaBH_4$, 16940-66-2; Bu_3SnCl, 1461-22-9; Me_3SnCl, 1066-45-1.

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Reduction of Epoxides to Olefins with Low Valent Titanium

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The reduction of epoxides to olefins is of some importance in synthesis, and a variety of methods have been devised to accomplish the transformation.[1] Among these methods has been the use of strongly reducing metals or