Tetrahedron Letters Vol. 21, pp 1527 - 1528
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0040-4039/80/0415-1527$02.00/0

NOVEL SYNTHESIS OF 2,3-DIARYLBUTA-1,3-DIENES FROM 1,4-DIMETHOXYBUTYNE-2

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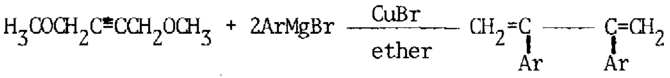
Summary: It was found that 2,3-diarylbuta-1,3-dienes were readily obtained in good to excellent yields through the S_N-2' type substitution of 1,4-dimethoxybutyne-2 with aryl Grignard reagents in the presence of a copper(I) salt.

Recently 2-butyne-1,4-diol and its derivatives have received extensive attention because of their much availability[1)] and interesting reactivities[2)], which have prompted us to explore useful application of these acetylenes to organic synthesis and effective industrial utilization.

In this study, we wish to describe a new synthetic method of 2,3-diarylbuta-1,3-dienes through the S_N-2' type substitution of 1,4-dimethoxybutyne-2 with aryl Grignard reagents in the presence of a copper(I) salt.



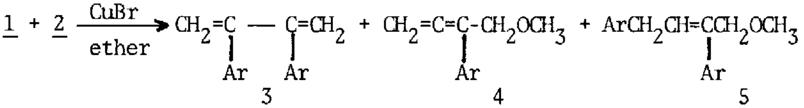
$$H_3COCH_2C{\equiv}CCH_2OCH_3 + 2ArMgBr \xrightarrow[\text{ether}]{\text{CuBr}} CH_2{=}\underset{Ar}{C}-\underset{Ar}{C}{=}CH_2$$

1 2 a-g 3 a-g

It was well established that copper-catalyzed Grignard reagents[3)] or cuprates[4)] react with propargyl alcohol derivatives to give allenes. To our knowledge, however, none of one-pot synthesis of buta-1,3-dienes from acetylenic compounds has been reported.

A typical procedure is described as follow: To a solution of 0.03 mole of p-chlorophenylmagnesium bromide in 50 ml of anhydrous ether containing 0.45 g(0.003 mole) of cuprous bromide was added 1.14 g(0.01 mole) of 1,4-dimethoxybutyne-2(1)[2c)] dissolved in 20 ml of anhydrous ether dropwise at 0 °C with vigorous stirring under nitrogen atmosphere, and was stirred at 0 °C for 2 hr and was gradually warmed to room temperature, and was allowed to stand at room temperature for 1 hr[5)]. After usual work-up of the mixture, 2,3-di(p-chlorophenyl)buta-1,3-dienes(3b) was isolated in a 98 % yield through column chromatograph; mp 64-65 °C, IR(KBr disk, cm^{-1}): $\nu_{C=C}$ 1616, 1603, NMR(CCl_4, ppm): δ=5.40[doublet(J=2.0 Hz), 2H], 5.60[doublet(J=2.0 Hz), 2H], 7.30-7.42[multiplet, 8H], MASS: molecular peak m/e=274.

Under the similar conditions, the nucleophilic substitution of 1 with 2 in the presence of cuprous bromide[6)], in principle, gave three types of products, namely 2,3-diarylbuta-1,3-dienes(3), 3-aryl-4-methoxybuta-1,2-dienes(4), and 1,3-diaryl-4-methoxybut-2-enes(5).



$$1 + 2 \xrightarrow[\text{ether}]{\text{CuBr}} CH_2{=}\underset{Ar}{C}-\underset{Ar}{C}{=}CH_2 + CH_2{=}C{=}\underset{Ar}{C}-CH_2OCH_3 + ArCH_2CH{=}\underset{Ar}{C}CH_2OCH_3$$

3 4 5

All of the products were isolated and identified by spectroscopic methods(IR, NMR, MASS) and/or elemental analyses. The results with each Grignard reagent are summarized in Table I[7].

Table I The reaction of 1 with 2 in the presence of cuprous bromide*

	Ar in ArMgBr	Isolated Yield (%)		
	2	3	4	5
2a	C_6H_5	66	+	19
2b	p-ClC_6H_4	98	+	+
2c	m-ClC_6H_4	100	0	0
2d	p-FC_6H_4	81	8	7
2e	p-$CH_3C_6H_4$	58	+	34
2f	p-$CH_3OC_6H_4$	70	+	7
2g	α-$C_{10}H_7$	16	+	75

* at 0 °C in ether + a trace amount

As shown in Table I, the introduction of an electron-withdrawing group into a phenyl ring of 2 brought about the exclusive formation of 3 in almost quantitative yields while an elecrtron-donating group on a phenyl ring of 2 led to the considerable increase in the yields of 5. Preferential formation of 5g to 3g in the reaction with 2g would be attributed to the steric hindrance of a bulky α-naphthyl group on the attack of 2g to the inner carbon atom of 4g, the initially formed allenic ether.

2,3-Diarylbuta-1,3-dienes(3) are of much use in organic synthesis[8]. For example, Diels-Alder reaction of 3c with dimethyl acetylenedicarboxylate yielded the adduct in a 77.2 % yield.

Finally, from the viewpoint of facile one-pot synthesis of a variety of buta-1,3-dienes from a common inexpensive acetylene derivatives, the present method may possess high potentiality in organic synthesis and industrial chemistry.

References and Notes

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5)3-Phenyl-4-methoxybuta-1,2-diene(4a) was obtained in a 88 % yield as a sole product when 1.50 equivalent moles of phenylmagnesium bromide(2a) was used in this nucleophilic substitution of 1.

6)Substitution of cuprous bromide with cuprous iodide or chloride as a catalyst in the reaction of 1 with 2a also led to the formation of 3a in 64 and 56 % yields, respectively.

7)The reaction of 1 with alkyl Grignard reagents in the presence of a copper(I) salt gave the corresponding 2,3-dialkylbutadienes and/or allenic ethers in low yield(20-48 %). Further study is on progress.

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(Received in Japan 16 January 1980)