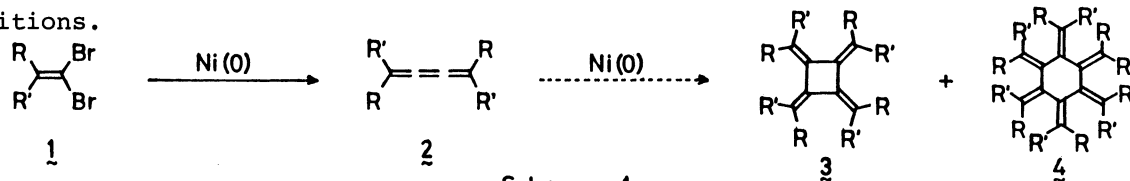


A NEW AND CONVENIENT SYNTHESIS OF ARYL-SUBSTITUTED BUTATRIENES USING
NICKEL-CATALYZED COUPLING OF ARYL-SUBSTITUTED 1,1-DIBROMOETHENES

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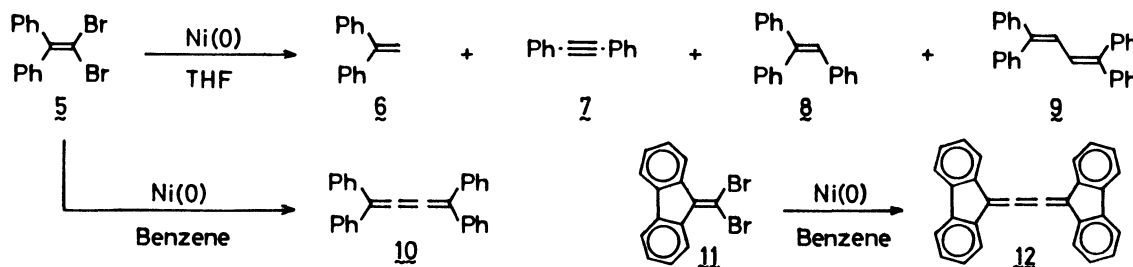
The reactions of aryl-substituted 1,1-dibromoethenes with in situ generated tetrakis(triphenylphosphine)nickel(0) in the presence of tetraethylammonium iodide give aryl-substituted butatrienes.

In the course of studies on radialenes (3 and 4),¹⁾ we have investigated a new and convenient synthetic method of butatrienes (2)²⁾ which seemed to be potential precursors of the radialenes (3 and 4). It was found that the nickel-catalyzed coupling of 1,1-dibromoethenes (1) in benzene affords butatrienes in moderate yields. This method possesses the synthetic utility, because readily available 1,1-dibromoethenes can be converted into aryl-substituted butatrienes under mild reaction conditions.



Scheme 1.

The reaction of 1,1-dibromo-2,2-diphenylethene (5) with $\text{Ni}(\text{PPh}_3)_4$, which was prepared in situ by reduction of $\text{NiBr}_2(\text{PPh}_3)_2$ with zinc,³⁾ in THF at 50 °C gave a mixture of 6 (3%), 7 (1%), 8 (28%), and 9 (29%). Similar treatment of 5 with $\text{Ni}(\text{PPh}_3)_4$ in DMF afforded also a mixture of 6 , 8 , and 9 in low yields. In contrast to the results in THF and DMF, similar reaction of 5 with $\text{Ni}(\text{PPh}_3)_4$ in benzene at 50 °C gave tetraphenylbutatriene (10 , 60%) as the sole product. The reaction of 11 having fluorene ring as a terminal group afforded the corresponding butatriene (12 , 67%) under the same conditions.



Scheme 2.

It is known that iodide ion is effective for the nickel-catalyzed coupling reactions.⁴⁾ In accord with these findings, the coupling of aryl-substituted 1,1-dibromoethenes is accelerated in the presence of Et_4NI . The reaction of 5 with in situ generated $\text{Ni}(\text{PPh}_3)_4$ in the presence of Et_4NI in benzene proceeded at room

temperature to give 10 (60%). Similar reaction of 5 in THF, however, afforded again a mixture of 6 (29%), 8 (21%), and 9 (40%).

The effect of Et_4NI in these reactions is remarkable when 1,1-dibromo-2-arylpropenes (13)⁵⁾ are used as substrates. As summarized in Table 1, the reactions of 13a-d with $\text{Ni}(\text{PPh}_3)_4$ in the presence of Et_4NI gave the corresponding 2,5-diarylhexa-2,3,4-trienes (14a-d), although the reactions of 13a-d in the absence of Et_4NI gave no identifiable products. The new hexatrienes (14a-d) decomposed gradually on exposure to air at room temperature.

A typical procedure is as follows. A mixture of $\text{NiBr}_2(\text{PPh}_3)_2$ (2 mmol), PPh_3 (4 mmol), activated zinc powder (20 mmol), Et_4NI (4 mmol), and 1,1-dibromo-2-(4-cyanophenyl)propene (13c, 2 mmol) in benzene under argon atmosphere was stirred at 50 °C for 17 h. After filtration, the filtrate and washings were chromatographed on silica gel (act. V, eluent: degassed benzene) to give 170 mg (60%) of 2,5-di(4-cyanophenyl)hexa-2,3,4-triene (14c) which is a 1:1 mixture of (E)- and (Z)-isomers.

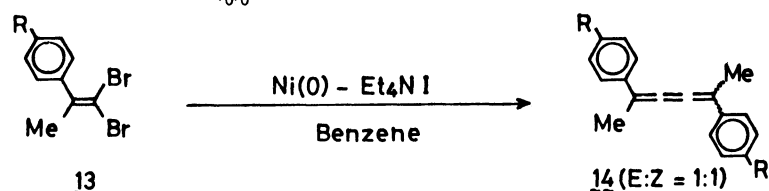
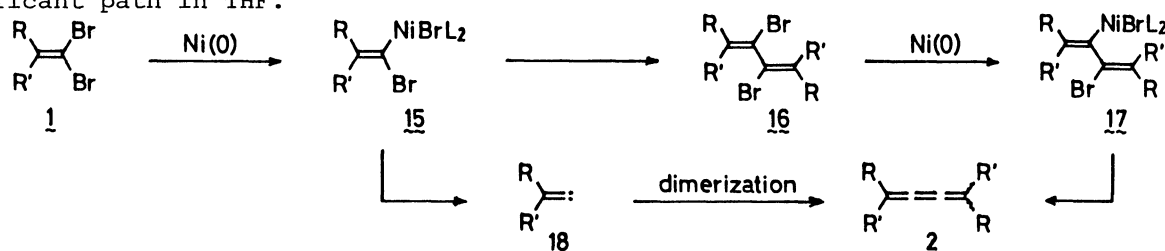


Table 1. Coupling of 1,1-dibromo-2-arylpropenes (13) with $\text{Ni}(\text{PPh}_3)_4$

1,1-Dibromopropene	Conditions		Product	Yield %	°C
	Temp /°C	Time/h			
<u>13a</u> : R=H	50	24	<u>14a</u> : R=H	29	115-122 ^{a)} , 2)
<u>13b</u> : R=OMe	rt	38	<u>14b</u> : R=OMe	41	184-187 ^{b)}
<u>13c</u> : R=CN	50	17	<u>14c</u> : R=CN	60	233-239 ^{a)}
<u>13d</u> : R=CO ₂ Me	50	19	<u>14d</u> : R=CO ₂ Me	44	201-202 ^{b)}

a) Yellow prisms. b) Pale yellow prisms.

A possible mechanism involves the coupling of the carbenoid complex (15), followed by the reduction of 16 via 17 to give 2 (Scheme 3). However, the reaction may proceed by a different mechanism, which involves the methylene carbene (18) via 15. Although the formation of diphenylacetylene (7) suggests the formation of the carbene (18), the yield is very low and the hydrogenative debromination of 1 is significant path in THF.



Scheme 3.

References

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- 5) 1,1-Dibromo-2-arylpropenes (13) can be easily prepared by the Wittig reaction (CBr_4 , PPh_3 , benzene, reflux) of acetophenone derivatives.

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