

One-step Synthesis of Fulgides by Palladium-catalyzed
Carbonylation of Substituted 2-Butyne-1,4-diols

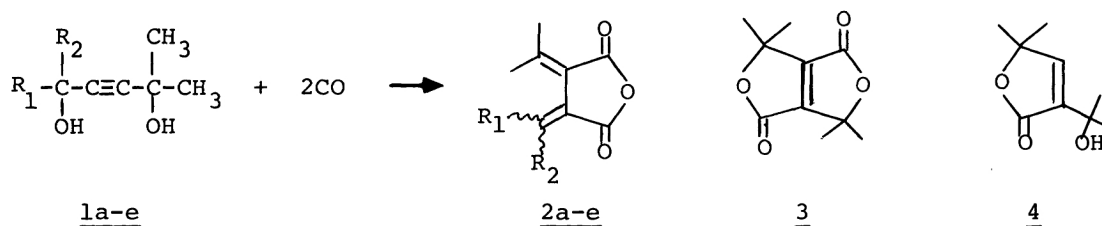
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The reaction of carbon monoxide with substituted 2-butyne-1,4-diols by $\text{Pd}(\text{OAc})_2/\text{I}_2$ catalyst gives derivatives of dimethylenesuccinic anhydride, "fulgides", in high yields.

Fulgide is a term used to derivatives of dimethylenesuccinic anhydride.¹⁾ It shows photochromic properties, which result from photocyclization on exposure to activating radiation and reverse process occurring either thermally or on irradiation at a different wavelength.²⁾ Recently, the possible application of photochromic organic compounds to a photochemical memory device has been pointed out³⁾ and fatigue-free photochromic system attracts attention.^{4,5)} From these viewpoints some fulgides are potential molecules for use in the optical information stores.

Since fulgides are synthesized stepwisely via the Stobbe condensation, more simple synthetic methods are desired. Tsuji and Nogi⁶⁾ have reported that the palladium-catalyzed carbonylation of 2,5-dimethyl-3-hexyne-2,5-diol (1a) gives diisopropylidenesuccinic anhydride (2a) and dilactone 3. The carbonylation,



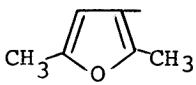
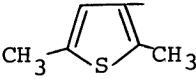
although still a potential reaction to one-step synthesis of fulgides, has found less application, since it requires so high concentration of HCl/PdCl_2 that difficulties are usually encountered in the carbonylation in a stainless steel autoclave and the yield of 2a does not exceed 50%. In the present study, we intended to improve the catalytic carbonylation, so that it can be applied to a synthetic route to fulgides and succeeded in one-step synthesis of photochromic fulgides.

One way to improve the catalysis is to promote the displacement of the OH group by carbon monoxide with rearrangement to allenecarboxylate.⁶⁾ Since iodine and iodides are thought to promote the reaction of alcohols with carbon monoxide,⁷⁾ we reasoned that facile synthesis of fulgides by catalytic systems other than

HCl/PdCl₂ may be possible. Indeed, though palladium acetate itself had no catalytic activity, the carbonylation of 1a with Pd(OAc)₂/I₂ (molar ratio, 1:1) proceeded smoothly. Absorption of carbon monoxide was completed within a few hours and fulgide 2a was obtained in a high yield. While dilactone 3 was not formed under these conditions, presence of triphenylphosphine as an auxiliary ligand to the palladium reduced the successive carbonylation to 2a and lactone 4 was the major product.

This carbonylation could be extended to other substituted 2-butyne-1,4-diols. The results are summarized in Table 1. Interestingly, fatigue-free

Table 1. Synthesis of fulgides

<u>1</u>	R ₁	R ₂	Catalyst	<u>1</u> /Pd ^{a)}	Time/h	Yield of <u>2</u> / % ^{b)}
<u>a</u>	CH ₃ ⁻	CH ₃ ⁻	PdCl ₂	10	5	60 ^{c)}
<u>a</u>	CH ₃ ⁻	CH ₃ ⁻	Pd(OAc) ₂ /I ₂	100	4	86 ^{c)}
<u>a</u>	CH ₃ ⁻	CH ₃ ⁻	PdCl ₂ (PPh ₃) ₂	25	6	18 (<u>4</u> , 61% ^{d)})
<u>b</u>	C ₆ H ₅ ⁻	C ₆ H ₅ ⁻	PdCl ₂	7.8	19.5	18 ^{d)}
<u>c</u>	CH ₃ ⁻	C ₆ H ₅ ⁻	Pd(OAc) ₂ /I ₂	7.3	5	81 ^{c)}
<u>d</u>	CH ₃ ⁻		Pd(OAc) ₂ /I ₂	10	12	≈50 ^{e)}
<u>e</u>	CH ₃ ⁻		Pd(OAc) ₂ /I ₂	10	17	48 ^{e)}

Solvent, benzene; CO, 72-85 kg/cm²; temperature, 90-100 °C

a) Molar ratio

b) Isolated yield by c) distillation, d) recrystallization, and e) TLC.

photochromic compounds (2d and 2e) possessing heterocyclic substituents, which can be used for the optical information stores, were readily synthesized. Fulgides 2c-e obtained by the carbonylation were a mixture of the corresponding Z and E isomers (2c, Z/E≈40/60; 2e, Z/E≈55/45).

In order to find optimum conditions the reactions with other solvents are now in progress.

References

- 1) H. Stobbe, Chem. Ber., 38, 3673 (1905).
- 2) H. G. Heller and S. Oliver, J. Chem. Soc., Perkin Trans. 1, 1981, 202.
- 3) Y. Hirshberg, J. Am. Chem. Soc., 68, 2304 (1956).
- 4) H. G. Heller, Chem. Ind., 1978, 193.
- 5) A. P. Glaze, S. A. Harris, H. G. Heller, W. Johncock, S. N. Oliver, P. J. Strydom, and J. Whitfall, J. Chem. Soc., Perkin Trans. 1, 1985, 957.
- 6) J. Tsuji and T. Nogi, Tetrahedron, 25, 4099 (1969).
- 7) D. Forster, J. Am. Chem. Soc., 98, 846 (1976) and references cited therein.

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