

Reaction of Silyl Enol Ethers with Arenediazonium Salts. Part 1. α -Arylation of Ketones

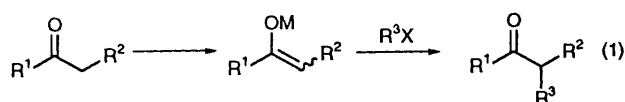
Toshiyasu Sakakura,^a Masayasu Hara^a and Masato Tanaka^{*,a,b}

^a National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan

^b Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

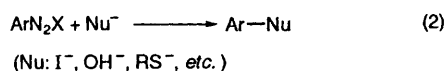
α -Arylation of ketones is accomplished by the use of arenediazonium salts as aryl-cation equivalents. The reaction of silyl enol ethers with arenediazonium tetrafluoroborates proceeds in the presence of palladium(0) catalysts and tetraphenylborate anion to give α -aryl ketones in moderate yields. Alternatively, silyl enol ethers smoothly react with arenediazonium tetrafluoroborates in pyridine even without palladium catalysts and tetraphenylborate anion, affording arylated ketones in good yields. A mechanism involving addition of an aryl radical to a silyl enol ether is proposed for the latter process.

The reaction of metal enolates with alkyl halides is an established and markedly useful synthetic method to form carbon-carbon bonds [eqn. (1)].¹ However, this procedure



M: alkali metals, Si, etc.

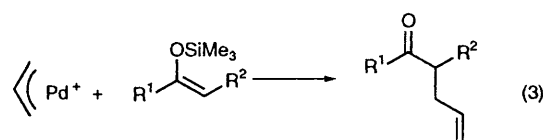
cannot be applied to the introduction of an aryl group because aryl halides are generally resistant to nucleophilic substitution. In order to circumvent the problem, several arylation reactions have been devised with the assistance of transition-metal complexes,² although each of them still has drawbacks, such as unsatisfactory yields or a requirement for special reagents. Another approach to the introduction of an aryl group to ketones through the reaction of metal enolates is the development of more efficient aryl-cation equivalents than aryl halides. Several compounds, such as arylidonium salts, and aryllead and arylbismuth reagents, have been proposed for this purpose.³ In this context, arenediazonium salts also appear to deserve attention because they are easily available and formally behave as aryl cations toward some nucleophiles [eqn. (2)],



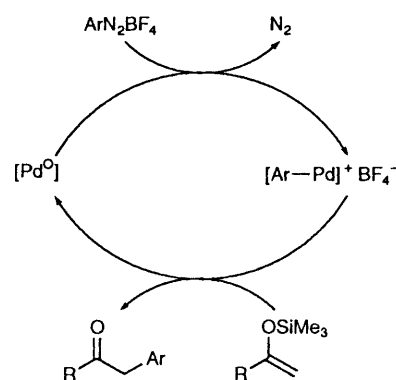
although a mechanism involving radicals rather than cations is operative in many cases.⁴ So far, the reactions of diazonium salts with various carbon nucleophiles, such as Grignard reagents,⁵ lithium enolates,⁶ enamines,⁷ alkyl enol ethers⁸ and active methylene compounds,⁹ have all resulted in the formation of azo or hydrazono compounds without releasing dinitrogen. In striking contrast, we have found that the reaction with silyl enol ethers of ketones in pyridine leads to α -aryl ketones instead of azo or hydrazono compounds.¹⁰ Here we report the details of this reaction.

Results and Discussion

Palladium-catalysed Reaction.—Tsuji reported an allylation of ketones *via* the reaction of silyl enol ethers using cationic π -allylpalladium complexes as electrophiles [eqn. (3)].¹¹ On the other hand, Kikukawa described the formation of cationic arylpalladium complexes by the reaction of Pd⁰ and ArN₂BF₄.¹² Hence, we first expected the formation of α -aryl



ketones through the reaction of silyl enol ethers with diazonium salts in the presence of palladium(0) complexes as depicted in Scheme 1. The reactions between 1-phenyl-1-(trimethylsiloxy)-



Scheme 1

ethene and benzenediazonium salts are summarized in Table 1. Although PhN₂BF₄ did not yield 1,2-diphenylethanone in the presence of Pd(PPh₃)₄, the corresponding tetraphenylborate, PhN₂BPh₄, gave the desired product in 14% yield (entries 1 and 2). Possible reasons for the superiority of PhN₂BPh₄ to PhN₂BF₄ are the higher tendency to release dinitrogen[†] and the higher solubility in a non-polar organic solvent (toluene). Since dry PhN₂BPh₄ is dangerous to handle because of its tendency to explode,[‡] we next tried to generate PhN₂BPh₄ *in situ* from PhN₂BF₄ and NaBPh₄. The reaction proceeded as expected to give 1,2-diphenylethanone in 22% yield (entry 3). On the other hand, the ketone was not formed at all when the reaction was run in the absence of the palladium catalyst or when iodobenzene was used in place of PhN₂BF₄ (entries 4 and 5). This is consistent with the hypothesis that the key species is a cationic palladium complex. Another typical palladium(0)

[†] PhN₂BPh₄ decomposes at a lower temperature (83–85 °C) than does PhN₂BF₄ (114–116 °C); see ref. 13.

[‡] Two of several attempts to dry PhN₂BPh₄ resulted in an explosion.

Table 1 Synthesis of α -phenyl ketone from silyl enol ether and benzenediazonium salts in the presence of catalysts^a

Entry	Catalyst	Diazonium salt	Additives ^b	Yield of PhCOCH ₂ Ph (%)
1	Pd(PPh ₃) ₄	PhN ₂ BF ₄	no	0
2	Pd(PPh ₃) ₄	PhN ₂ BPh ₄	no	14 ^c
3	Pd(PPh ₃) ₄	PhN ₂ BF ₄	yes	22
4	None	PhN ₂ BF ₄	yes	0
5	Pd(PPh ₃) ₄	<i>d</i>	yes	0
6	Pd(dba) ₂	PhN ₂ BF ₄	yes	20
7	PhPdI(PPh ₃) ₂	PhN ₂ BF ₄	yes	< 1 ^e
8	CuCl ₂	PhN ₂ BF ₄	yes	0

^a Ph(Me₃SiO)C=CH₂ (2.0 mmol), diazonium salt (2.6 mmol), catalyst (0.02 mmol), toluene (6 cm³), 0 °C, 2 h. Yields are based on silyl enol ether and were determined by GLC using an internal standard.

^b NaBPh₄ (2.6 mmol), 15-crown-5 (2.6 mmol). ^c Ph(Me₃SiO)C=CH₂ (1.2 mmol), diazonium salt (1.0 mmol), catalyst (0.013 mmol), benzene (3 cm³), room temperature, 0.5 h. ^d Iodobenzene was used in place of benzenediazonium salt. ^e The yield was 35% after 59 h at room temperature.

Table 2 Solvent effect on palladium-catalysed synthesis of α -phenyl ketones^a

Solvent	Yield (%)
Pyridine	74
THF ^b	36
DMF ^c	25
Toluene	22
MeCN	14

^a Ph(Me₃SiO)C=CH₂ (2.0 mmol), PhN₂BF₄ (2.6 mmol), Pd(PPh₃)₄ (0.02 mmol), NaBPh₄ (2.6 mmol), 15-crown-5 (2.6 mmol), solvent (6 cm³), 0 °C, 2 h. Yields are based on silyl enol ether. ^b Tetrahydrofuran. ^c *N,N*-Dimethylformamide.

Table 3 Solvent effect on the reaction of 1-phenyl-1-(trimethylsiloxy)ethene with benzenediazonium tetrafluoroborate^a

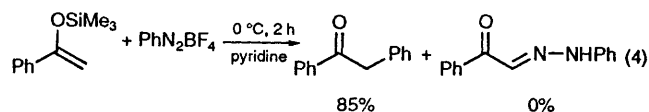
Solvent	Yield of PhCOCH ₂ Ph (%)
Pyridine	85
HMPA	11
DMSO	6
MeCN	2
DMF	< 1
Dichloromethane	0
Toluene	0
THF	0
2,4,6-Trimethylpyridine	0

^a Ph(Me₃SiO)C=CH₂ (2.0 mmol), PhN₂BF₄ (2.6 mmol), solvent (6 cm³), 0 °C, 2 h.

complex, Pd(dba)₂ (dba = dibenzylideneacetone), also catalysed the reaction as well as did Pd(PPh₃)₄, while a Pd^{II} complex, PhPdI(PPh₃)₂, was much less effective (entries 6 and 7). Copper(II) chloride, which is known to be capable of catalysing the Meerwein arylation,¹⁴ was totally inactive under the same conditions (entry 8). This may be because of its low solubility in toluene.

Solvent Effects.—Since ionic reactions are much affected by reaction solvents in general, solvent effects were investigated for the reaction with PhN₂BF₄ in the presence of Pd(PPh₃)₄ and NaBPh₄ (Table 2). Although the reaction proceeded in a variety of solvents in moderate yield, the highest yield was achieved in

pyridine. Moreover, to our surprise, the reaction in pyridine was found to afford the phenylated ketone effectively even without Pd(PPh₃)₄ and NaBPh₄ [eqn. (4)]. A possible by-product formed without release of dinitrogen, 1-phenyl-2-(phenylhydrazono)ethanone, was not detected at all.



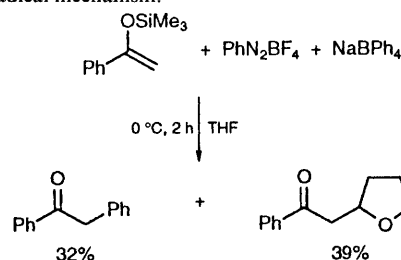
Since it was shown that palladium catalysts were not necessary in pyridine, solvent effects were re-examined in the absence of both palladium catalysts and NaBPh₄ (Table 3). Besides pyridine, the reactions in hexamethylphosphoric triamide (HMPA) and dimethyl sulfoxide (DMSO) yielded 1,2-diphenylethanone albeit in low yields. The other solvents were almost ineffective under the present conditions. These results are not explicable in terms of common solvent parameters such as dielectric constant or dipole moment. The role of pyridine is discussed later.

Reaction in Pyridine (Non-catalysed Reaction).—The applicability of the new α -arylation in pyridine was investigated using various diazonium salts and silyl enol ethers (Table 4). The diazonium salts having an electron-withdrawing (Cl⁻) or an electron-releasing (MeO⁻) group at the *para*-position gave almost the same yields as did the unsubstituted salt (PhN₂BF₄) (entries 1–3). On the other hand, the use of an *ortho*-substituted diazonium salt resulted in a lower yield, presumably because of steric hindrance (entry 4).

The reaction with benzenediazonium chloride gave only a trace amount of the desired product (entry 5). The lower yield may be partly ascribed to the low solubility and tight ion-pairing of the diazonium salt. The higher affinity of the BF₄ anion toward the silicon atom as compared with the chloride anion would also be important for the smooth progress of the reaction, especially for the cleavage of the silicon–oxygen bond. As a matter of fact, ready cleavage of silyl ethers by tetrafluoroborate anion has been reported.¹⁵

Substituents on silyl enol ethers exhibited quite a large influence on the yields of α -aryl ketones. When R¹ was an aryl or a heteroaryl group, the desired ketones were obtained in relatively good yields (entries 1, 6 and 7). However, when R¹ was alkyl (entries 8–10), reactions were sluggish; the yield was ~30% even after a prolonged reaction time in the presence of excess of diazonium salt (entry 9). The conjugated silyl enol ether (R¹ = vinyl) did not form an α -aryl ketone, probably because of polymerization (entry 11). The increase in steric hindrance (R² = Me rather than H) considerably reduced the reaction rate (entry 12). However, the use of a large excess of

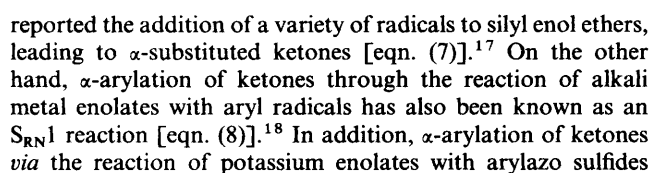
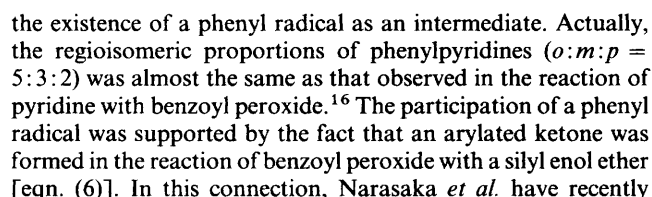
§ It is worth noting here that upon addition of NaBPh₄ (without a palladium catalyst), the reaction in THF afforded 1,2-diphenylethanone in moderate yield with concomitant formation of 1-phenyl-2-(tetrahydrofuran-2-yl)ethanone. This indicates the possibility of a new α -tetrahydrofuran-2-yl)ethanone. The reaction presumably proceeds through a radical mechanism.



Entry	R ¹ (Me ₃ SiO)C=CHR ²		Diazonium salt	Time (t/h)	Yield ^b (%)
	R ¹	R ²			
1	Ph	H	PhN ₂ BF ₄	2	72 (85)
2	Ph	H	<i>p</i> -ClC ₆ H ₄ N ₂ BF ₄	3.5	73
3	Ph	H	<i>p</i> -MeOC ₆ H ₄ N ₂ BF ₄	6	65
4	Ph	H	<i>o</i> -MeC ₆ H ₄ N ₂ BF ₄	2	49
5	Ph	H	PhN ₂ Cl	2	(2)
6	2-Thienyl	H	PhN ₂ BF ₄	2	58
7	2-Furyl	H	PhN ₂ BF ₄	2	47
8	n-C ₇ H ₁₅	H	PhN ₂ BF ₄	2	20
9 ^c	n-C ₇ H ₁₅	H	PhN ₂ BF ₄	5	(31)
10	Bu ^t	H	PhN ₂ BF ₄	2	21
11	Vinyl	H	PhN ₂ BF ₄	4	(0)
12	Ph	Me	PhN ₂ BF ₄	4.5	42
13 ^c	Ph	Me	PhN ₂ BF ₄	7	(72)
14	PhCH ₂	Ph	PhN ₂ BF ₄	5	(4)
15	PhC(OAc)=CHMe		PhN ₂ BF ₄	2	(0)

diazonium salt mitigated this drawback (entry 13). When R^2 was phenyl, the reaction was further hampered (entry 14). The enol acetate was much less reactive than the corresponding silyl enol ether and was recovered unchanged after the reaction (entry 15). The low reactivity may be associated with the difficulty of cleaving the oxygen-carbon bond under the reaction conditions.

(adduct of diazonium salts and thiols) has very recently been reported [eqn. (9)].¹⁹ The mechanism for such reactions is probably closely related to that for the present reaction.



If it is assumed that the present arylation proceeds *via* a radical, the unique solvent effect of pyridine (see Table 3) is understandable in terms of acceleration of radical formation from diazonium salts. It is known that aryl radicals are effectively formed from diazonium salts in pyridine *via* azo-type adducts [eqns. (10) and (11)].^{4,16} Another possible advantage of the pyridine solvent is its basic nature which prevents the silyl enol ethers from being hydrolysed. However, the role of pyridine cannot be explained as a simple proton acceptor, because 2,4,6-trimethylpyridine (collidine) failed to promote the reaction despite its basicity (pK_a) being similar to that of pyridine. The lack of the reaction in collidine is presumably due to the large steric hindrance around the nitrogen atom and the low solubility of diazonium salts. The second best solvent in Table 3 was HMPA. This is also consistent with a radical mechanism because it is known that solvents with large Koppel and Paju's parameters (*e.g.*, pyridine, HMPA and DMSO) are effective for homolytic decomposition of diazonium salts.^{4,20}

The radical thus formed may add to a silyl enol ether to give an arylated ketone [eqn. (12)], although it is unclear as to whether or not the cleavage of the oxygen-silicon bond occurs after the radical addition. The role of pyridine as a reagent

isolation step was not required, the reaction mixture was analysed by GC after addition of octadecane (200 mg, internal standard).

Analysis of Phenylpyridines.—Benzenediazonium tetrafluoroborate (2.2 mmol) was added to a pyridine solution (3 cm³) of 2-(trimethylsiloxy)non-1-ene (1.0 mmol). The mixture was stirred for 3 h at 0 °C, and benzene (30 cm³) was added. The solution was washed with water (30 cm³ × 2) to remove diazonium salts and was evaporated under reduced pressure. From an ethereal solution (30 cm³) of the resulting oil, phenylpyridines were extracted with 1.5 mol dm⁻³ hydrochloric acid (10 cm³ × 2). After the addition of NaOH (1.5 g), phenylpyridines were re-extracted with benzene (10 cm³ × 2). The benzene solution was dried over MgSO₄ and concentrated under reduced pressure. The resulting oil was purified by TLC [hexane–diethyl ether (1:1)] to give phenylpyridines. The *ortho*, *meta* and *para* isomers were identified by comparison of NMR and IR spectra with authentic data.³¹

Identification of the Products.—1,1,3-Triphenylpropan-2-one³² and 1-phenyl-2-(phenylhydrazono)ethanone³³ were analysed by the comparison of GLC retention times and mass fragmentation patterns with those of authentic samples synthesized according to the literature methods.

Physical, spectral and analytical properties of isolated α -aryl ketones are summarized below.

1,2-Diphenylethanone. B.p. 80 °C (0.3 mmHg, Kugelrohr); m.p. 55–56 °C (from hexane) (lit.,^{2a} 55–56 °C); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1680 (CO); δ_{H} 4.27 (2 H, s, CH₂) and 7.1–8.2 (10 H, m, Ph).

1-Phenylnonan-2-one.³⁴ $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 1718 (CO); δ_{H} 0.86 (3 H, t, J 6, Me), 1.1–1.8 (10 H, m, [CH₂]₅), 2.43 (2 H, t, J 6, CH₂CO), 3.67 (2 H, s, CH₂Ph) and 7.1–7.7 (5 H, m, Ph); m/z 218 (M⁺, 0.3%), 127 (C₇H₁₅⁺, 42) and 91 (PhCH₂⁺, 19).

2-Phenyl-1-(2-thienyl)ethanone.³⁵ B.p. 95 °C (0.3 mmHg, Kugelrohr); $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 1657 (CO); δ_{H} 4.18 (2 H, s, CH₂), 7.11 (1 H, m, C₄H₃S), 7.30 (5 H, s, Ph), 7.61 (1 H, dd, J 5 and 1, C₄H₃S) and 7.77 (1 H, dd, J 4 and 1, C₄H₃S); m/z 202 (M⁺, 4%), 111 (C₄H₃S–CO⁺, 100), 91 (PhCH₂⁺, 7) and 83 (C₄H₃S⁺, 6).

1-(2-Furyl)-2-phenylethanone.³⁶ B.p. 110 °C (18 mmHg, Kugelrohr); $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 1676 (CO); δ_{H} 4.10 (2 H, s, CH₂), 6.53 (1 H, dd, J 4 and 1.5, C₄H₃O), 7.22 (1 H, d, J 4, C₄H₃O), 7.30 (5 H, s, Ph) and 7.59 (1 H, d, J 1.5, C₄H₃O); m/z 186 (M⁺, 15%), 95 (C₄H₃O–CO⁺, 100), 91 (PhCH₂⁺, 14) and 67 (C₄H₃O⁺, 3).

1,2-Diphenylpropan-1-one. B.p. 125 °C (0.2 mmHg, Kugelrohr); m.p. 47–48 °C (from hexane) (lit.,³⁷ 53 °C); $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 1683 (CO); δ_{H} 1.52 (3 H, d, J 6, Me), 4.70 (1 H, q, J 6, CH) and 7.0–8.1 (10 H, m, Ph).

2-(4-Chlorophenyl)-1-phenylethanone. M.p. 137–138 °C (from hexane) (lit.,³⁸ 138 °C); $\nu_{\max}(\text{Nujol})/\text{cm}^{-1}$ 1685 (CO); δ_{H} 4.25 (2 H, s, CH₂) and 7.1–8.2 (9 H, m, ClC₆H₄ and Ph).

2-(4-Methoxyphenyl)-1-phenylethanone. M.p. 92–93 °C (from hexane) (lit.,³⁹ 94.4–95 °C); $\nu_{\max}(\text{Nujol})/\text{cm}^{-1}$ 1691 (CO); δ_{H} 3.75 (3 H, s, OMe), 4.20 (2 H, s, CH₂) and 6.7–8.2 (9 H, m, MeOC₆H₄ and Ph).

3,3-Dimethyl-1-phenylbutan-2-one.⁴⁰ $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 1718 (CO); δ_{H} 1.20 (9 H, s, Bu^t), 3.79 (2 H, s, CH₂) and 7.1–7.5 (5 H, m, Ph).

2-(2-Methylphenyl)-1-phenylethanone.⁴¹ M.p. 66.5–67 °C (lit.,⁴¹ 67 °C); $\nu_{\max}(\text{Nujol})/\text{cm}^{-1}$ 1689 (CO); δ_{H} 2.26 (3 H, s, Me), 4.30 (2 H, s, CH₂) and 7.1–8.2 (9 H, m, MeC₆H₄ and Ph).

1-Phenyl-2-(tetrahydrofuran-2-yl)ethanone.⁴² B.p. 100 °C (0.8 mmHg, Kugelrohr); $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 1685 (CO); δ_{H} 1.2–2.4 (4 H, m, CHCH₂CH₂CH₂O), 3.05 (1 H, dd, J_{gem} 16, J 7, PhCH₂CO), 3.39 (1 H, dd, J_{gem} 16, J 7, PhCH₂CO), 3.6–4.1

(2 H, m, CH₂O), 4.41 (1 H, quintet, J 7, CHO), 7.1–7.7 (3 H, m, Ph) and 7.9–8.1 (2 H, m, Ph); m/z 190 (M⁺, 15%), 162 (10), 147 (15), 120 (11), 105 (PhCO⁺, 100), 77 (Ph⁺, 59) and 71 (C₄H₇O⁺, 33).

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