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Synthesis of 2-Phenyl-1-(2-thienyl)- and 2-Aryl-1-(2-furyl)ethanones by the $S_{RN}1$ Mechanism. Relative Reactivities of Enolate Ions of Ketones

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The synthesis of α-aryl ketones has received much attention over the past two decades. Several arylation reactions have been devised with the assistance of transition metal catalysis, although each of them requires special reagents or gives unsatisfactory yields.[1] Beside aryl halides other reagents such as aryliodonium salts, aryllead, and arylbismuth reagent have been proposed for this purpose.[2] Also the reaction of silyl enol ether with arenediazonium salts in the presence of Pd(0) and tetraphenylborate anion gave α-aryl ketones.[3] Recently it has been reported that the arylation of ketone enolate ions with aryl bromides gave good yields of α-aryl ketones by a palladium-catalyzed coupling in the presence of Tol-BINAP or BINAP as a ligand.[4]

The $S_{RN}1$ mechanism is also an important route to achieve the synthesis of this type of compounds.[5] Good percentages of substitution are usually obtained with enolate ions of aliphatic ketones, mainly from acetone and pinacolone. These anions react with phenyl halides under photostimulation in liquid ammonia (−33 °C) or in DMSO at room temperature. In DMSO substitution can be achieved without photostimulation with substrates that are very good electron acceptors.[6]

Aromatic ketones behave somewhat different. For example, the enolate ion of acetophenone reacts with halobenzenes or halonaphthalenes in liquid ammonia under irradiation only under drastic conditions.[7] Heteroarylation of the anion can be achieved in this solvent either under irradiation or even in the dark with highly electrophilic substrates.[8,9] On the other hand, phenylation as well as heteroarylation of the anion is possible in DMSO under photostimulation.[10,11] A similar behavior has been observed with the enolate ions of 2-acetylnaphthalene[12] and other aromatic ketones such as 2-acetylfuran[8b,11] and 2-acetylthiophene. The latter carbanion has been reported to afford the substitution product only by reaction with phenyl azosulfides,[13] which are very good electron acceptors that react spontaneously or under laboratory light with different nucleophiles. The difference in reactivity between enolate anions of aromatic and aliphatic ketones toward phenyl halides in liquid ammonia has been attributed to the lower efficiency of the former in the photoinitiation step of the proposed mechanism (Scheme 1).[5] This situation can be overcome by employing other methods of initiation like solvated electrons from alkali metals, electrochemically, favoring the initial electron transfer at higher temperatures (DMSO, rt), or performing the reaction in the presence of added nucleophiles that are less reactive than the enolate anion of the aromatic ketone toward phenyl radicals (eq 3) but are better electron donors to initiate the chain (eq 1) (*entrainment reaction*).

Scheme 1

Initiation $$ArX + Nu^{-} \xrightarrow{h\upsilon} ArX^{-\bullet} + Nu^{\bullet} \quad 1.$$

Propagation $$ArX^{-\bullet} \longrightarrow Ar^{\bullet} + X^{-} \quad 2.$$

$$Ar^{\bullet} + Nu^{-} \longrightarrow ArNu^{-\bullet} \quad 3.$$

$$ArNu^{-\bullet} + ArX \longrightarrow ArNu + ArX^{-\bullet} \quad 4.$$

On this basis, we studied the reaction of the enolate ions of 2-acetylthiophene and 2-acetylfuran with different aryl halides to determine their reactivity, the initiation conditions that favor the substitution reaction, and the possibility of increasing their synthetic scope. Photoinitiation and initiation by ferrous ion were carried out. Ferrous ion (usually $FeSO_4$ in liquid ammonia and $FeCl_2$ or $FeBr_2$ in DMSO)[14] can provide an alternative and efficient method to initiate the reaction of carbanions with iodobenzene and other aryl halides. The relative reactivities of the enolate ions of 2-acetylthiophene and 2-acetylfuran with respect to the enolate ions of acetophenone and 2-acetylnaphthalene were determined.

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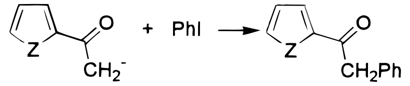
Table 1. Reaction of Aryl Halides with the Carbanions from 2-Acetylthiophene (1) and 2-Acetylfuran (2) in DMSO[a]

expt	Nu^-, $M \times 10^3$	ArX, $M \times 10^3$	*t*-BuOK, $M \times 10^3$	% X^- [b]	substit prod (%)[c]
1[d]	**1**, 15.4	**3**, 5.1	20.6	3	
2	**1**, 123.3	**3**, 44.8	133	6	
3[e]	**1**, 69.5	**3**, 22.3	185	53	38[f,g]
4[h]	**1**, 123.3	**3**, 44.9	173		53
5	**2**, 74.8	**3**, 26.4	103	11	
6[e]	**2**, 74.8	**3**, 22.3	177	82	78[g]
7[h]	**2**, 99.7	**3**, 35.7	156		88
8[e,i]	**2**, 74.8	**3**, 22.3	216	<9	
9	**2**, 74.8	**6a**, 24.0	148	72	69[j]
10[i]	**2**, 74.8	**6a**, 27.4	154	74	42
11[k]	**2**, 74.8	**6a**, 27.4	162	79	33
12[l]	**2**, 74.8	**6a**, 27.4	157	14	
13	**2**, 74.8	**6b**, 25.0	150	98	96
14[l]	**2**, 74.8	**6b**, 25.5	165	54	34
15[l,m]	**2**, 74.8	**6b**, 25.0	155	<3	
16[n]	**2**, 74.8	**6b**, 22.0	165		58
17	**2**, 74.8	**6c**, 25.9	165	81	56
18[l]	**2**, 74.8	**6c**, 26.7	150	71	63
19[n]	**2**, 74.8	**6c**, 26.8	144		42
20[k]	**2**, 74.8	**6c**, 25.7	147	84	46

[a] Photostimulated reactions (unless indicated), carried out under nitrogen at 40 °C. Irradiation time (180 min). [b] Determined potentiometrically on the basis of substrate concentration. [c] Determined by GLC and the internal standard method. [d] Reaction carried out in liquid ammonia. [e] Reaction performed in the presence of acetonate anion ($M \times 10^3 = 68$). [f] Benzene was detected but not quantified. [g] Traces of phenylacetone (<1%). [h] Dark reaction in the presence of $FeBr_2$ (40 mmol %). Reaction time (30 min). Temperature (25 °C). [i] *p*-Dinitrobenzene (30 mmol %). [j] Naphthalene was quantified (4%). [k] Di-*tert*-butylnitroxide (30 mmol %). [l] Dark reaction. [m] *p*-Dinitrobenzene (60 mmol %). [n] Dark reaction, $FeBr_2$ (80 mmol %).

Results

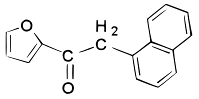
Enolate Ions of 2-Acetylthiophene (1) and 2-Acetylfuran (2). The enolate ions **1** and **2** failed to react with iodobenzene (**3**) under photoinitiation either in liquid ammonia or DMSO in the presence of excess *t*-BuOK (Table 1, expts 1, 2, and 5, respectively). The degree of dehalogenation obtained in these reactions increased when they were performed in DMSO and in the presence of good electron donors such as the enolate ion of acetone (*entrainment reaction*). Under these conditions the highest percentage of substitution products **4** (38%) and **5** (78%), from anions **1** and **2**, respectively, were obtained with a substrate:nucleophile:acetonate ion ratio of 1:3:3 (Table 1, expts 3 and 6).



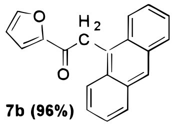
1, Z= S **3** **4, Z= S**
2, Z= O **5, Z= O**

The dark reactions of anions **1** and **2** with **3**, in the presence of 40% of $FeBr_2$, afforded 53% and 88% of substitution products, respectively (Table 1, expts 4 and 7). These percentages of substitution, higher than the ones obtained under photostimulation, were achieved without the need of added nucleophiles and with the advantage of no side products from their possible photostimulated decomposition.

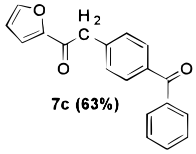
The anion **2** reacted with better electron acceptor substrates such as 1-iodonaphthalene (**6a**), 9-bromoanthracene (**6b**), and 4-bromobenzophenone (**6c**) to afford the following yields of ketones **7a**−**c**, respectively.



7a (69%)



7b (96%)



7c (63%)

Compounds **6a** and **6b** afforded the indicated yields of substitution under irradiation (Table 1, expts 9 and 13). No substitution product was formed in the dark reaction of **6a**, and the degree of substitution obtained with compound **6b** decreased to 34% under this condition (Table 1, expts 12 and 14). However, this percentage increased to 58% by addition of $FeBr_2$ (Table 1, expt 16).

Similar yields of substitution were obtained in the reactions of substrate **6c** with the enolate ion **2** under photostimulation (56%) or in the dark (63%). Added $FeBr_2$ did not improved the degree of substitution in the dark (Table 1, expts 17, 18, and 19).

The percentage of substitution obtained in these reactions not only decreased in the absence of irradiation but also usually in the presence of radical or radical anion traps such as di-*tert*-butylnitroxide (DTBN) and *p*-DNB, respectively (Table 1, expts 8, 10, 11, 15, and 20).

The relative reactivities of anions **1** and **2** and the enolate ions of acetophenone (**8**) and 2-acetylnaphthalene (**9**) were determined in competition experiments under photoinitiation as well as under iron(II) initiation. The relative reactivities were estimated according to the approximation previously reported.[15]

In the photostimulated reaction of **3** with nucleophiles **8** and **9** in excess, we determined a $k_{\mathbf{9}}/k_{\mathbf{8}} = 1.11$[16] (Table 2). The enolate ion of 2-acetylthiophene (**1**) was 0.5 times less reactive than the enolate ion of acetophenone (**8**). The enolate ion of 2-acetylfuran (**2**) was 0.8 times less reactive than the enolate ion of acetophenone.[17]

In the iron(II)-induced competition reactions the enolate ion **1** was 0.6 times less reactive than carbanion **8** and the enolate anion **2** had the same reactivity as the enolate ions **8** and **9** (Table 3).

On the basis of the present experimental evidences, the entrainment of the photoinitiated reactions by added acetone enolate anion and the inhibition of the reactions by radical and radical anion scavengers, we propose that the enolate anions of 2-acetylfuran and 2-acetylthiophene react with aryl halides by the $S_{RN}1$ mechanism. The low reactivity of these anions in photoinitiated reactions with **3** and the considerable higher reactivity observed in the presence of the enolate ion of acetone indicate that they

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[15] The equation used in the relative reactivity determination of pairs of nucleophiles vs a radical is

$$\frac{k_1}{k_2} = \frac{\ln([Nu_1]_0/[Nu_1]_t)}{\ln([Nu_2]_0/[Nu_2]_t)}$$

where $[Nu_1]_0$ and $[Nu_2]_0$ are initial concentrations and $[Nu_1]_t$ and $[Nu_2]_t$ are concentration at time *t* of both nucleophiles. This equation is based on a first-order reaction of both anions with the phenyl radicals, see: Bunnett, J. F. In *Investigation of Rates and Mechanisms of Reactions*, 3rd ed.; Lewis, E. S., Ed.; Wiley-Interscience: New York, 1974; Part 1, p 159.

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[17] This relative reactivity order is obtained when the enolate ions **8** and **2** are present in aproximatelly a 3-fold excess with respect to the substrate; however when they are present at a concentration similar to that of the substrate the relative reactivity is ca. 1.5 and the total percentage of reaction decreases to less than 20%. This dependence of the percentage of substitution with the nucleophile: substrate ratio was observed only under photostimulation.

Table 2. Photostimulated Relative Reactivity of Enolate Ions of Ketones toward PhI[a]

carbanions from	Nu_1:Nu_2,[b] mmol	% X^- [c]	substit prod (%)		rel reactivity		av
			$PhNu_1$	$PhNu_2$			
2-acetylfuran (**2**)	2.8:3.0	17	5	7		0.76	
vs	6.7:3.8	50	29	19		0.86	
acetophenone (**8**)	4.4:5.7	62	27	40		0.87	
					k_2/k_8		0.83 ± 0.06
2-acetylthiophene (**1**)	6.2:3.8	95	50	58		0.51	
vs							
acetophenone (**8**)	4.1:5.7	81	20	58		0.47	
					k_1/k_8		0.49 ± 0.03
2-acetylnaphthalene (**9**)	3.0:3.0	47	29	23		1.27	
vs	2.2:4.1	52	18	36		0.93	
acetophenone (**8**)	5.1:8.7	49	22	33		1.14	
					k_9/k_8		1.11 ± 0.17

[a] Reactions carried out at 40 °C in 40 mL of DMSO with 1 mmol of PhI. Irradiation time 120 min. [b] Nu_2 = enolate anion of acetophenone. [c] On the basis of substrate concentration.

Table 3. Relative Reactivity of Enolate Ions of Ketones toward PhI in the Presence of $FeBr_2$[a]

carbanions from	Nu_1:Nu_2,[b] mmol	substit prod (%)		rel reactivity		av
		$PhNu_1$	$PhNu_2$			
2-acetylfuran (**2**)	6.7:4.4	64	43		0.98	
vs	5.6:5.5	53	51		1.02	
acetophenone (**8**)	4.4:6.7	40	59		1.03	
				k_2/k_8		1.01 ± 0.03
2-acetylthiophene (**1**)	6.6:6.3	28	46		0.57	
vs						
acetophenone (**8**)	4.5:6.7	18	45		0.59	
				k_1/k_8		0.58 ± 0.01
2-acetylnaphthalene (**9**)	7.4:4.9	22	16		0.91	
vs	5.6:5.5[c]	14	12		1.15	
acetophenone (**8**)	4.7:6.7	13	22		0.84	
				k_9/k_8		0.97 ± 0.16

[a] Reactions carried out at 25 °C in 40 mL of DMSO with 1 mmol of PhI. [b] Nu_2 = enolate anion of acetophenone. [c] Temperature (60 °C).

are unable to initiate the process with this substrate. The electron transfer capability of enolate anions in the initiation has been shown to roughly follow the same order as that of the pK_a of the conjugated acids of the carbanions.[18] Even though the pK_a of the conjugated acids of carbanions **1**, **2**, and **9** have not been reported, they are expected to be lower than the pK_a of acetophenone and acetone (pK_a = 24.7 and 26.5, respectively).[19] These facts would explain their higher reactivity toward more electrophilic and thus better electron acceptor compounds such as 1-iodonaphthalene, 9-bromoanthracene, 4-bromobenzophenone, 5-chloro-7-iodo-8-isopropoxyquinoline,[9a] and 6-iodo-9-ethylpurine.[9a]

The relative reactivities determined indicate that the enolate ions **1** and **2** are more efficient than the enolate ion of acetone in the coupling reaction of the process (eq 3). The enolate ions from 2-acetylfuran, 2-acetylnaphthalene, and acetophenone have a similar reactivity toward phenyl radicals while the carbanion from 2-acetylthiophene is half as reactive.

Comparison of the relative reactivities determined for the anions of acetophenone and 2-acetylnaphthalene toward **3** with the value reported toward iodonorcarane ($k_9/k_8 = 1.7$)[20] is another piece of evidence indicating that phenyl radicals are less selective than norcaranyl radicals in their reaction toward carbanions. Similar results were obtained for the reaction of phenyl and 1-adamantyl radicals toward enolate ions of ketones.[21]

The possibility of initiating these reactions with Fe(II) salts is an interesting synthetic possibility. Under these conditions no special photochemical device is required, and the formation of products from photochemical decomposition of the carbanions is avoided. On the other hand, the similar relative reactivity order obtained in competition experiments under light and iron(II) initiation, previously reported with other pair of nucleophiles,[14c] can be taken as an indication of the presence of the same reaction intermediates under both methods of initiation.

Experimental Section

General Method. Irradiation was conducted in a reactor equipped with two 400-W lamps emitting maximally at 350 nm (Philips Model HPT, air and water refrigerated). Potentiometric titration of halide ions was performed with a pH meter using a Ag/Ag^+ electrode.

Materials. PhI, $FeBr_2$, 4-bromobenzophenone, 9-bromoanthracene, 1-iodonaphthalene, and *t*-BuOK were commercially available and used as received. DMSO was distilled under vacuum and stored under molecular sieves (4 Å). Acetophenone was distilled and stored with molecular sieves (4 Å). 2-Acetylthiophene and 2-acetylfuran (Aldrich) were distilled. 2-Acetylnaphthalene (Jonhson Matthey Alfa Products) was recrystallized from petroleum ether.[22]

Photostimulated Reaction of Enolate Ions with 3. The following procedure is representative. The reactions were carried out in a 100 mL three-neck round-bottomed flask

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equipped with nitrogen inlet and magnetic stirrer. To 40 mL of dry and degassed DMSO under nitrogen were added 6.0 mmol of *t*-BuOK and 5.0 mmol of 2-acetylthiophene. After 15 min **3** (1.5 mmol) was added and the reaction mixture was irradiated for 3 h. The reaction was quenched with an excess of ammonium nitrate and water (120 mL). The mixture was extracted twice with methylene chloride (40 mL), and the organic extract was washed twice with water, dried, and quantified by GLC. The iodide ions in the aqueous solution were determined potentiometrically.

The solvent was removed under reduced pressure. The residue after column chromatography on silica gel and eluted with petroleum ether/diethyl ether (90:10) gave a mixture of 2-acetylthiophene and 2-phenyl-1-(2-thienyl)ethanone. This mixture was distilled under reduced pressure in the Kügelrohr apparatus to give **2-phenyl-1-(2-thienyl)ethanone (4)**: ^{1}H NMR[3] (Cl_3CD) δ 4.1 (s, 2H); 7.1 (dd, 1H, $J = 3.8, 4.9$); 7.2−7.3 (m, 5H); 7.6 (dd, 1H, $J = 1.0, 4.9$); 7.7 (dd, 1H, $J = 1.0, 3.8$).

1-(2-Furyl)-2-Phenylethanone (5) was isolated by column chromatography and eluted with petroleum ether/dietyl ether (90:10). The liquid isolated was distilled in the Kügelrohr apparatus: ^{1}H NMR[3] (Cl_3CD) δ 4.05 (s, 2H); 6.45 (dd, 1H, $J = 3.5, 1.8$); 7.1 (dd, 1H, $J = 3.5, 0.7$); 7.15−7.25 (m, 5H); 7.5 (dd, 1H, $J = 1.8, 0.8$).

1-(2-Furyl)-2-(1-naphthyl)ethanone (7a) was isolated by column chromatography and eluted with petroleum ether/diethyl ether (90:10): ^{1}H NMR[23] (Cl_3CD) δ 4.58 (s, 2H), 6.48−6.55 (dd, 1H); 7.19−7.24 (dd, 1H); 7.39−7.61 (m, 5H); 7.72−7.89 (m, 2H); 7.94−7.85 (m, 1H); ^{13}C NMR (Cl_3CD) δ 42.9, 112.7, 117.9, 124.0, 125.4, 125.7, 126.3, 127.9, 128.2, 128.7, 130.7 (c), 132.39 (c), 133.9 (c), 146.0, 152.8 (c), 186.5 (c); MS (relative intensity) *m/e* 238 (0.7), 237 (5.2), 236 (29.9), 143 (0.7), 142 (11.3), 141 (86.1), 115 (31.1), 97 (0.3), 96 (2.7), 95 (47.3), 89 (3), 63 (6.2), 51 (8.3), 40 (3.4), 39 (100).

2-(9-Anthryl)-1-(2-furyl)ethanone (7b) was isolated by column chromatography and eluted with petroleum ether/diethyl ether (90:10): mp 172−173.5 °C; ^{1}H NMR (Cl_3CD) δ 5.16 (s, 2H); 6.49−6.55 (dd, 1H); 7.20−7.25 (dd, 1H); 7.33−7.56 (m, 5H); 7.56−7.70 (m, 1H); 7.69−7.80 (m, 4H); ^{13}C NMR (Cl_3CD) δ 38.5, 112.6, 117.8, 124.1, 124.8, 126.1, 127.4, 129.0, 130.6 (c), 131.6 (c), 146.3, 152.2 (c), 186.2 (c); MS (relative intensity) *m/e* = 288 (0.4), 287 (3.4), 286 (18.5), 193 (1.3), 192 (16.5), 191 (100.0), 190 (13.4), 189 (35.2), 165 (8.3), 95 (14.0), 38 (19.1); HRMS calcd for $C_{20}H_{14}O_2$ 286.0994, found 286.0994.

2-(4-Benzoylphenyl)-1-(2-furyl)ethanone (7c) was isolated by column chromatography and eluted with petroleum ether/acetone (90:10): ^{1}H NMR (Cl_3CD) δ 4.22 (s, 2H); 6.53−6.58 (dd, 1H); 7.25−7.30 (dd, 1H); 7.37−7.65 (m, 6H); 7.73−7.83 (m, 4H); ^{13}C NMR (Cl_3CD) δ 45.2, 112.5, 118.0, 128.2, 129.5, 130.5, 132.1, 136.0 (c), 137.7 (c), 139.0 (c), 146.9, 152.1 (c), 185.6 (c), 196.1 (c); MS (relative intensity) *m/e* = 292 (0.1), 291 (0.9), 290 (5.0), 196 (0.2), 195 (0.8), 168 (0.8), 167 (5.7), 106 (0.3), 105 (3.0), 97 (0.6), 96 (4.6), 95 (100), 78 (0.7), 77 (8.7), 76 (0.4), 53 (0.8), 52 (0.7), 51 (8.7); HRMS calcd for $C_{19}H_{14}O_3$ 290.0943, found 290.0939.

Fe(II)-Induced Reaction of 2 with 3. To 30 mL of dry and degassed DMSO under nitrogen were added 6.0 mmol of *t*-BuOK, 5.0 mmol of 2-acetylthiophene, and 0.6 mmol of $FeBr_2$. After a few minutes **3** (1.5 mmol) was added. The reaction was quenched after 30 min.

Competition Reactions of Two Different Enolates Ions toward 3. To estimate the relative reactivities of these nucleophiles, photostimulated reaction and $FeBr_2$ induced reactions were carried out. In 40 mL of dry and degassed DMSO under nitrogen, 12 mmol of *t*-BuOK, 4 mmol of acetophenone, and 6 mmol of 2-acetylfuran were added. Then 1 mmol of $FeBr_2$ was added. After a few minutes, 1 mmol of **3** was added. After a reaction time of 30 min ($FeBr_2$-induced reaction) or 3 h (under photostimulation), the reaction was quenched by addition of ammonium nitrate in excess.

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Supporting Information Available: ^{1}H NMR spectra for compounds **7b** and **7c** (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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