814 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.26 (overlapping d, 6 H), 3.6 [s, ketonic H at C(2)], 5.05 [s, enolic H at C(2)], 5.1–5.2 (m, 1 H), 5.53 (app t, 1 H), 5.93–6.46 (m, 2 H), 11.9 (s, enol O*H*); MS, *m*/*z* 157 (MH$^+$). Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.76. Found: C, 61.76; H, 7.93.

***tert*-Butyl 3-oxo-4-pentenoate (1d)**: bp 49 °C/0.72 mmHg (oven temperature; lit.[12] bp 80–82 °C/5 mmHg); R_f (hexanes:ethyl acetate 3:1) 0.61; IR (film) 2982, 2934, 1736, 1658, 1587, 1418, 1370, 1254, 1146, 814 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.45 (m, 9 H), 3.51 [(s, ketonic H at C(2)], 4.96 [s, enolic H at C(2)], 5.47 (t, J = 6 Hz, 1 H), 5.9–6.4 (m, 2 H), 11.9 (s, enol O*H*); MS, *m*/*z* 171 (MH$^+$).

Bornyl 3-oxo-4-pentenoate (1e): Compound **1e** was prepared as described above; however, ether was used as the reaction solvent. Purification was achieved by Kugelrohr distillation utilizing a preheated oven (150 °C) at 0.51 mmHg. R_f (hexanes:ethyl acetate 3:1) 0.59; IR (film) 2953, 1740, 1657, 1588, 1420, 1244, 1150, 1040, 812 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.8–1.0 (m, 9 H), 1.0–1.1 (m, 1 H), 1.2–1.4 (m, 2 H), 1.6–2.0 (m, 3 H), 2.3–2.45 (m, 1 H), 3.7 [s, ketonic H at C(2)], 4.9–5.0 (m, 1 H), 5.15 [s, enolic H at C(2)], 5.35 (app t, 1 H), 6.0–6.5 (m, 2 H), 11.85 (s, enol O*H*). Anal. Calcd for $C_{15}H_{21}O_3$: C, 72.25; H, 8.51. Found: C, 72.28; H, 8.58.

Compounds 4a and **4b** were prepared in an analogous fashion.

Ethyl 4-methyl-3-oxo-4-pentenoate (4a): bp 48 °C/0.37 mmHg (oven temperature; lit.[4,19] bp 88–92 °C/12 mmHg); R_f (hexanes:ethyl acetate 3:1) 0.61; IR (film) 2984, 1741, 1672, 1636, 1601, 1421, 1239, 1152, 1040, 968 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.2–1.4 (m, 3 H), 1.82–1.95 (m, 3 H), 3.54 [s, ketonic H at C(2)], 4.15–4.23 (m, 2 H), 4.93 [s, enolic H at C(2)], 5.75–6.2 (m, 1 H), 6.6–7.0 (7, 1 H), 11.86 (s, enol O*H*). Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.76. Found: C, 61.69; H, 7.95.

Ethyl 5-methyl-3-oxo-4-pentenoate (4b): bp 78 °C/1.60 mmHg (oven temperature; lit.[4,19,20] bp 95–98 °C/mmHg); R_f (hexanes:ethyl acetate 3:1) 0.49; IR (film): 3101, 2986, 1743, 1682, 1595, 1456, 1420, 1379, 1345, 1294, 1250, 1095, 1034, 941 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.2–1.35 (m, 3 H), 1.86 (s, 3 H), 3.70 [s, ketonic H at C(2)], 4.15–4.25 (m, 2 H), 5.18 [s, enolic H at C(2)], 5.3–5.9 (m, 2 H), 12.0 (s, enol O*H*). Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.76. Found: C, 61.55; H, 7.78.

Acknowledgment. R.Z. acknowledges the Camille and Henry Dreyfus Foundation for a Distinguished New Faculty Grant and the American Cancer Society, Inc., for a Junior Faculty Grant. This work was supported by the Biomedical Research Support Grant Program (S07 RR07068-23), Division of Research Resources, National Institutes of Health and Syracuse University.

Supplementary Material Available: ^{13}C NMR data (recorded at 125 MHz) for all products (2 pages). Ordering information is given on any current masthead page.

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(19) Couffignal, R.; Moreau, J.-L. *J. Organomet. Chem.* **1977**, *127*, C65.

(20) Bodalski, R.; Pietrusiewicz, K. M.; Monkiewicz, J.; Koszuk, J. *Tetrahedron Lett.* **1980**, *21*, 2287.

Oxidation of 4-(Phenylazo)-1,2-naphthalenediol

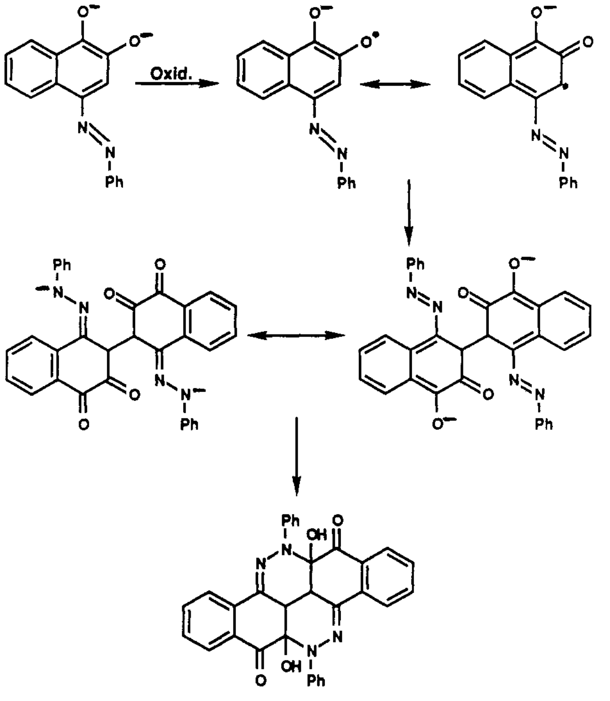
Paul T. MacGregor*[,1] and Myron S. Simon

Chemical Research Division, Polaroid Corporation,
730 Main Street, Cambridge, Massachusetts 02139

Received March 17, 1989

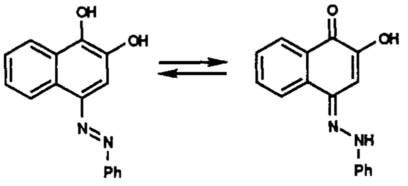
An alkaline solution of 4-(phenylazo)-1,2-naphthalenediol (**1**) can develop silver in an exposed photographic emulsion and produce a lemon-yellow image.[2]

Scheme I. Possible Mechanism for the Formation of 2



2

Under appropriate conditions, after neutralization, an apparently colorless image against an orange background of the unreacted dye can be obtained.[3] The oxidation of **1** in aqueous alkali has been reported twice, originally by Zincke and Wiegand in 1895,[4] and again by Shemyakina, Bogoslovsky, and Shemyakin.[5] The deep blue alkaline solution of the dye turns brown on exposure to air and deposits a yellow solid which was described in each case as 4-(phenylazo)-1,2-naphthoquinone.



1a **1b**

To understand the photographic experiments we have oxidized **1** with silver nitrate in potassium hydroxide solution. Workup of the alkaline mixture without neutralization yielded the yellow product in 37% yield after recrystallization.[6] The yellow product was shown by IR and ^{1}H NMR spectroscopy and by TLC to be identical with the product of air oxidation, and also (by TLC and MS only) with a yellow product obtained by extraction of some of the apparently colorless image material mentioned above.

The mass spectrum of the yellow product showed it to be a dehydro dimer with a molecular ion at *m*/*e* 526 (EI) and little evidence of fragmentation except for a small peak at *m*/*e* 490. The IR spectrum (CCl$_4$) contained a strong carbonyl band at 1698 cm^{-1} and an NH or OH band at 3480 cm^{-1}. The proton NMR spectrum showed a nonex-

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(1) Present address: Anitec Image Corp., 40 Charles St., P.O. Box 4444, Binghamton, NY 13902-4444.

(2) Friedman, J. S. *History of Color Photography*; Focal: New York, 1968; p 367.

(3) Rogers, H. G., Personal communication.

(4) Zincke, T.; Wiegand P. *Ann. Chem.* **1895**, *286*, 58.

(5) Shemyakina, O. M.; Bogoslovsky, B. M.; Shemyakin, M. M. *Zh. Obshch. Khim.* **1952**, *22*, 675 (Engl. transl. p 739).

(6) The same result is obtained using $K_3Fe(CN)_6$ in aqueous KOH.

0022-3263/89/1954-4719$01.50/0

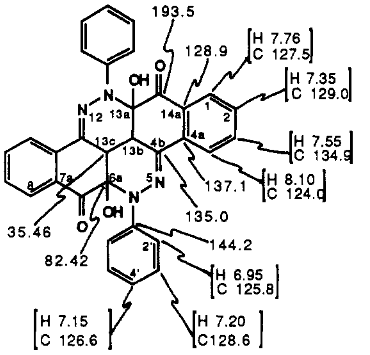
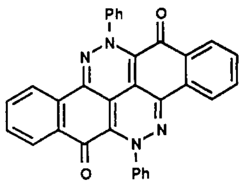


Figure 1. NMR assignments for 2.

changable two-proton singlet at δ 3.73 ppm, suggesting a symmetrical structure with two protons bound to sp^3 hybridized carbon atoms. The ^{13}C NMR spectrum was also consistent with a symmetrical dimer, showing only 14 lines, including one carbonyl singlet at δ 193.6 ppm. It also contained a doublet at 35.46 ppm, in accord with the ^{1}H NMR spectrum, and a singlet at 84.42 ppm.

We propose that the yellow product is the hexacyclic dimer 2 and arises from initial coupling at the 3-position of 1, as shown in Scheme I. The dye in 1 N KOH is present as the dianion as indicated by the strong absorption band at 600 nm (ϵ 21 400).[7] We postulate that one-electron oxidation produces a semiquinone with some radical character at the 3-position, leading to carbon–carbon bond formation. Analogous couplings are often encountered in the oxidation of naphthol derivatives.[8,9] The failure of the dimer to re-aromatize or oxidize further results from the closure to the hemiaminal, which accounts for the absence of a second carbonyl band in the ^{13}C NMR spectrum and the presence of the singlet at 84.42 ppm. Precipitation of 2, which is less acidic than 1, prevents any further base-catalyzed reactions. The presence of a two-proton (exchangeable) resonance at 5.27 ppm in the NMR spectrum and the 3480 cm^{-1} IR band are consistent with the hemiaminal structure.

The proposed structure 2 is further supported by its dehydration in concentrated sulfuric acid. The cyan-colored solution (λ_{max} = 638 nm) yields a purple solid on dilution with water. The mass spectrum of this product shows a molecular ion at *m/e* 491 (FAB$^+$), consistent with double dehydration to 3. (Elemental analysis shows the absence of any sulfate ion and the probable presence of 1 mol of water of hydration.) The IR spectrum of 3 contains a pair of strong bands at 1595 and 1625 cm^{-1}, which are strikingly similar to bands shown by the starting dye. These are absent in the spectrum of 2 and may be associated with the keto hydrazone structures of **1b** and 3.[10]



3

Experimental Section

General. Analytical TLC's were performed with 1:1 cyclohexane/CH_2Cl_2 or 5% acetone/CH_2Cl_2 on Analtech silica gel plates no. 02031 and preparative TLC on Analtech taper plates no. 81013. Elemental analyses were performed by Galbraith Laboratories. NMR spectra were obtained on a Varian XL 300 FT NMR, UV-vis spectra on a Hewlett-Packard 8452A diode array spectrophotometer, and IR spectra on a Nicolet 20DXC FT IR spectrophotometer.

4-(Phenylazo)-1,2-naphthalenediol (1).[13] Aniline sulfate (8.50 g, 0.060 mol) in 50 mL of H_2O and 4.7 mL of concentrated H_2SO_4 was diazotized at −5 °C with sodium nitrite (4.53 g, 0.066 mol) in 15 mL of H_2O, and the resulting solution was treated with sulfamic acid until gas evolution ceased. Aluminum sulfate octadecahydrate (20.12 g, 0.03 mol) in 50 mL of H_2O was added to the cold solution. 1,2-Naphthalenedione (8.59 g, 0.054 mol) in 150 mL of ethanol was hydrogenated over 0.2 g of 5% Pd/C in a Parr shaker until the theoretical uptake of H_2 was complete.[14] The solution was filtered and added all at once to the cold diazotization solution. After being stirred for 1 h, the mixture was filtered and the cake was washed repeatedly with water and then partitioned between water and ethyl acetate. The organic layer was washed repeatedly with H_2O, dried over $MgSO_4$, and evaporated. Recrystallization from acetonitrile yielded 4.73 g (29%) of red dye 1 solvated with 1 mol of acetonitrile. Electronic spectrum (THF): λ_{max} 476 (ϵ 40 700), 244 nm (ϵ 27 800). IR (KBr): 1625, 1600, 1540, 1455, 1405 cm^{-1}. NMR (DMSO-d_6): δ 2.08 (s, 3 H, acetonitrile), 6.98 (t, 1 H), 7.36 (t, 2 H), 7.47–7.55 (m, 3 H), 7.59 (s, 1 H), 7.71 (t, 1 H), 8.12 (d, 1 H), 8.57 (d, 1 H), 10.01 and 11.13 (s, 1 H each, exchangeable).

Silver Nitrate Oxidation. 1·CH_3CN (1.5 g, 4.91 mmol) in 6 mL of THF was added to 60 mL of deaerated 1 N NaOH under nitrogen. Silver nitrate (2.00 g, 11.8 mmol) in 5 mL of H_2O was added rapidly to the stirred dark blue solution. After 3 min the blue color had been discharged. The mixture was filtered through Celite to give a red filtrate. The cake was washed with several portions of water and then with ethyl acetate. The cake was further washed with THF until the washes were almost colorless. The THF was evaporated, and the residue taken up in ethyl acetate, combined with the EtOAc washes, washed several times with water, dried over $MgSO_4$, and evaporated to a solid. Recrystallization from toluene gave 0.662 g (36.9%) of yellow dimer, mp 217–225 °C dec.[15] UV spectrum: λ_{max}(THF) 312 (ϵ 24 300), 360 nm (sh, ϵ 11 600). IR (CCl_4): 3480 (m, sh), 2880, 2840 (w), 1698 (s, sh), 1602, 1582, 1498 cm^{-1}. IR (KBr): 1695 (C=O), 1600, 1495 cm^{-1}. MS (EI): *m/e* 526, 490. ^{1}H NMR ($CDCl_3$): δ 8.10 (d, 2 H, H-4), 7.76 (d, 2 H, H-1), 7.56 (t, 2 H, H-3), 7.36 (t, 2 H, H-2), 7.3–7.1 (m, 6 H, H-4′ and H-3′), 6.98 (d, 4 H, H-2′), 5.2 (s, 2 H, exchangeable), 3.73 (s, 2 H, H-13c). ^{13}C NMR ($CDCl_3$): δ 193.63 (s, C-14), 144.16 (s, C-1′), 137.32 (s, C-4a), 135.46 (s, C-4b), 134.88 (d, C-3), 129.02 (d, C-2), 128.93 (s, C-14a), 128.60 (d, C-3′), 127.51 (d, C-1), 126.55 (d, C-4′), 125.79 (d, C-2′), 124.00 (d, C-4), 84.42 (s, C-6a), 35.46 (d, C-13b). 2D NMR ($CDCl_3$ 3 bond H–H correlation signals): δ, δ 8.11, 7.57 (H-4–H-3), 7.78, 7.37 (H-1–H-2), 7.57, 7.37 (H-3–H-2), 7.21, 6.97 (H-3′–H-2′), H-3′–H-4′ was unresolvable. 2D NMR ($CDCl_3$ 1 bond H–C correlation signals): δ, δ, 8.10, 124.0 (CH-4), 7.76, 127.5 (CH-1), 7.55, 134.9 (CH-3), 7.35, 129.0 (CH-2), 7.20, 128.6 (CH-3′), 7.15, 126.6 (CH-4′), 6.95, 125.8 (CH-2′). 2D NMR ($CDCl_3$, 3 bond H–C correlation signals in the

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(7) In pH 9 buffer 1 gives a pale magenta solution. An alkaline solution of 4-(phenylazo)-1-naphthol has an absorption band at 500 nm. Griffiths, J. *J. Soc. Dyers Colourists* **1972**, 106.

(8) For a recent review on the oxidative dimerization of naphthalene derivatives, see: Tisler, M. *Org. Prep. Proc. Int.* **1986**, *18*, 17.

(9) The dimerization of lawsone is an interesting parallel. Chandrasenan, K.; Thomson, R. H. *Tetrahedron* **1971**, *27*, 2529.

(10) The tautomeric composition of 1 has not been established, although the Russian workers attributed its nonoxidative hydrolysis (to lawsone and phenylhydrazine) to the hydrazone structure.[5] On the other hand, 4-(phenylazo)-1-naphthol has been extensively studied,[11] and its solutions display a solvent-dependent equilibrium between the two tautomers. One report claims that the solid in a KCl pellet is predominantly in the hydrazone form.[12]

(11) See, for example: Kishimoto, S.; Kitahara, S.; Manabe, O.; Hiyama, H. *J. Org. Chem.* **1978**, *43*, 3882.

(12) Millefiori, S.; Fasone, S. *Boll. Sedute Accad. Gioenia Sci. Natur. Catania* **1971**, *10*, 733; *Chem. Abstr.* **1973**, *78*, 28946*x*.

(13) The present preparation is probably less efficient than that of Zincke from 1a,7a-dihydronaphth[2,3-*b*]oxirene-2,7-dione.[4] See also Neunhoeffer, O.; Wenzel, M. *Z. Physik. Chem. (Leipzig)* **1958**, *209*, 94.

(14) **CAUTION!** The reduction product is a potent skin irritant.

(15) Shemyakina, et al. reported 205–207 °C and Zincke 250 °C. In our experience the decomposition point depended on the rate of heating, with discoloration occurring as low as 190 °C.

aromatic region): δ 8.06 (H-4) with 128.6 (C-14a or C-2), 135.0 (C-4b); 7.75 (H-1) with 134.3 (C-3), 193.5 (C-14), none for 137.1 (C-4a); 7.53 (H-3) with 137.1 (C-4a), 127.3 (C-1); 7.33 (H-2) with 123.7 (C-4), 128.7 (C-14a); 7.20 (H-3′) with 128.4 (C-5′); 7.17 (H-3′) with 143.9 (C-1′); 7.14 (H-4′) with 125.49 (C-2′); no signals obtained for 6.99 ppm (H-2′). Subsequent neutralization and extraction of the aqueous mother liquor yielded a complex mixture of other colored products which was not examined further.

Air Oxidation. To 1 (150 mg, 0.51 mmol) in 2 mL of EtOH was added 20 mL of 1 N KOH. The solution was stirred vigorously in an open flask for about 30 min, until the blue color appeared to have completely changed to red. The mixture was extracted with EtOAc, and the organic layer was washed three times with H_2O, dried over $MgSO_4$, and evaporated to a yellow solid, which was recrystallized from a 1:1 mixture of toluene and cyclohexane. The IR and PMR spectra and TLC were indistinguishable from the $AgNO_3$ oxidation product 2.

Photographic Experiment. A clear polyester sheet was coated with a photographic silver halide emulsion and coated in turn with a layer of gelatin containing 1. After exposure of a portion of the sheet to light, this was developed with a KOH solution containing 2-(4-methylphenyl)hydroquinone, causing the coated material first to become blue and then bleach in the exposed areas. Subsequent washing with dilute acetic acid yielded a transparent orange color in the unexposed areas and a transparent neutral image in the exposed areas. Several samples of the exposed (and developed) areas were extracted with both EtOAc and THF. The extracts were combined and evaporated to a yellow gum. Repeated preparative TLC yielded a yellow solid, which on TLC showed only a trace of a colorless impurity at higher R_f. The yellow spot was indistinguishable from 2 by TLC, and both spots turned deep cyan when treated with concentrated H_2SO_4, fading to purple after standing exposed to air. MS (DCI, NH_3): *m/e* 527, 509 (weak), 265.

Sulfuric Acid Dehydration. Compound 2 (150 mg, 0.29 mmol) was dissolved in about 2 mL of concentrated H_2SO_4 to give a dark cyan solution (λ_{max} 638 nm), stirred for 10 min, diluted with 10 mL of H_2O, and centriguged. The precipitate was washed several times with H_2O and vacuum dried for 16 h at 60 °C over P_2O_5 to yield 109 mg of purple solid. Vis spectrum: λ_{max}(pyridine) 566 nm. IR (KBr): 1625, 1595 cm^{-1}. MS (FAB^+): *m/e* 491. Anal. Calcd for $C_{32}H_{20}N_4O_3$: C, 75.58; H, 3.96; N, 11.02. Found: C, 75.56; H, 3.55; N, 10.80.

Acknowledgment. We are indebted to Dr. H. F. Evans for preparation and discussion of the 2D NMR spectra and to other members of the Polaroid Central Analytical Facility for UV–vis, IR, and mass spectra.

Studies of the Furan–Carbonyl Photocycloaddition Reaction: Vinylic Substitution Reactions

Stuart L. Schreiber* and John A. Porco, Jr.

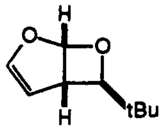
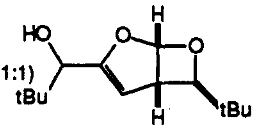
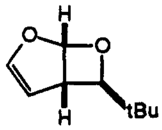
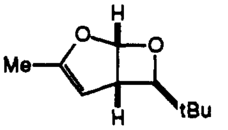
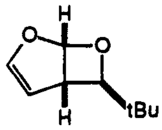
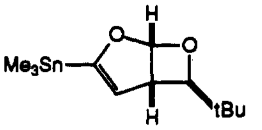
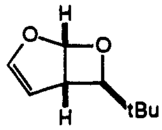
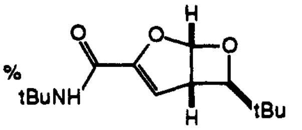
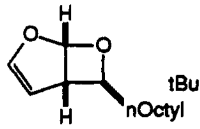
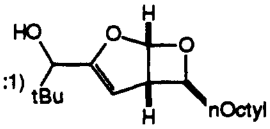
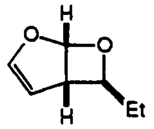
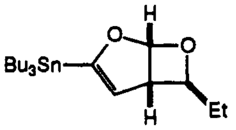
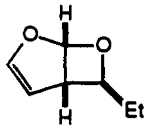
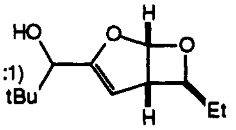
Sterling Chemistry Laboratory, Yale University,
New Haven, Connecticut 06511

Received March 14, 1989

In a previous communication from these laboratories, the influence of main-group metals (Sn, Si) on the chemoselectivity of the furan–carbonyl photocycloaddition reaction was reported.[1] In this note, we describe an alternative solution to the synthesis of photoproducts that are not readily obtained by the direct photoreaction of unsymmetrically substituted furans.

The metalation of cyclic enol ethers with tBuLi and subsequent reaction with electrophiles has been reported by Boeckman.[2] Attempts to apply these conditions to the Paterno–Büchi photoadduct of benzaldehyde and furan resulted instead in the formation of 2-furylphenylcarbinol. However, the conditions recently described by Hanessian[3] for the formation of *C*-glycosides from glucals with use of Schlosser's base (nBuLi, KOtBu, THF, −78 °C) were found to be successful for metalation of the oxetane containing enol ethers *provided that approximately 2.3 equiv of base was employed.* A similar need for excess tBuLi was noted in deprotonation reactions of alkoxy-substituted dihydrofurans and pyrans.[2]

Table I. Functionization of α-Vinylic Hydrogen

entry	enol ether	electrophile	yield	product
1		tBuCHO	66% (1:1)	
2		MeI	41%[b]	
3		Me_3SnCl[c]	65%	
4		tBuNCO	61%	
5		tBuCHO	63% (1:1)	
6		Bu_3SnCl[c]	50%	
7		tBuCHO	72% (1:1)	

[a] Metalations were conducted by adding nBuLi in hexanes (2.3 equiv, 2 M) to a solution of dry KOtBu (2.1 equiv) and the photoadduct (1.0 equiv) in THF at −78 °C (3 h) and subsequently adding the electrophile in THF. [b] Low isolated yield is due in part to product volatility. [c] Metalation was conducted in hexane (−78 °C, 5 h), followed by the addition of electrophile in THF.

The results of metalation/functionalization studies with several representative photoproducts are reported in Table I. Although modest yields are observed in most instances, this reaction sequence gives rise to products that, when the direct photoaddition of the corresponding unsymmetrically substituted furan is attempted, are produced as mixtures (entries 1, 2, 5, and 7) or not formed at all (entry 4).[4] A limitation of the deprotonation reaction was found when the photoaddition product of benzaldehyde and fu-

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(1) Schreiber, S. L.; Desmaele, D.; Porco, J. A., Jr. *Tetrahedron Lett.* **1988**, *29*, 6689.

(2) (a) Boeckman, R. K.; Bruza, K. J. *Tetrahedron Lett.* **1977**, *18*, 4187. (b) Boeckman, R. K.; Bruza, K. J. *Tetrahedron* **1981**, *37*, 3997.

(3) Hanessian, S.; Martin, M.; Desai, R. C. *J. Chem. Soc., Chem. Commun.* **1986**, *12*, 926.

(4) Schreiber, S. L.; Hoveyda, A. H.; Wu, H.-J. *J. Am. Chem. Soc.* **1983**, *105*, 660.

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