The crude product was further purified via column chromatography on neutral alumina (hexane eluent); this procedure afforded pure 8 [749 mg, 26.2% based on consumed (unrecovered) 6] as a colorless, sweet-smelling oil, bp ca. 50° (0.14 mm, microdistillation). An analytical sample of 8 was obtained via preparative VPC [0.25 in. × 10 ft column, 20% FFAP on Chromasorb W, all VPC components (injector, column, and detector) at 140°, He flow rate 100–110 ml/min]: NMR ($CDCl_3$) δ 1.13 (m, 2 H, 5,6-endo ring protons), 1.26 (t, $J \approx 6$ Hz, 3 H, $-OCH_2CH_3$), 1.90 (m, 2 H, 5,6-exo ring protons), 4.07 (q, $J = 6$ Hz, 2 H, $-OCH_2CH_3$), 4.74 [m, 2 H, 1,4 (bridgehead) protons], 6.24 [unsymmetrical t, 2 H, 2,3 (vinyl) protons]; ir (film) 3020 (w), 2995 (w), 1710 (s, br), 1270 (m), 690 cm^{-1} (m); mass spectrum *m/e* 167 (molecular ion), 139, 94, 80, 66, 41, 39 (base peak).

Anal. Calcd for $C_9H_{13}NO_2$: C, 64.65; H, 7.84. Found: C, 64.88; H, 7.87.

***N*-Methyl-7-azanorbornene (2).** *N*-Carbethoxy-7-azanorbornene (8, 749 mg, 4.49 mmol) was dissolved in benzene (30 ml). To the resulting solution was added a benzene solution (23 ml) of diisobutylaluminum hydride (0.61 mmol/ml). After stirring for 4 hr at room temperature, an additional 5 ml of the benzene solution of diisobutylaluminum hydride was added (total 28 ml, 17.1 mmol of diisobutylaluminum hydride). After stirring for an additional 4 hr at room temperature, the reaction was quenched with excess methanol until precipitation of aluminum methoxide was complete. The reaction mixture was then filtered and combined with an equal volume of a saturated solution of picric acid in 95% ethanol, whereupon yellow crystals of *N*-methyl-7-azanorbornene picrate precipitated almost immediately. Recrystallization from 95% ethanol afforded the pure picrate (1.30 g, 85.6%) as yellow needles, mp 225° dec.

Anal. Calcd for $C_{13}H_{14}N_4O_7$: C, 46.16; H, 4.17. Found: C, 45.93; H, 3.98.

The free base (2) was obtained by treating the above picrate with concentrated, aqueous KOH solution. The resulting mixture was extracted with chloroform, and the free amine (2) was isolated via preparative VPC [0.25 in. × 4 ft column, 28% Pennwalt 223 on 80/100 mesh Gas-Chrom R containing 4% KOH, all VPC components (injector, column, and detector) at 100–110°, *nitrogen* carrier gas, N_2 flow rate ca. 100–110 ml/min]: NMR ($CDCl_3$) δ 0.98 (m, 2 H, 5,6-endo ring protons), 1.87 (m, 2 H, 5,6-exo ring protons), 2.05 (s, 3 H, NCH_3), 3.70 [m, 2 H, 1,4 (bridgehead) protons], 5.98 [br s, 2 H, 2,3 (vinyl) protons]; ir (film) 3080 (w), 2990 (w), 690 cm^{-1} (m); mass spectrum *m/e* 109 (molecular ion), 94, 81, 80, 66, 53, 42, 39 (base peak).

***N*-Tosyl-7-azanorbornane-*endo,endo*-2,3-dicarboxylic Acid (5).** Compound 5 was prepared using the same procedure which was previously employed for the synthesis of 6. Hydrogenation–hydrogenolysis of 3 (10.0 g, 36.9 mmol) followed by treatment of the resulting solution with excess *p*-toluenesulfonyl chloride afforded crude 5 (12.0 g, 95.5%). The crude product was further purified by sublimation at 150° (0.05 mm), which afforded the corresponding acid anhydride (9). Compound 9 recrystallized from acetone to afford a colorless, microcrystalline solid, mp 230–232°. Hydrolysis of 9 afforded pure 5: NMR (pyridine-d_5) δ 1.53–2.50 (m, 4 H, 5,6-exo and endo ring protons), 2.30 (s, 3 H, $ArCH_3$), 3.90 (m, 2 H, 2,3-exo ring protons), 4.70 [m, 2 H, 1,4 (bridgehead) protons], 5.50 (s, 2 H, –COOH), 7.63 (AA′BB′ pattern, 4 H, aryl ring protons). Compound 5 was further characterized via the corresponding anhydride (9); ir of 9 (KBr) 3070 (w), 2980 (w), 1865 (s), 1785 (s), 1335 (sh), 1140 (sh), 1590 (w), 905 cm^{-1} (s); mass spectrum *m/e* 321 (molecular ion), 223, 166, 155, 122, 91, 68 (base peak).

Anal. Calcd for $C_{15}H_{15}NO_5S$: C, 56.06; H, 4.70. Found: C, 56.16; H, 4.92.

***N*-Tosyl-7-azanorbornene (7).** Compound 5 (2.3 g, 6.8 mmol) was dissolved in an electrolyte solution (100 ml) which was prepared as described previously for the synthesis of 8 from 6. A direct current (80 V, initial current 160 mA) was passed through this solution for 12 hr while the solution temperature was maintained at 20° via external cooling. At the conclusion of the electrolysis, the current had dropped to 50 mA. Work-up of the reaction was carried out as described for the synthesis of 8 from 6. The crude product was purified via elution chromatography on neutral alumina (hexane eluent). Compound 7 (204 mg, 12.1%) was thereby obtained. Recrystallization of 7 from hexane afforded an analytical sample as colorless needles: mp 91.5–92.0°; NMR ($CDCl_3$) δ 1.07 (m, 2 H, 5,6-endo ring protons), 2.03 (m, 2 H, 5,6-exo ring protons), 2.42 (s, 3 H, $ArCH_3$), 4.64 [m, 2 H, 1,4 (bridgehead) protons], 5.73 [unsymmetrical t, 2 H, 2,3 (vinyl) protons], 7.41 (AA′BB′ pattern, 4 H, aryl ring protons); ir (KBr) 3090 (w), 2995 (w), 2960 (w), 1590 (w), 1335 (s), 1150 (s), 690 cm^{-1} (s); mass spectrum *m/e* 249 (molecular ion), 221, 155, 106, 91 (base peak), 65, 58.

Anal. Calcd for $C_{13}H_{15}NO_2S$: C, 62.62; H, 6.06. Found: C, 62.50; H, 5.99.

7-Azanorbornene (1). Compound 7 (204 mg, 0.82 mmol) was dissolved in a solution of diethyl ether (10 ml) in liquid ammonia (20 ml). Excess, clean sodium metal was added portionwise until the blue color of solvated electrons persisted for 1 min. The reaction mixture was then concentrated, and the residue was dissolved in diethyl ether and extracted with dilute aqueous hydrochloric acid. The aqueous phase was rendered strongly basic (KOH) and the resulting solution was extracted with chloroform (10 ml). The chloroform extracts were dried and carefully concentrated, affording 1 as a colorless liquid (70 mg, 90%): NMR ($CDCl_3$) δ 1.02 (m, 2 H, 5,6-endo ring protons), 1.75 (m, 2 H, 5,6-exo ring protons), 1.76 (s, 1 H, –NH, disappears upon addition of D_2O), 4.12 [m, 2 H, 1,4 (bridgehead) protons], 6.23 [unsymmetrical t, 2 H, 2,3 (vinyl) protons]; ir (film) 3250 (br), 3070 (w), 2960 (s), 1650 (br), 1260 (m), 790 cm^{-1} (s); mass spectrum *m/e* 95 (molecular ion), 80, 67, 66, 51, 42, 39 (base peak), 28. Compound 1 was further characterized via its picrate. When 1 was added to a solution of picric acid (excess) in 95% ethanol, precipitation of 7-azanorbornene picrate occurred almost immediately. Recrystallization of the picrate from 95% ethanol afforded yellow needles, mp 208–210° dec.

Anal. Calcd for $C_{12}H_{12}N_4O_7$: C, 44.45; H, 3.73; N, 17.28. Found: C, 44.21; H, 3.85; N, 17.30.

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Registry No.—1, 55590-24-4; 1 picrate, 55590-25-5; 2, 55590-26-6; 2 picrate, 55590-27-7; 3, 34354-00-2; 4, 55658-14-5; 5, 55658-15-6; 6, 55590-28-8; 7, 55590-29-9; 8, 55258-01-0; 9, 17037-46-6; 10, 55590-30-2.

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Addition of *tert*-Butylcyanoketene to Imino Ethers. Steric Effects on Product Formation

Donald H. Aue* and Darryl Thomas

Department of Chemistry, University of California, Santa Barbara, Santa Barbara, California 93106

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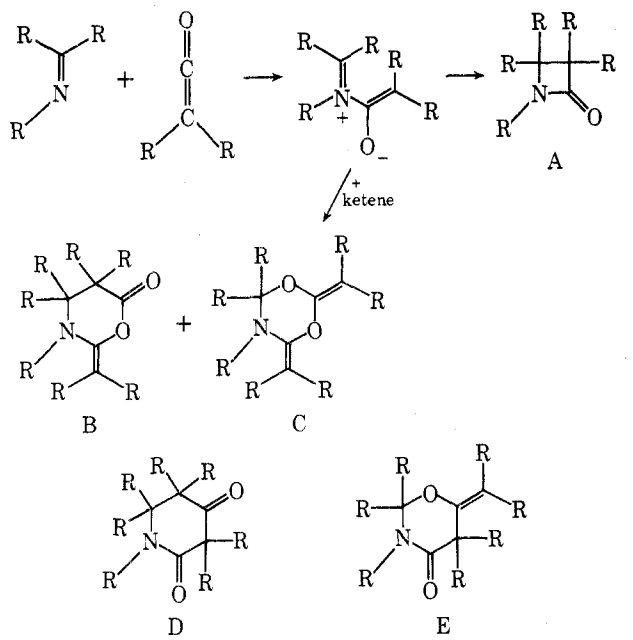
In connection with a series of studies on additions to imino ethers,[1] we have investigated ketene additions to cyclic and acyclic imino ethers here. Ketenes were first shown by Staudinger to add to imines to give β-lactams A in 1907.[2] In many cases 2:1 adducts are formed at the expense of the β-lactam, however.[3-17] Although originally assigned the piperidinedione structure D,[4-9] most 2:1 adducts have since been shown to be oxazinones B.[3,10-13] In a few cases the dioxazines C have been formed too.[14-17] Compounds of structure E are known,[18-26] but not from 1,4-dipolar addi-

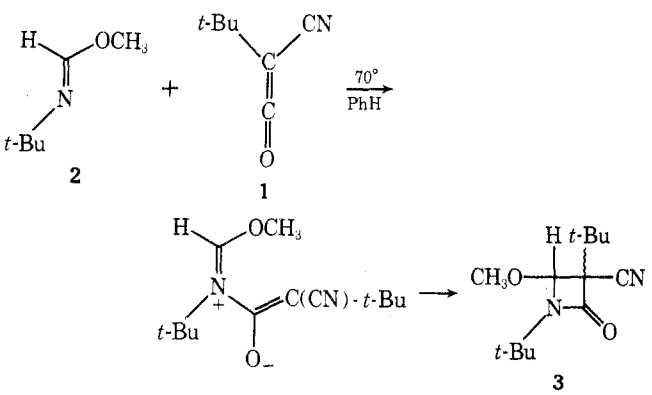


tions. With unhindered imines in the presence of Lewis acid catalysts, a few 1:2 adducts from addition of a second molecule of imine to the 1,4 dipole are obtained;[3,27,28] and a 1:1:1 adduct from trapping of a 1,4 dipole with phenyl isocyanate is known.[29,30]

The pattern of reactivity in these reactions indicates that 1:1 β-lactams are usually preferred over 2:1 adducts when there are bulky groups on nitrogen and in solvents of low polarity.[3,13] In addition, it appears that dioxazines C are favored over oxazinones B when the iminium ion is strained[16,17] or when there is steric hindrance to ring closure through carbon.[17] Steric hindrance at nitrogen in the imino ethers **2** and **5** might particularly favor β-lactam formation, so additions to **5** were tried in an attempt to make the bicyclic β-lactam **4**.

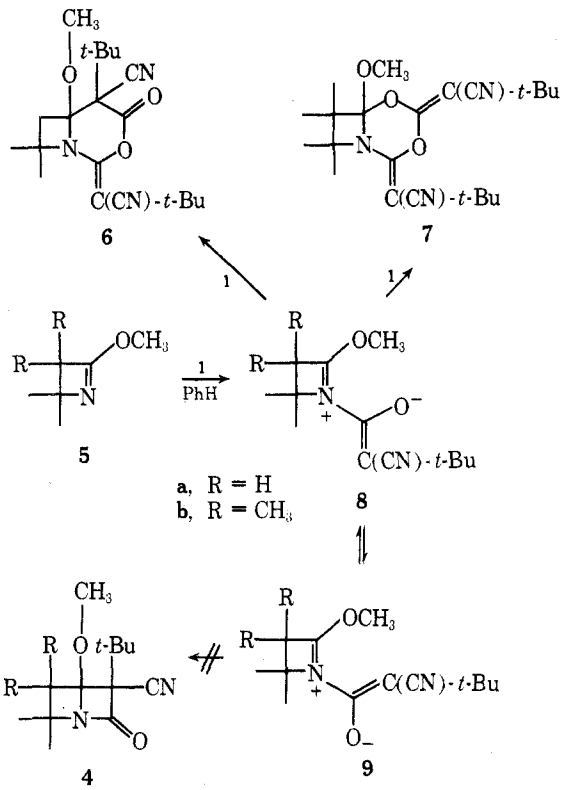
Results and Discussion

A convenient source of a sterically hindered ketene, *tert*-butylcyanoketene (**1**), is from thermolysis of 2,5-diazido-3,6-di-*tert*-butylquinone.[31] Treatment of methyl *N*-*tert*-butylformimidate (**2**) with a slight excess of ketene **1** in refluxing benzene results in a 90% isolated yield of 1,3-di-*tert*-butyl-3-cyano-4-methoxy-2-azetidinone (**3**). This reaction is analogous to those of imines with bulky substituents on nitrogen which yield β-lactams.[1-3,13] No 2:1 cycloadducts were detected; the reaction gives only **3** from NMR and ir analysis of the crude reaction mixture.



To study the steric effect and to look for the interesting bicyclic amide **4**, additions to methoxyazetines **5** were tested. These 4,4-dimethyl substituted methoxyazetines represent analogs of **2** where the *tert*-butyl group is effectively pulled back by incorporation into the azetine ring. Treatment of 2-methoxy-4,4-dimethylazetine (**5a**) with 2 equiv of **1** at room temperature in benzene resulted in the isolation by chromatography of a crystalline 2:1 adduct in low yield. The oxazinone structure **6** for this adduct was chosen on the basis of the infrared bands at 1755 and 1700 cm^{-1}, although the 1755-cm^{-1} band was much weaker.[3,10-12] It was also noted that this adduct melted with decomposition and vigorous evolution of a gas shown to be isobutylene by mass spectrometry. The presence of a carbonyl in **6** was confirmed by the occurrence of a ^{13}C NMR peak at 187.4 ppm. The rest of the ^{13}C spectrum was also consistent with structure **6**. The ultraviolet spectrum showed only end absorption as expected for **6**. The desired β-lactam **4** could not be detected by NMR or ir spectroscopy in the reaction mixture.

Treatment of 2-methoxy-3,3,4,4-tetramethylazetine (**5b**) with ketene **1** showed no evidence of β-lactam formation, but resulted in formation of the 2:1 adduct **7** in moderate yield. Lack of even a weak band from 1700 to 1800 cm^{-1} in the infrared spectrum and lack of any carbonyl band in the ^{13}C spectrum led to the assignment of the dioxazine structure **7** to this adduct rather than an oxazinone structure analogous to **6**. The ^{13}C spectral bands and the infrared bands at 1705 and 1625 cm^{-1} are consistent with structure **7**.[14-17] A strong ultraviolet band at 232 nm with a shoulder at 275 nm also distinguishes the dioxazine structure **7** from the oxazinone structure of **6**.



Formation of the β-lactam **3** is favored[3,13] over formation of 2:1 adducts. This is probably because the 1,4-dipolar ion prefers the conformation shown, which cannot give the usual oxazinone B or dioxazine C adducts by concerted 1,4-dipolar addition of another ketene. Although the carbon of the ketene is quite hindered, the imino ether carbon is not very hindered in **2**; and C–C closure to give the β-lactam **3** occurs readily. The dipolar ions **8** and **9** from the cyclic imino ethers **5** feel enough relief of the steric hindrance of the bulky *gem*-dimethyl substituents next to nitrogen that conformer **8** may now be preferred over **9**. Greater ste-

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]

E. J. Corey* and J. William Suggs

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

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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-