

Palladium-catalysed 1,4-Arylation/Alkylation of Buta-1,3-diene

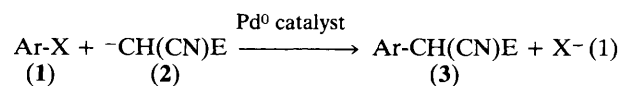
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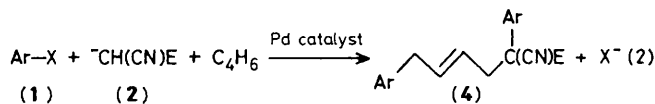
Palladium-catalysed reactions of butadiene with halogeno-arenes and stabilized anions give arylation/alkylation products of the diene in which two carbon-carbon bonds are formed from three components in one catalytic cycle.

Many reports have appeared on organic syntheses using palladium-catalysed reactions in which a π -allylpalladium species acts as a key intermediate.¹ Recently we have shown that stabilized anions such as $^{-}\text{CH}(\text{CN})_2$ and $^{-}\text{CH}(\text{CN})\text{CO}_2\text{R}$ react smoothly with some halogeno-arenes in the presence of a palladium catalyst to give the coupled products (3) (equation 1).² The mechanism of this reaction may reasonably be explained by postulating the initial formation of a Pd-Ar intermediate, which may be able to undergo insertion of dienes to afford π -allylpalladium species. We now report that a palladium-phosphine complex catalyses the 1,4-arylation/alkylation of buta-1,3-diene with halogeno-arenes and malonitrile or cyanoacetates in which two carbon-carbon bonds

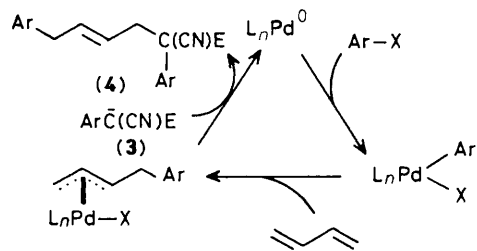
are formed from three components in one catalytic cycle (equation 2). Catalytic arylation/alkylation reactions of 1,3-dienes have not been reported previously.³



Thus, in the presence of dichlorobis(triphenylphosphine)-palladium catalyst (0.3 mmol) a mixture of iodobenzene (30 mmol) and malonitrile anion (2: E = CN), generated *in situ* from malonitrile (10 mmol) and sodium hydride, was allowed to react with a large excess of butadiene (*ca.* 120



- a; E = CN, Ar = Ph
 b; E = CN, Ar = *p*-MeC₆H₄
 c; E = CN, Ar = *p*-ClC₆H₄
 d; E = CO₂Et, Ar = Ph
 e; E = CO₂Me, Ar = Ph
 f; E = CO₂Me, Ar = *p*-MeC₆H₄



Scheme 1

mmol) in tetrahydrofuran at 70 °C for 67 h. After quenching with dilute hydrochloric acid, the product was extracted with diethyl ether, and then purified by column chromatography on silica gel using hexane and chloroform as eluents. A 1,4-arylation/cyanoalkylation product of butadiene, *trans*-5,5-dicyano-1,5-diphenylpent-2-ene (**4a**) was obtained in 62% yield (based on malononitrile employed) which was identified by spectroscopic analyses.† *p*-Iodotoluene similarly reacted to give the corresponding product, but *p*-chloriodobenzene required higher temperature and longer reaction time. The reactivity of the halogeno-arenes was in the same order as observed previously in the dicyanomethylation of halogeno-arenes, I > Br ≫ Cl. Cyanoacetates (**2**, E = CO₂R) similarly reacted to give (**4d-f**) in about 40% yield (Table 1).

† C₆H₅CH₂CH=CHCH₂C(C₆H₅)(CN)₂ (**4a**): *m/z* 272 (*M*⁺); ¹H n.m.r. (CDCl₃, 360 MHz): δ 7.1–7.6 (10H, m), 5.88 (1H, dt, *J* 15, 7 Hz), 5.51 (1H, dt, *J* 15, 7 Hz), 3.41 (2H, d, *J* 7 Hz), and 2.92 (2H, d, *J* 7 Hz).

Table 1. 1,4-Arylation/alkylation of butadiene.

Run	Ar-X	CH ₂ (CN)E E	Conditions		Product	Yield ^a (%)
			Temp./°C	Time/h		
1	Ph-I	CN	70	67	(4a)	62
2	Ph-Br	CN	70	48	(4a)	10 ^b
3	<i>p</i> -MeC ₆ H ₄ -I	CN	70	48	(4b)	46
4	<i>p</i> -ClC ₆ H ₄ -I	CN	80	120	(4c)	36
5	Ph-I	CO ₂ Et	70	72	(4d)	40
6	Ph-I	CO ₂ Me	70	45	(4e)	42
7	<i>p</i> -MeC ₆ H ₄ -I	CO ₂ Me	70	45	(4f)	47

^a Isolated yield based on CH₂(CN)E. ^b Catalyst, (Ph₂PCH₂CH₂PPh₂)-PdCl₂; solvent, dimethoxyethane; the yield was determined by g.l.c.

Under the same conditions the use of phenylmalononitrile instead of malononitrile afforded (**4a**) in 70% yield, indicating that the reaction step incorporating the diene proceeds after the dicyanoalkylation of halogeno-arenes, *i.e.*, initial formation of arylmalononitrile (**3**) from the reaction between malononitrile and halogeno-arenes (equation 1), and then attack of the anion on the π-allylpalladium intermediate yields the products (**4**).

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