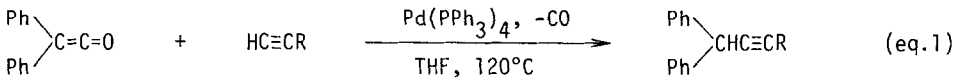
Tetrahedron Letters,Vol.26,No.31,pp 3697-3698,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

PALLADIUM COMPLEX CATALYZED REACTION OF DIPHENYLKETENE WITH TERMINAL ACETYLENES GIVING DISUBSTITUTED ACETYLENES

Take-aki Mitsudo, Mamoru Kadokura, and Yoshihisa Watanabe*
Department of Hydrocarbon Chemistry, Faculty of Engineering,
Kyoto University, Sakyo-ku, Kyoto 606, Japan

Summary: The reaction of diphenylketene with terminal acetylenes catalyzed by tetrakis-(triphenylphosphine)palladium gave disubstituted acetylenes in high yields.

Ketenes are known to undergo a variety of charactaristic reactions and to form complexes with transition metals.[1] A currently important area in organometallic chemistry is the synthesis and the utilization of transition metal carbene complexes.[2] It has been reported that diphenylketene is a good precursor of a carbene ligand.[3] However, no application of this feature to organic synthesis has been reported. Here we report the first example of palladium complex catalyzed organic synthesis using a ketene as a source of a carbene moiety. The reaction of diphenylketene with terminal acetylenes in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0) gave disubstituted acetylenes (eq. 1).



(eq.1)

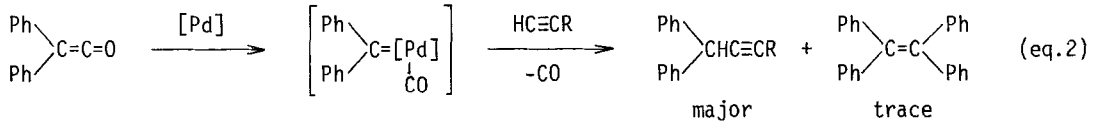
The reaction of diphenylketene with 1-pentyne is typical. A mixture of diphenylketene (1mmol), 1-pentyne (1mmol), and $Pd(PPh_3)_4$ (0.05mmol) in 5 ml THF was placed in a 50 ml stainless autoclave under an argon atmosphere and stirred at 120°C for 5 h. The product was isolated by Kugelrohr distillation and identified as 1,1-diphenyl-2-hexyne by means of ^1H NMR, ^{13}C NMR, FT-IR, and MS.

Representative results are summarized in Table. The reactions of a variety of terminal acetylenes proceeded similarly giving disubstituted acetylenes in high yields. With internal acetylenes, the reaction did not occur under same conditions. When the reaction was carried out under a pressure of carbon monoxide (5 $kg \cdot cm^{-2}$), diphenylketene was not consumed. Several cycloaddition reactions of diphenylketene and acetylenes have been known,[4] however, such reactions were not observed. In all cases, a trace amount of tetraphenylethylene was produced and the product having a carbonyl group was not detected.

Table. Palladium Catalyzed Reaction of Diphenylketene with Terminal Acetylenes.[a)]

run	acetylene	product	yield(%)[b)]
1	$HC{\equiv}CCH_2CH_2CH_3$	$Ph_2CHC{\equiv}CCH_2CH_2CH_3$	89(60)[c)]
2	$HC{\equiv}C(CH_2)_5CH_3$	$Ph_2CHC{\equiv}C(CH_2)_5CH_3$	81
3	$HC{\equiv}CC(CH_3)_3$	$Ph_2CHC{\equiv}CC(CH_3)_3$	74
4	$HC{\equiv}CPh$	$Ph_2CHC{\equiv}CPh$	44
5	$HC{\equiv}CCH_2OCH_3$	$Ph_2CHC{\equiv}CCH_2OCH_3$	32
6	$HC{\equiv}CSi(CH_3)_3$	$Ph_2CHC{\equiv}CSi(CH_3)_3$	78

a) Diphenylketene (1 mmol), acetylene (1 mmol), $Pd(PPh_3)_4$ (0.05 mmol), THF 5 ml, 120°C, 5 h.
b) Determined by glc using an internal standard. c) Isolated yield.



These results show that diphenylketene is catalytically decarbonylated by the palladium complex. Taking into account the decarbonylation reaction of ketenes by transition metal complexes,[3),5)] the reaction may be rationalized by assuming the formation of a diphenylcarbene palladium complex as a reaction intermediate (eq. 2).

In contrast with the reaction of triplet diphenylcarbene, which was generated from diazodiphenylmethane, with terminal acetylenes,[6)] indenes were not obtained in the present reaction. This fact also seems to support the existence of the metal-coordinated carbene species.

In the reaction with ethylphenylketene, 1-phenyl-1-propene was obtained quantitatively either in the presence or absence of acetylenes. This result may be accounted for by a fast 1,2-hydrogen shift of the carbene ligand[7)].

Application of the present reaction and the study on the mechanism are now in progress.

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(Received in Japan 4 April 1985)