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A NOVEL PALLADIUM-CATALYZED REARRANGEMENT OF ACETYLENIC KETONES TO FURANS

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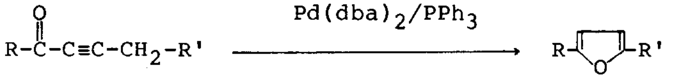
Abstract: A novel rearrangement of 1-aryl-4-alkyl-2-butyn-1-one in the presence of $Pd(dba)_2$-PPh_3 catalyst gave 2,4-substituted furans in moderate yields.

In studying palladium-catalyzed [3+2] cycloaddition reaction[1,2] of methylenecyclopropane with 1-aryl-4-alkyl(or aryl)-2-butyn-1-one compounds[3],we found that the yields of desired addition products were quite low. Contrary to our expectation, most of acetylenic ketones underwent rearrangement to 2,4-substituted furans. Further experiments showed that the butynones themselves have been cyclized by palladium catalyst according to equation(1).



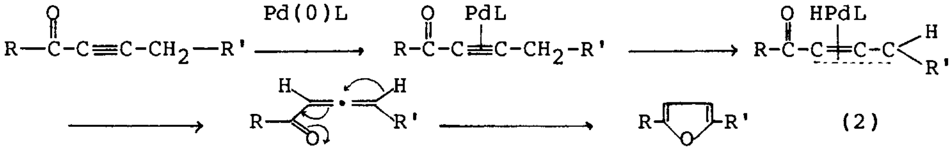
(1)

The experimental conditions and the yields of the products are listed in Tab. 1.

Since the preparation of substituted furans is of current interest,various methods have been adopted for this purpose[4-8]. In this paper we present a new route for preparing these compounds,the yields of which were about 40%.

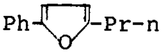
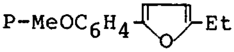
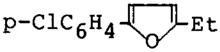
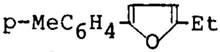
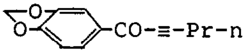
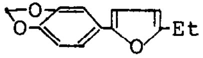
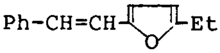
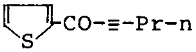
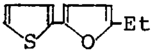
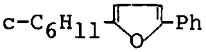
In equation 1,when R is aryl group(including heterocyclic aryl),the rearrangement is satisfactory,but when R is simple alkyl group(e.g.,R=Me,R'=Pr-n) no substituted furans is obtained.

Possible mechanism of this rearrangement is suggested as follows(Eqn.2): By means of palladium-catalyst,the butynones were at first rearranged into allenyl ketones and then cyclized to furans[6].Whether Palladium participates the allenyl ketone coordination is not sure now.Further mechanistic investigation is in progress.



(2)

Table 1. Palladium-catalyzed Rearrangement of Butynones[a)]

Entry	Butynone	hr.	Substituted furan formed	M.P. or B.P.(°C/Torr)	Isolated yield(%)
1	Ph-CO-≡-Bu-n	6		104-105/0.7	44
2	Ph-CO-≡-Pr-n	6		85-88/1	48
3	p-MeOC$_6$H$_4$-CO-≡-Pr-n	6		115-120/0.5	40
4	p-ClC$_6$H$_4$-CO-≡-Pr-n	8		28-29	37
5	p-MeC$_6$H$_4$-CO-≡-Pr-n	6		88-90/1	44
6		6		43-43.5	59
7	Ph-CH=CH-CO-≡-Pr-n	6		108-111/0.7	37
8		6		78-80/0.7	41
9	Ph-CO-≡-CH$_2$-Ph	7		87-88	25
10	Ph-CO-≡-CH$_2$-C$_6$H$_{11}$-c	12		58-59	33[b)]
11	Me-CO-≡-Bu-n	12			0

a) All the reactions were carried out at 100°C for 6-12 hr,under N_2,and the products were identified by ^{1}H-nmr,IR and MS.

b) Based on the recovered starting material.

Typical procedure: To the flask charged with Pd(dba)$_2$(1-2 mol%),a mixture of 1,4-diphenyl-2-butyn-1-one(1-2 mmol),PPh$_3$(1-2 mol%) and 1 ml toluene was added under nitrogen. The resulting mixture was heated to 100°C. The progress of the reaction was followed by TLC(silica gel,eluted with petroleum ether) without any prior concentration or treatment. Spectral and analytical data of the product are as follows: ^{1}H-nmr 7.8-7.1(m,10H),6.6(s,2H). MS,m/e(%)M$^+$ 220(100),191 (15),115(43),105(30). ^{13}C-nmr 107.2,123.8,127.3,128.7,130.9,153.5. IR,(KBr)3040, 1610,1485,1020,795,760,690,670.Calcd. for $C_{16}H_{12}O$,: C,87.24;H,5.49. Found: C,87.57;H,5.31.

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