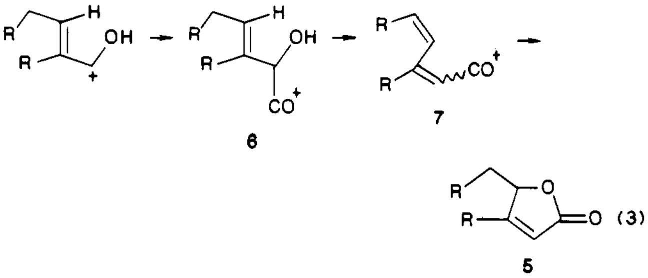
protonation of **2** yields **4**, which then cyclizes to **1**. The regioselectivity of CO incorporation is rather puzzling. In principle, both termini of **3** can react with CO. Reaction at the aldehydic carbon should lead to the isomeric **5** (eq 3). Since an α-OH group is supposed to stabilize a carbenium ion,[10] **5** may be expected to be the major product on the basis that Koch reaction products are generally determined by the relative stabilities of the intermediate carbenium ions. However, **5** was not observed in any of the reactions studied. It is, of course, possible that carbonylation is reversible and that **6** is less thermodynamically stable than **4** or either **6** or **7** is unstable under the reaction conditions. The real cause for the absence of **5** will have to await further study.



(3)

2(5*H*)-Furanones occur as natural products[11] and are versatile synthetic intermediates since, e.g., they react readily as Michael acceptors[12] and can be reduced to furans.[13,14] A large body of literature is available on the synthesis of these compounds,[15] but none is comparable to our method with respect to simplicity and availability of starting materials.

Experimental Section

Nuclear magnetic resonance spectra were recorded on a Varian EM360 or a JEOL FX90 spectrometer. Infrared spectra were recorded on a Beckmann AccuLab instrument. Mass spectra were obtained by use of a Finnigan 4000 GC/MS system operating in the chemical ionization mode with methane. Gas chromatographic analysis utilized a Hewlett-Packard 5700A instrument with 6 ft × $^1/_8$ in. columns packed with 5% Carbowax 20M or SE 30. Elemental analyses were performed by the Analytical Laboratories, Michigan Division, The Dow Chemical Co.

General Method. All reactions were run under identical conditions and are illustrated by the procedure for the carbonylation of *n*-propanal. Sulfuric acid (96%, 100 mL, 1.81 mol) was placed in a 300-mL stainless steel autoclave equipped with a high-speed stirrer and heated to 50 °C. After the vessel was closed and flushed with nitrogen, carbon monoxide was introduced until the pressure reached 6.9 MPa. With stirring at 1700 rpm, *n*-propanal (17.4 g, 0.3 mol) was added at a rate of 0.15 mol per hour by means of a modified HPLC pump. Stirring and heating were continued for 2 more h after all the aldehyde had been added. The vessel was then cooled to room temperature and the excess carbon monoxide vented. The contents were cautiously added to 200 g of ice. The aqueous solution was saturated with ammonium chloride and extracted with ether (2 × 300 mL). After the mixture was dried with anhydrous MgSO$_4$, the solvent was removed on a rotary evaporator at room temperature and the resulting residue distilled at reduced pressures to give **1b** (8.32 g, 44%): bp 100–103 °C (10 mmHg) [lit.[16] bp 112–118 (12 mmHg)]; ^{1}H NMR (CDCl$_3$) δ 4.63 (s, 2 H), 2.30 (q, 2 H, J = 7.0 Hz), 2.05 (s, 2 H), 1.1 (t, 3 H, J = 7.0 Hz); ^{13}C NMR (CDCl$_3$) δ 174.6 (C=O), 155.8 (C-3), 128.7 (C-4), 72.4 (C-5), 16.7, 12.6, 12.0 (Et, Me); IR (neat) 1750, 1680 cm^{-1}; MS, (m + 1)/z 127 (M).

3-*n*-Propyl-4-ethyl-2(5*H*)-furanone (1c). The carbonylation of *n*-butanal (21.6 g, 0.3 mol) gave 8.9 g (38.5%) of **1c**: bp 125–130 °C (12 mmHg); ^{1}H NMR (CDCl$_3$) δ 4.76 (s, 2 H), 2.38 (m, 4 H), 1.52 (m, 2 H), 1.03 (m, 6 H); ^{13}C NMR (CDCl$_3$) δ 175.1, 161.9, 126.2, 70.7, 25.3, 21.3, 20.2, 13.7, 12.2; IR (neat) 1750, 1670 cm^{-1}; MS, (m + 1)/z = 155 (M). Anal. Calcd for C$_9$H$_{14}$O$_2$: C, 70.13; H, 9.09. Found: C, 70.35; H, 9.11.

3-*n*-Hexyl-4-*n*-pentyl-2(5*H*)-furanone (1d). From *n*-heptanal (34.2 g, 0.3 mol) was obtained 8.6 g (24%) of **1d**: bp 142–146 °C (1 mmHg); ^{1}H NMR (CDCl$_3$) δ 4.55 (s, 2 H), 2.26 (m, 4 H), 1.31 (m, 14 H), 0.89 (m, 6 H); ^{13}C NMR (CDCl$_3$) δ 175.09, 160.51, 127.09, 71.13, 31.63, 31.52, 29.14, 28.06, 27.57, 27.03, 23.56, 22.53, 13.97, 13.81; MS (m + 1)/z = 239 (M). Anal. Calcd for C$_{15}$H$_{26}$O$_2$: C, 75.63; H, 10.92. Found: C, 75.90; H, 10.71.

3,4-Dimethyl-2(5*H*)-furanone (1a). The carbonylation of 2-methyl-2-butenal[9] gave 54.6% of **1a**: bp 99–102 °C (10 mmHg) [lit.[16] bp 103–112 °C (14 mmHg)]; ^{1}H NMR (CDCl$_3$) δ 4.51 (s, 2 H), 2.00 (s, 3 H), 1.81 (s, 3 H); ^{13}C NMR (CDCl$_3$) δ 175.1, 156.4, 122.5, 72.3, 11.9, 7.9.

Registry No. **1a**, 1575-46-8; **1b**, 35594-14-0; **1c**, 103563-97-9; **1d**, 103563-98-0; **2a**, 1115-11-3; **2b**, 623-36-9; **2c**, 64344-45-2; CH$_3$CH$_2$CHO, 123-38-6; CH$_3$(CH$_2$)$_2$CHO, 123-72-8; CH$_3$(CH$_2$)$_5$CHO, 111-71-7; H$_2$SO$_4$, 7664-93-9; CO, 630-08-0.

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Aryl-Activated Carbon–Chlorine Bond Cleavage at the Bridgehead Positions in 1-Chloro- and 1,4-Dichloro-7,7-dimethoxybenzonorbornene[1]

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There have been several reports of the photolytic cleavage of bridgehead iodides by direct photolysis of the carbon–halogen chromophore.[2] The cleavage of simple benzylic systems (such as benzyl chloride), through light absorbed by the aromatic ring, has also been extensively studied.[3] Our own interest has been in the photochemical intramolecular activation of remote (frequently UV transparent) functional groups,[1,4] and, in this context, we noted calculations[5] that indicated significant $\pi,\pi^*/\sigma,\sigma^*$ interaction[1,6] might occur in a bridgehead-substituted benzonorbornene. This suggested one might observe photolytic cleavage of a 1-chlorobenzonorbornene derivative despite the unfavorable location of the halogen.

As a prototypical example, we prepared 1,4-dichloro-7,7-dimethoxybenzonorbornene (**1**) by using published

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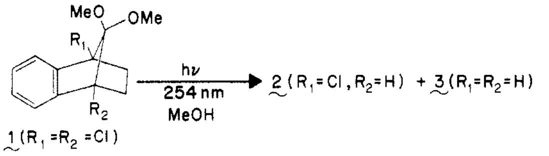
procedures.[7] The presence of the methoxy groups is a matter of synthetic convenience and there is no spectral evidence for interaction with the benzene ring. Photolysis of a 0.02 M solution of **1** in methanol, using a low-pressure mercury source (254 nm), led to the formation of two major products observable by GLC (eq 1). At 72% loss of **1**, the ratio of **2**/**3** was 2.6; there is no evidence of the bridgehead ethers one might expect from heterolytic cleavage.[2,8] At higher conversion (84%) the ratio of **2**/**3** diminished to 1.7, indicating that **2** was fragmenting to **3**. This was confirmed by photolysis of the monochloro photoproduct wherein clean reduction to **3** was observed.[9]



(1)

The quantum efficiency (ϕ) for photofragmentation of **2** to **3** was determined using the photosolvolysis of *exo*-2-chlorobenzonorbornene in methanol ($\phi = 0.55$)[6] as a secondary actinometer. The measured value of 0.024 may be compared with ϕ's reported for (unconstrained) benzyl chloride (0.26–1.0, depending on the solvent)[10] and to the 0.55 observed for the homobenzylic 2-position (see above).

Experimental Section

^{1}H NMR were obtained with a Perkin Elmer R-32 (90 MHz), a Varian XL-200 (200 MHz), or a Nicolet NT-470 (470 MHz) spectrometer. ^{13}C NMR spectra were recorded on the Varian XL-200 spectrometer at 50 MHz. Mass spectra were obtained with a Finnigan automated gas chromatography EI/CI mass spectrometer. Vapor-phase chromatography utilized Varian Model 90-P, A-90-P, and A-700 chromatographs for preparative work and Model 1200 or 1400 FID chromatographs with a Hewlett-Packard 3380 or 3380-A digital integrator for quantitative studies. Photochemical studies mainly employed a rotating turntable with quartz tubes and a Hanovia Model 68814-45 low-pressure mercury arc lamp.

Photolysis of 1,4-Dichloro-7,7-dimethoxybenzonorbornene (1).[7] In a typical procedure, 500 mg (1.8 mmol) of **1** was dissolved in 100 mL of methanol (Burdick and Jackson Spectroquality, sparged with argon for 30 min, and irradiated for 440 min, with constant argon bubbling, using the 254-nm lamp. After addition of some solid Na_2CO_3 to reduce acidity, the methanol was removed on a rotary evaporator and the residue taken up in dichloromethane. Analysis by a 20 ft × $^1/_4$ in. 10% FFAP on 60/80 mesh Chromosorb W (AW-DMCS) column at 210 °C (90 mL of He/min) showed compounds **2** (t_r 25 min) and **3** (t_r 12.4 min)[7] plus ethylene glycol (t_r 4.8 min) and traces of an unidentified product (t_r 19 min).

1-Chloro-7,7-dimethoxybenzonorbornene (**2**) has hitherto been reported and was isolated by preparative VPC: ^{1}H NMR ($CDCl_3$, 470 MHz) δ 7.20–7.40 (m, 4 H, Ar), 3.51 (s, 3 H, anti OCH_3), 3.30 (d, 1 H, bridgehead H), 3.20 (s, 3 H, syn OCH_3), 2.35 (dd, 2 H, CH exo), 1.45 (dd, 2 H, CH endo); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 25.89 (C-3), 34.84 (C-2), 45.22 (C-4), 50.63, 51.96 (OCH_3), 74.76 (C-1), 115.32 (C-7), 119.87, 120.97, 126.59, 127.19, 141.50 (Ar); mass spectrum (70 eV) 238, 240 ($M^{\bullet+}$), 163, 165 (base peak + isotope peak, M – $CH(OCH_3)_2$).

Anal. Calcd for $C_{13}H_{15}ClO_2$: C, 65.40; H, 6.33; Cl, 14.85. Found: C, 65.81; H, 6.35; Cl, 14.44.

Quantum Efficiency for Conversion of 2 to 3. Compound **2** was made up as a 8.04 × 10^{-3} M solution in methanol and charged (5.0 mL) into two matched quartz tubes. Two other matched tubes were charged with 5.0 mL of 1.00 × 10^{-2} M *exo*-benzobicyclo[2.2.1]hepten-2-yl chloride (**4**) in methanol. The five tubes were degassed with argon for 30 min and the three solutions of **2** irradiated for 181 min. One of the solutions of **4** was irradiated for the intial 10.3 min (lamp prewarmed for 50 min) and the other for the final 10.3 min. Analysis of **4** was by a 10 ft × $^1/_8$ in. 10% Carbowax 20 M column at 130 °C by comparison with unirradiated solution. Analysis of **3** was on the same column using bibenzyl as an internal standard; both tubes gave the same $\phi_3 = 0.024$.

Acknowledgment. We thank the National Science Foundation (Grant CHE-8318825) for support of this research. The carbon-13 NMR data were obtained on an instrument provided by NSF Grant CHE 8004246, the 470-MHz data were obtaiend through the Purdue University Biological Magnetic Resonance Laboratory (Grant NIH-RR01077), and the GC–Ms data were obtained on an instrument provided by NSF Grant CHE-8010832.

Registry No. 1, 34201-94-0; 2, 103620-91-3; 3, 29370-70-5.

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[9] Earlier studies[6] have shown that, for example, *exo*-2-chloronorbornane, is not susceptible to *inter*molecular aryl sensitization.

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Ketovinylation of Arylthallium Compounds Catalyzed by Lithium Tetrachloropalladate

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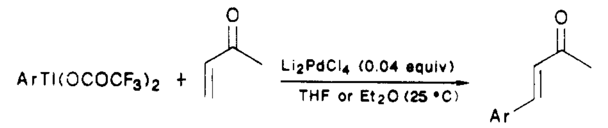
We report here the results of our study in which methyl vinyl ketone is β-arylated by a Li_2PdCl_4-catalyzed reaction with various thallated aromatic compounds.



The palladium(II)-catalyzed olefinatioin of arylthallium compounds was first reported by Spencer and Thorpe in 1975.[1] Since then, numerous examples and variations of this reaction have been reported.[2] Except for one isolated case,[3] however, none of those examples have involved the use of a vinyl ketone as the olefin.[4] That one isolated case was the Pd(II)-catalyzed reaction of methyl vinyl ketone with a thallated indole. It involved the use of a high

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