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HECK REACTION OF 1-ARYLTRIAZENES

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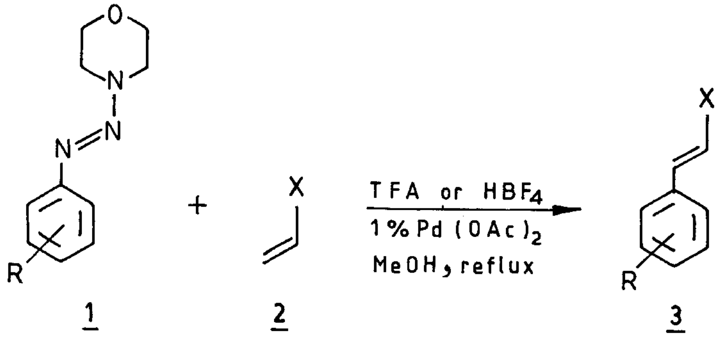
ABSTRACT : 1-Aryl triazenes upon treatment with TFA or HBF_4 undergo Heck reaction via in-situ generated aryldiazonium salts.

Palladium catalyzed arylation of olefins (Heck reaction)[1] is a prominent landmark in the field of transition metal mediated organic synthesis.[2] Methodological refinement of the Heck reaction still continues, focussing on ligand effects,[3] additives[4] and reactivity of heterosubstituted olefins.[5] However, little attention has been paid to the aromatic components of Heck reaction which, for all practical purposes, remain confined to the halides and triflates. In addressing this limitation, we[6] and others[7] have studied the aryldiazonium tetrafluoroborates as non-conventional Heck-substrates and have shown that they hold many synthetic and operational advantages over the aryl halides and triflates. However, diazonium tetrafluoroborates are prone to decomposition on storage, in view of which we decided to investigate the Heck reaction of 1-aryltriazenes[8] as aryldiazonium surrogates.

1-Aryltriazenes are readily available, shelf-stable diazonium surrogates which are easily purified and are soluble in most organic solvents. Although known for a century now,[8] their synthetic utility remained virtually unexplored until recently, when they found use in halodeamination reactions[9] and as anilino-protecting groups.[10] Apart from these, occasional uses in the Gomberg-Bachmann reaction[11] concludes their synthetic role. Nothing special was known about transition metal applications on these triazenes[12] which, in fact, provided additional impetus to study their reactivity in the Heck reaction.

In the event, the triazene **1a** failed to undergo Heck reaction with ethyl acrylate under the standard conditions [$Pd(OAc)_2/PPh_3/Et_3N$] either in CH_3CN or DMF. However, addition of two equivalents of TFA or 42% HBF_4 and conducting the reaction in refluxing methanol (or ethanol) with 1% $Pd(OAc)_2$ was successful **(Scheme 1)**. Although TFA and HBF_4 are equally effective (cf. entries 3 & 4, **Table 1**), mineral acids including DOWEX-50W-X8 resin are poor mediators for this reaction. Alcohols were found to be the preferred solvents (over benzene, CH_3CN or DMF). Even alcoholic solvents can be omitted in favour of water when 42% HBF_4 is used, a case which truly reflects an aqueous Pd-catalyzed process.[13]



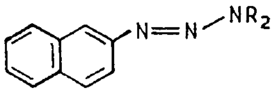
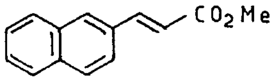
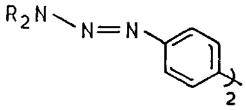
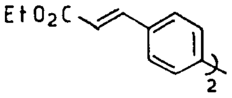
a; R = H b; R = p – Cl c; R = m – Cl d; R = p – OMe e; R = o – OMe

SCHEME - 1

Synthetic efficacy of this reaction was studied with a series of triazenes[14] (**Table 1**). All triazenes irrespective of their substitution pattern reacted efficiently within a short reaction time (30-45 mins) with the exception of the nitro-substituted triazenes, which have so far failed to participate under a variety of conditions. The benzidine derived bis-triazene (entry 9, **Table 1**) underwent bis-coupling, thus promising further scope in the synthesis of various symmetrical (possibly unsymmetrical) para-phenylene derivatives. Regarding olefinic partners, although acrylates were routinely used, unactivated olefins such as cyclopentene (entry 7, **Table 1**) can be equally effective.

In summary, 1-aryltriazenes undergo Heck reaction in the presence of TFA or HBF_4 via an operationally simple procedure which bypasses the hazards usually associated

Table 1 : Heck Reaction of 1-Aryltriazenes (Scheme 1).

	Triazene	Olefin[a]/ Acid	Product *	Yield (%)
1)	1a	EA/TFA	3a	76
2)	1b	EA/TFA	3b	69
3)	1c	EA/TFA	3c	85
4)	1c	EA/HBF_4	3c	79
5)	1d	EA/TFA	3d	80
6)	1e	EA/HBF_4	3e	75
7)	1b	CP/TFA	p-chlorophenyl-cyclopentene	72[b,c]
8)		MA/TFA		70[b]
9)		EA[d]/TFA[e]		66

[a] EA = Ethyl acrylate, MA = Methyl acrylate, CP = Cyclopentene ; [b] at 25°C; [c] 5:1 mixture of 3- and 1-arylcyclopentene; [d] 2.5 equivalents; [e] 4 equivalents.

$-NR_2$ = Morpholinyl

* All compounds gave satisfactory spectral(IR, NMR) data consistent with the assigned structures.

with isolated diazonium salts. Further exploitation of this reaction is currently under study.

Typical experimental procedure : TFA (0.52g, 4.5 mmol) was added dropwise to an ice-cold solution of **1d** (0.5 g, 2.2 mmol) in methanol (5 ml). Ethyl acrylate (0.28 g, 2.8 mmol) and $Pd(OAc)_2$ (5 mg) were then added and the mixture was heated to reflux for 45 mins. Standard work-up with ether followed by silica-gel chromatography gave **3d**(0.37 g, 80%), IR (neat) : 1700, 1630, 1600 cm^{-1}; ^{1}HNMR ($CDCl_3$) : 1.33 (3H, t, J=7 Hz), 3.84 (3H, s), 4.26 (2H, q, J=7 Hz), 6.25 (1H, d, J=16 Hz), 6.90 (2H, d, J=8 Hz), 7.50 (2H, d, J=8 Hz), 7.65 (1H, d, J=16 Hz).

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