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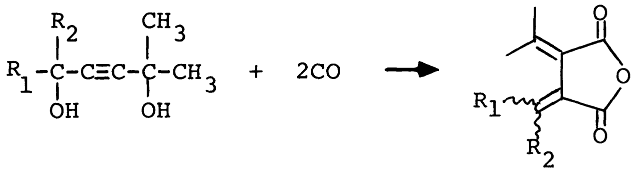
One-step Synthesis of Fulgides by Palladium-catalyzed Carbonylation of Substituted 2-Butyne-1,4-diols

Jitsuo KIJI, Hisatoshi KONISHI, Tamon OKANO,
Shinji KOMETANI, and Akio IWASA
Department of Environmental Chemistry and Technology,
Faculty of Engineering, Tottori University, Tottori 680

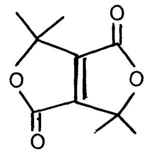
The reaction of carbon monoxide with substituted 2-butyne-1,4-diols by $Pd(OAc)_2/I_2$ catalyst gives derivatives of dimethylenesuccinic anhydride, "fulgides", in high yields.

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 sunthesis 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.



1a-e 2a-e



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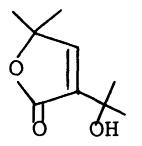

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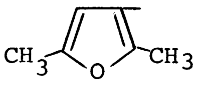
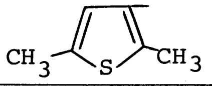
One way to improve the catalysis is to promote the displacement of the OH group by carbon monoxide with rearrangement to allenecarboxylate.6) Since iodine and iodides are thought to promote the reaction of alcohols with carbon monoxide,7) we reasoned that facile synthesis of fulgides by catalytic systems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

$HCl/PdCl_2$ may be possible. Indeed, though palladium acetate itself had no catalytic activity, the carbonylation of 1a with $Pd(OAc)_2/I_2$ (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 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).

Table 1. Synthesis of fulgides

1	R_1	R_2	Catalyst	1/Pd[a]	Time/h	Yield of 2/%[b]
a	CH_3-	CH_3-	$PdCl_2$	10	5	60[c]
a	CH_3-	CH_3-	$Pd(OAc)_2/I_2$	100	4	86[c]
a	CH_3-	CH_3-	$PdCl_2(PPh_3)_2$	25	6	18 (4, 61%[d])
b	C_6H_5-	C_6H_5-	$PdCl_2$	7.8	19.5	18[d]
c	CH_3-	C_6H_5-	$Pd(OAc)_2/I_2$	7.3	5	81[c]
d	CH_3-		$Pd(OAc)_2/I_2$	10	12	≈50[e]
e	CH_3-		$Pd(OAc)_2/I_2$	10	17	48[e]

Solvent, benzene; CO, 72-85 kg/cm^2; temperature, 90-100 °C

a) Molar ratio

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

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

References

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