

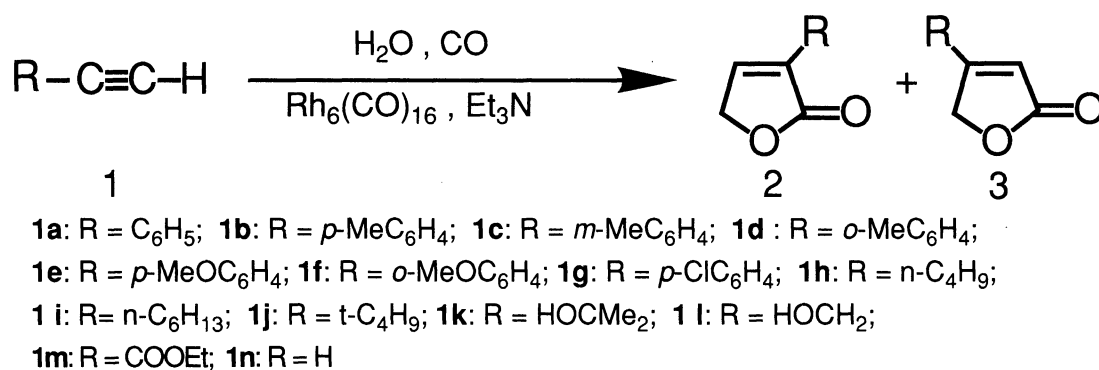
Reductive Carbonylation of Acetylenes under Water-Gas Shift Reaction Conditions.
Synthesis of Furan-2(5H)-ones from Terminal and Non-substituted Acetylenes

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Under water-gas reaction conditions terminal and non-substituted acetylenes are selectively converted into furan-2(5H)-ones by catalysis with a rhodium carbonyl cluster.

There have been numerous reports on the metal-catalyzed carbonylation of acetylenes.¹⁾ Recent examples include palladium(II)-catalyzed dicarbonylation of terminal acetylenes with formic acid and water,²⁾ and palladium(0)-catalyzed cyclocarbonylation of alkynols to furan-2(5H)-ones.³⁾ Previously, we have reported the catalytic preparation of 3,4-disubstituted furan-2(5H)-ones from internal acetylenes by rhodium-catalyzed reductive carbonylation under water-gas shift reaction conditions.⁴⁾ But attempts to obtain furanones from terminal and non-substituted acetylenes were not successful. In general, acetylenes having an active C-H bond may often cause complex reactions due to side reactions via oxidative addition.⁵⁾ Furan-2(5H)-ones are one of the most important synthetic targets because they are useful synthetic intermediates and an important class of naturally occurring compounds, some derivatives of which possess significant biological activities. Thus, we have performed the re-investigation of reaction conditions for terminal and non-substituted acetylenes and found that the reaction may be extended to a general method for the selective synthesis of furan-2(5H)-ones from such acetylenes (Scheme1).



Scheme 1.

The following improvement of the reaction conditions has been made: 1) The reaction temperature was decreased to 80 °C from 100 °C. 2) The solvent was changed to dioxane from tetrahydrofuran. 3) The amount of added amine was decreased. 4) The concentration of substrate was reduced. Then, phenylacetylene gave a mixture of 3- and 4- phenylfuran-2(5H)-ones in good yields under these conditions. In a typical procedure, phenylacetylene (**1a**) (15 mmol) was treated with water (86 mmol) and carbon monoxide (100 atm) in dioxane (45 ml) containing triethylamine (2.2 mmol) at 80 °C for 5 h in the presence of Rh₆(CO)₁₆ (9.4 × 10⁻³ mmol). The reaction proceeded smoothly and gave 3-phenylfuran-2(5H)-ones (**2a**) (50% yield) and 4-phenylfuran-2(5H)-one (**3a**) (43% yield). The reaction took place even at 50°C, although the reaction rate was decreased.

It was also found that the reaction activity and the selectivity were markedly influenced with the nature of solvents. Solvents with a smaller dielectric constant gave good results. Figure 1 shows dependence of the yield of furanones on the dielectric constant of solvents. In spite of immiscibility with water, benzene and chloroform showed also good results, but the reaction did not take place in hexane perhaps due to insolubility of the catalyst.

Other terminal acetylenes such as 1-hexyne and propargyl alcohol similarly gave the corresponding furanones except ethyl propiolate which gave no furanone derivatives and produced mainly cyclic trimers. It is noticeable that non-substituted acetylene (**1n**), which is highly reactive and often produce a polymeric material in other systems, also afforded furanone (**2n**) in a good yield under this reaction condition. The results obtained in the present work are summarized in Table 1. The

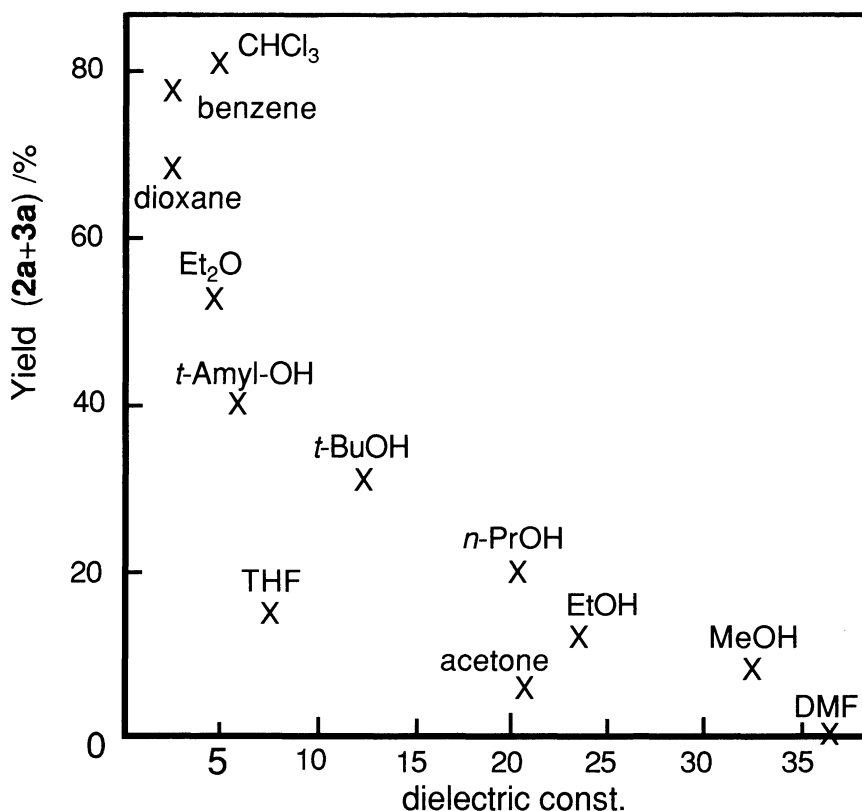


Fig. 1. Effect of the solvent.

isomer ratio of the furanones formed is about 1 and seems to be not affected by the electronic and steric nature of the substituents on the phenyl ring (**1a-1g**), contrary to the previous observation in the case of internal acetylenes.^{4b)}

The mild reaction conditions and use of a suitable solvent which were found in the present study may depress the side reactions and promote the reductive carbonylation of terminal and non-substituted acetylenes. Consequently, not only internal acetylenes but also terminal and non-substituted acetylenes can be selectively converted to furan-2(5H)-ones by the catalysis with $\text{Rh}_6(\text{CO})_{16}$ under water-gas shift reaction conditions and the present reaction may offer one of the useful synthetic methods of furan-2(5H)-ones. Further investigations including the mechanistic study are now in progress.

Table 1. Synthesis of Furan-2(5H)-ones from acetylenes^{a)}

Entry	R-C≡C-H	Conversion/%	Furanone	Yield/% ^{b)}	2:3 ^{c)}
1	1 a	100	2a+3 a	93	54:46
2	1 b	100	2b+3 b	87	54:46
3	1 c	100	2c+3 c	98	47:53
4	1 d	100	2d+3 d	91	37:63
5	1 e	100	2e+3 e	75	49:51
6	1 f	93	2f+3 f	71	42:58
7	1 g	100	2g+3 g	85	49:51
8	1 h	100	2h+3 h	92	30:70
9	1 i	100	2i+3 i	99	34:66
10	1 j	100	2j+3 j	99	73:27
11	1 k	100	2k+3 k	88	61:39
12	1 l	100	2l+3 l	60	45:55
13d)	1 m	100	-	0	-
14e)	1 n	-	2 n	71f)	-

a) Reaction conditions: Rh₆(CO)₁₆, 9.4 x 10⁻³ mmol; Substrate, 15 mmol; H₂O, 86 mmol; NEt₃, 2.2 mmol; dioxane, 45 ml; CO, 100 atm; 80 °C; 5 h. b) Determined by GC analysis. c) Molar ratio of the structural isomers, **2** and **3**. d) Cyclic trimers were obtained as the main products. e) Reaction was carried out at 50 °C for 5 h. f) Isolated yield.

References

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