Acylation of 2-Methoxynaphthalene with Acyl Chlorides in the Presence of a Catalytic Amount of Lewis Acids

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The regiochemistry of the reaction of 2-methoxynaphthalene **1** with benzoyl chloride **2a** using a catalytic amount of a Lewis acid is strongly influenced by the identity of the acid catalyst employed as well as by the reaction temperature. By using $InCl_3$, $FeCl_3$, $SnCl_4$ or $ZnCl_2$ and heating at 160 °C, 2-benzoyl-6-methoxynaphthalene **4a** is selectively produced along with 1-benzoyl-7-methoxynaphthalene **5a**, while in the case of $AlCl_3$, $SbCl_5$ or $TiCl_4$, 1-benzoyl-2-methoxynaphthalene **3a** is the major product. 2-Acyl-6-methoxynaphthalenes **4b–e** can be selectively obtained using $InCl_3$ and the corresponding acyl chlorides **2b–e** in place of **2a**. In the presence of a stoichiometric amount of $InCl_3$, the reaction of **1** with **2a** also gives **4a** as the predominant product along with **5a** even at 50 °C. This reaction appears to involve isomerisation of **3a** to **4a** and **5a**.

The Friedel–Crafts acylation has a long history and has been to date of great importance for the synthesis of aromatic carbonyl compounds.[1] While the reaction is usually carried out using a stoichiometric amount of aluminium chloride, reactive aromatic compounds are known to undergo acylation in the presence of a catalytic amount of Lewis acid.[2] Recently, several effective catalyst systems for the acylation of anisole and its derivatives have also been developed.[3]

The reaction of naphthalene derivatives is of special interest because of the dichotomy of 1- *versus* 2-substitution. Recently, acetylation of naphthalene with aluminium chloride in dichloroethane has been thoroughly studied and the mechanism of 2-substitution in the reaction system has been clearly distinguished from that of the 1-substitution on the basis of the kinetic analysis.[4] On the other hand, selective synthesis of 2,6-disubstituted naphthalenes is also of considerable interest, since such compounds have become increasingly important in industrial uses.[5]

As part of our study of catalytic derivatisation reactions of aromatic compounds,[6] we have undertaken selective acylation of 2-methoxynaphthalene with acyl chlorides in the presence of a catalytic amount of Lewis acids. It was found that 2-acyl-6-methoxynaphthalenes could be produced as the predominant products along with 1-acyl-7-methoxynaphthalenes by using certain medium strength acids, typically $InCl_3$, as the catalyst.

Results and Discussion

Catalytic Reaction of 2-Methoxynaphthalene **1** *with Benzoyl Chloride* **2a**.—When **1** (2 mmol) was treated with an equimolar amount of **2a** in the presence of $AlCl_3$ (0.1 mmol, 5 mol%) in nitrobenzene at 50 °C for 3 h it gave 1-benzoyl-2-methoxynaphthalene **3a** as the major product along with 2-benzoyl-6-methoxy- and 1-benzoyl-7-methoxy-naphthalenes, **4a** and **5a**, the composition of **3a–5a** being 63:25:12 [Table 1 and Scheme 1 (R = Ph)]. The conversion of **1** and the combined yield of **3a–5a**, based on **1** consumed, were 56 and 91%, respectively. With $InCl_3$ in place of $AlCl_3$, **3a** was obtained in a higher selectivity of 88%. On increasing the temperature in the reaction with $InCl_3$, the product composition was drastically changed and **4a** was the predominant product formed at 160 °C with 84% selectivity, whereas the reaction with $AlCl_3$ was less sensitive to temperature variation.

The reaction of **1** with **2a** catalysed by various metal chlorides at 160 °C was also examined (Table 1). Among the metal species tested, $FeCl_3$, $ZnCl_2$ and $SnCl_4$ selectively afforded **4a** as well as $InCl_3$, whilst $SbCl_5$ and $TiCl_4$ gave **3a** as the major product. With the less acidic chlorides $MnCl_2$, $CoCl_2$ and $CuCl_2$, **3a** was the predominant product. It was confirmed that no benzoylated products were formed without the presence of a catalyst even at 160 °C. It is noted that in some cases, a very small amount of 2-benzoyl-3-methoxynaphthalene **6a** (less than 1%) was detected.

In order to examine the solvent effect on the product distribution, the benzoylation reaction using $InCl_3$ was performed in 1,2-dichlorobenzene or without solvent. The product composition was essentially the same as that in nitrobenzene, although the total product yield was somewhat reduced (Table 1). This suggests that the 'complexing effect'[1]

Table 1 Reaction of 2-methoxynaphthalene **1** with benzoyl chloride **2a**[a]

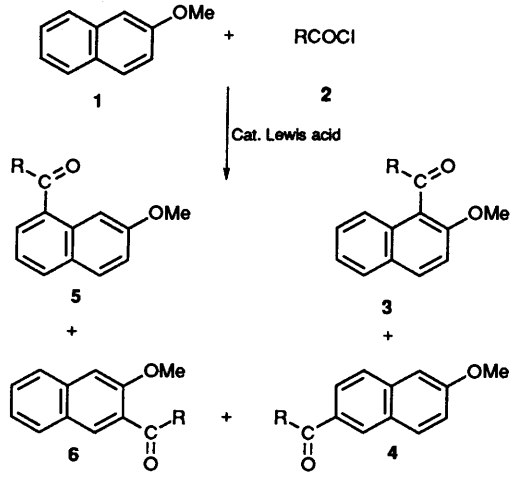
Catalyst	*T*/°C	Conversion of **1** (%)[b]	Total yield of **3a–5a** (%)[b,c]	Product distribution (%)[b,d]		
				3a	**4a**	**5a**
$AlCl_3$	50	56	91	63	25	12
$AlCl_3$	100	57	88	62	26	12
$AlCl_3$	160	62	82	43	41	16
$InCl_3$	50	58	99	88	9	3
$InCl_3$	100	65	79	29	56	15
$InCl_3$	160	72	79		84	16
$InCl_3$[e]	160	66	71		87	13
$InCl_3$[f]	160	58	57		87	13
$InCl_3$[g]	160	73	64		91	9
$InCl_3$[h]	160	88	59	27	58	15
$InCl_3$[i]	160	72	85	8	75	16
$SbCl_5$	160	56	89	70	22	8
$TiCl_4$	160	53	83	86	9	5
$ZrCl_4$	160	54	80	30	53	16
$FeCl_3$	160	66	82		80	20
$FeCl_3$[f,j]	160	27	91	70	19	11
$SnCl_4$	160	70	80	4	77	19
$ZnCl_2$[g]	160	73	84	1	85	14
$MnCl_2$	160	49	99	94	4	2
$CoCl_2$	160	55	99	93	5	2
$CuCl_2$	160	52	85	93	5	2

[a] *Reaction conditions:* [**1**]:[**2a**]:[catalyst] = 2:2:0.1 (in mmol), $PhNO_2$ (5 cm^3), 160 °C, 3 h, under N_2. [b] Determined by GLC analysis. [c] Based on **1** consumed. [d] In some reactions, a very small amount of 2-benzoyl-3-methoxynaphthalene **6a** (less than 1%) was formed. [e] In 1,2-dichlorobenzene. [f] Without solvent. [g] [Catalyst] = 0.2. [h] [**2a**] = 4. [i] Reaction for 0.5 h. [j] [**1**]:[**2**]:[catalyst] = $3:1:10^{-5}$.

Table 2 Reaction of naphthalenes **1**, **7** and **10** with benzoic anhydride **2a'** and acyl chlorides **2a–e** using $InCl_3$ [a]

Naphthalene	2	Conversion of naphthalene (%) [b]	Total yield of ketones (%) [b,c]	Products	Ratio
1	**2a'**	60	78	**4a:5a**	76:24
1	**2b**	67	82	**4b:5b**	80:20
1	**2c**	73	79	**4c:5c**	79:21
1	**2d**	66	62	**4d:5d**	90:10
1	**2e**	56	82	**4e:5e**	93:7
7	**2a**	63	81	**8:9**	84:16
10	**2a**	67	85	**11:12**	57:43

[a] *Reaction conditions:* [**1**]:[**2**]:[$InCl_3$] = 2:2:0.1 (in mmol), $PhNO_2$ (5 cm^3), 160 °C, 3 h, under N_2. [b] Determined by GLC analysis. [c] Based on **1** consumed.



a R = Ph, **b** R = 4-$MeOC_6H_4$, **c** R = 4-BrC_6H_4, **d** R = $PhCH_2$, **e** R = C_6H_{13}, **f** R = Me, [**2a'** = $(PhCO)_2O$, **2f'** = $(MeCO)_2O$]

Scheme 1 *Reagents and conditions:* $PhNO_2$, 50–160 °C, under N_2

of the nitro compound in determining the acylation regiochemistry is not important in the present reaction.

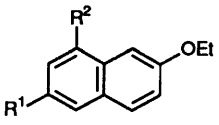
One example of the reaction of **1** with **2a** using a catalytic amount of $FeCl_3$ without solvent was previously described, in which in contrast to our observation, **3a** was reported to be the predominant product.[3,7] The difference in the product distribution appeared to be owing to the amount of the catalyst used. Indeed, with 0.01 mol% of $FeCl_3$, **3a** was the major product, suggesting that the amount of catalyst also affects the product distribution.

Catalytic Reaction of 2-Methoxynaphthalene **1** *with Benzoic Anhydride* **2a'** *or Acyl Chlorides* **2b–e** *and other Naphthalene Compounds* **7**, **10** *and* **13** *with* **2a**.—The reactions of **1** with **2a'** or acyl chlorides **2b–e** using 5 mol% of $InCl_3$ at 160 °C afforded the corresponding 2-acyl-6-methoxynaphthalenes **4a–e** with good selectivity along with **5a–e**, as did the reaction of **1** with **2a** (Scheme 1 and Table 2). It is worth noting that selective aroylation at the 2-position of naphthalene compounds has not yet been reported, while aliphatic acyl chlorides are known to react with naphthalene compounds in the presence of a stoichiometric amount of $AlCl_3$ in complexing solvents such as nitromethane and nitrobenzene to give the corresponding 2-acylated naphthalenes as the major products.[1] The reaction of 2-ethoxynaphthalene **7** with **2a** under the same conditions gave 2-benzoyl-6-ethoxynaphthalene **8**, selectively. However, naphthalene **10** itself reacted with **2a** to give a mixture of 1- and 2-benzoylnaphthalenes, **11** and **12**, in comparable amounts. The reaction of 2-methylnaphthalene **13** with **2a** gave a mixture of five kinds of monobenzoylated products in a ratio of 26:12:5:12:45; the structural assignment of these products has not been made.

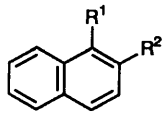
Table 3 Treatment of ketones **3a–5a**, **3e**, **3f** and **11** with $InCl_3$ [a]

Ketone	$InCl_3$ (mol%)	Products [yield (%)] [b]	Recovery of ketone (%)
3a	5	**1** (39), **4a** (42), **5a** (9)	
4a	5		100
5a	5	**1** (47), **4a** (2)	47
3e	5	**1** (52), **4e** (11), **5e** (9)	
3f [c]	100	**1** (52), **4f** (32), **5f** (6)	18
3f [c,d]	100	**1** (38), **4f** (23), **5f** (8)	13
11	5		100

[a] *Reaction conditions:* [**1**]:[**2**]:[$InCl_3$] = 1:1:0.05 (in mmol), $PhNO_2$ (2.5 cm^3), 160 °C, 3 h. [b] Determined by GLC analysis. [c] Reaction at 50 °C. [d] Reaction for 12 h.



7 $R^1 = R^2 = H$
8 $R^1 = COPh$, $R^2 = H$
9 $R^1 = H$, $R^2 = COPh$



10 $R^1 = R^2 = H$
11 $R^1 = COPh$, $R^2 = H$
12 $R^1 = H$, $R^2 = COPh$
13 $R^1 = H$, $R^2 = Me$

Product Isomerisation and Deacylation.—When ketone **3a** was treated with 5 mol% of $InCl_3$ in nitrobenzene at 160 °C for 3 h, **3a** completely disappeared and a mixture of **4a** and **5a** in a ratio of 82:18 (51%) was formed together with **1** (39%) (Table 3). This product composition parallels that in the corresponding catalytic reaction of **1** with **2a**, indicating that **3a**, if formed in the benzoylation, may be transformed into **4a** and **5a**. In the product mixture, benzoic acid (30%) was also detected. Thus, the debenzoylation of **3a** to give **1** could be due to its reaction with adventitious water. In contrast to the behaviour of **3a**, treatment of **5a** with $InCl_3$ gave **4a** in only 2% yield together with a significant amount of **1** (47%). A prolonged reaction time did not change the product yield. No isomerised and debenzoylated products were formed on treatment of **4a** with $InCl_3$. Treatment of **3e** under the same conditions gave **4e** (11%) together with **5e** (9%) and **1** (52%). This ketone yield is considerably lower than that in the reaction of **1** with **2e**. These results indicate that the precedence of the deacylation and the isomerisation and their ease depend on the identity of the acyl groups and their substitution position on the naphthalene ring.

1-Benzoylnaphthalene **11** was stable under the present conditions, however it is known that **11** is isomerised into the corresponding isomer **12** in polyphosphoric acid.[8] The ratio of the product mixture from the reaction of **13** with **2a** did not change by treatment with $InCl_3$. Thus, activation by the

Table 4 Reaction of 2-methoxynaphthalene **1** with benzoyl chloride **2a**, acetyl chloride **2f** or acetic anhydride **2f'** using a stoichiometric amount of $InCl_3$[a]

2	Catalyst	Solvent	T/°C	t/h	Conv. of 1 (%)[b]	Total yield of 3a–5a (%)[b,c]	Product distribution (%)[b] 3	4	5
a	$InCl_3$	$PhNO_2$	20	6	69	98	81	15	4
a	$InCl_3$	$PhNO_2$	50	1	64	90	47	44	9
a	$InCl_3$	$PhNO_2$	50	3	64	84	3	80	17
a	$InCl_3$	$(CH_2Cl)_2$	50	1	70	77	66	30	4
a	$InCl_3$	$(CH_2Cl)_2$	50	3	63	64	12	76	12
a	$AlCl_3$	$PhNO_2$	50	3	94	60	63	35	2
a	$AlCl_3$	$(CH_2Cl)_2$	50	3	83	84	92	6	2
f	$InCl_3$	$PhNO_2$	40	1	61	90	41	49	10
f	$InCl_3$	$PhNO_2$	40	5	64	71		91	9
f	$InCl_3$	$(CH_2Cl)_2$	40	1	59	78	33	54	12
f	$InCl_3$	$(CH_2Cl)_2$	40	5	66	58		87	13
f	$AlCl_3$	$(CH_2Cl)_2$	40	5	88	90	84	15	1
f'	$InCl_3$	$(CH_2Cl)_2$	50	3	64	80	53	31	16
f'	$InCl_3$	$(CH_2Cl)_2$	50	6	—[d]	—	27	60	13
f'	$InCl_3$	$(CH_2Cl)_2$	50	12	—	—	7	79	14
f'	$InCl_3$	$(CH_2Cl)_2$	50	24	62	77		83	17

[a] *Reaction conditions:* [1]:[2]:[catalyst] = 2:2:2 (in mmol), under N_2. [b] Determined by GLC analysis. [c] Based on **1** consumed. [d] Not determined.

methoxy group in **1** seems to be the key for the isomerisation and debenzoylation to occur.

It has also been reported that 1-acetyl-2-methoxynaphthalene **3f** is transformed into **4f** in only 2% yield in the presence of 2 equiv. of $AlCl_3$ and 1 equiv. of acetyl chloride **1f** in refluxing chloroform and hence, it was concluded that isomerisation was not important in the acetylation of **1** using $AlCl_3$.[9] Consequently, **3f** was treated with a stoichiometric amount of $InCl_3$ at 50 °C to compare the catalyst properties. It was observed that **3f** was much more efficiently isomerised to a mixture of **4f** and **5f** along with formation of **1** in both nitrobenzene and 1,2-dichloroethane without addition of **2f** (Table 3).

Stoichiometric Reactions of 2-Methoxynaphthalene **1** *with Acyl Chlorides* **2a** *and* **2f**.—In connection with the above isomerisation experiments, the reactions of **1** with **2a** and **2f** using a stoichiometric amount of $InCl_3$ or $AlCl_3$ at 40–50 °C in either 1,2-dichloroethane or nitrobenzene were carried out (Table 4). In the reaction of **1** with **2a** using $InCl_3$ for 3 h, **4a** was the major product in both the solvents, while a significant amount of **3a** was detected after a reaction time of 1 h. The fact that the conversion of **1** after 1 h was essentially the same as that after 3 h indicates that isomerisation of **3a** to **4a** occurs in the reaction medium. By contrast, the reaction of **1** with **2a** using $AlCl_3$ gave **3a** as the major product even after 3 h.

The reaction of **1** with either **2f** or acetic anhydride **2f'** in the presence of $InCl_3$ was similar to that with **2a**, suggesting that it may also involve the isomerization of **3f** to **4f**. The stoichiometric reaction of **1** with **2f** using $AlCl_3$ in nitrobenzene was previously reported, where **4f** was formed as the major product.[9] It was confirmed that **3f** was the major product in dichloroethane as well as in carbon disulfide.

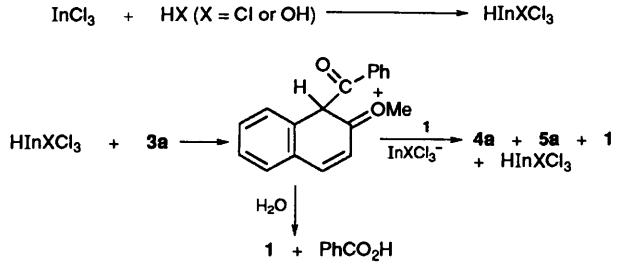
MO Calculations.—The results for the acylation of **1** and the isomerisation and the deacylation of the product ketones suggest that C-1 is the most reactive position and that ketones **4** are more stable than the corresponding isomers **3** and **5**, which parallels the usual electrophilic substitution of naphthalenes having an electron donating substituent at the 2-position.[1] To obtain numerical information on the relative reactivity of the carbons of **1** and relative stability of the product ketones, semi-empirical MO calculations on **1** and **3a**–**6a** were carried out using the AM1 method.[10,11] The charge densities of C-1, C-3, C-6 and C-8 of **1** were calculated to be −0.21, −0.14, −0.14 and −0.13 and heats of formation of **3a**, **4a**, **5a** and **6a** were 6.43, 1.74, 4.05 and 6.67 kcal mol^{-1},* respectively. These data suggest that (a) based on the negative charge, C-3, C-6 and C-8 carbons have similar reactivity, while C-1 is the most reactive position as expected and (b) the stability order of the ketones follows the sequence **4a** > **5a** > **3a** > **6a**. These conclusions seem to be consistent with the observations that (a) the reaction of **1** with **2a** using $InCl_3$ at low temperature or using $AlCl_3$ gave **3a** as the major product, (b) **3a** could be transformed to **4a** and **5a** in the presence of $InCl_3$, (c) **4a** was stable against the treatment with $InCl_3$, while **5a** could be debenzoylated, and (d) **6a** was a very minor product.

Reaction Mechanism.—Two factors, electronic and steric effects, are usually taken into consideration in the Friedel–Crafts acylation of naphthalene compounds:[1] the 1-position is electronically more reactive as discussed above, whilst it is sterically more hindered compared with the 2-position because of the presence of a *peri*-hydrogen. A recent study on the acetylation of naphthalene has suggested that the structure of the intermediary σ-complexes between naphthalene and acetyl chloride coordinated by aluminium chloride is also significant in determining the substitution regiochemistry, which is mainly determined by steric effects in the intermediates.[4] These arguments have been made based on the premise that the acylation proceeds without isomerisation of product naphthalene ketones. Although a reasonable reversible mechanism for the acylation of naphthalene compounds has also been proposed,[1] it has been regarded to be of less importance, since isomerisation of acylated naphthalene derivatives is not significant under normal reaction conditions using $AlCl_3$.[1,4] The present results for the acylation of **1**, especially when using $InCl_3$, which is apparently less acidic than $AlCl_3$,[1,12] may provide typical examples involving the reversible acylation as the most significant reaction path. The reactions of **1** with **2a** and **2f** (or **2f'**) in the presence of a stoichiometric amount of $InCl_3$ at 50 °C may be clear representatives (Table 4). Although a rather effective *trans*-acetylation in polymethylbenzenes using $AlCl_3$ was previously described,[13] such examples in the acylation of naphthalene compounds have, to our knowledge,

* 1 cal = 4.184 J.

not yet been reported. The catalytic benzoylation of **1** could also proceed by the isomerisation mechanism at least to some extent: (a) formation of **3a** could be detected at the early stages of the reaction of **1** with **2a** (Table 1) and (b) the treatment of **3a** under catalytic conditions gave a mixture of **4a** and **5a** in a comparable ratio with that in the corresponding benzoylation. The results for the catalytic reaction of **1** with **2a** using various metal chlorides also suggest that certain metal chlorides having medium acidity[1,12] may be suitable for the selective formation of **4a**. On the other hand, strong acids and/or those having high affinity for oxygen seem to be less effective for the isomerisation of **3a**. They could form stable complexes with the two oxygen atoms in **3a**. There is, however, a possibility that under catalytic conditions using medium strength acids, the primary acylation of **1**, especially with aliphatic acyl chlorides, would preferentially occur at the 6 position: (a) in the reaction with **1e**, only a very small amount of **3e** (*ca.* 1%) could be detected at the early stages and (b) the catalytic isomerisation of **3e** to **4e** was less efficient than that expected from the corresponding acylation. Thus, an alternative explanation for the selective formation of **4** could be that the σ-complex of **1** with **2** coordinated by medium strength acids at C-1 of **1** is less stable than that with **2** coordinated by strong acids and hence, the acylation under the catalytic conditions at elevated temperature preferentially takes place at C-6. Further, less acidic catalysts may in any case be too weak to react preferentially at the less negative 6 position of **1** and have no isomerisation ability.

It should be pointed out that isomerisation was the major reaction in the treatment of **3a** with $InCl_3$, whereas in the case of **5a** debenzoylation was predominant. A possible explanation for this difference is that protonated **3a**, which seems to be more stable than that from **5a** because of the presence of the neighbouring methoxy group, could transfer the benzoyl group to **1** generated in the medium before the liberation of benzoyl cation and/or its equivalent (Scheme 2). This could also participate in the catalytic benzoylation reaction.



Scheme 2

Experimental

^1H NMR spectra were obtained with a JEOL JNM-GSX-400 spectrometer for $CDCl_3$ solutions. *J* Values are given in Hz. GLC–MS data were obtained with a Shimadzu QP-2000A spectrometer. GLC analysis was carried out with a Shimadzu GC 8A gas chromatograph equipped with a Silicon OV-17 glass column (2.6 mm × 1.5 m) or with a CBP-1 capillary column (0.5 mm × 25 m).

2-Ethoxynaphthalene **7** was prepared by the reaction of 2-naphthol with diethyl sulfate in the presence of sodium hydroxide. Other starting materials were commercially available. It should be noted that aluminium chloride used was a white lot provided by Wako Pure Chem. Ind. (99.9%). When a lower grade lot was used, the product distribution in the catalytic reaction of **1** with **2a** was somewhat different: at 160 °C in nitrobenzene, the ratio **3a**:**4a**:**5a** was 72:21:7. Solvents were purified by standard methods before use. The following experimental details may be regarded as typical in methodology and scale.

Reaction of 2-*Methoxynaphthalene* **1** *with Benzoyl Chloride* **2a** *in the Presence of* $InCl_3$.—A mixture of **1** (316 mg, 2 mmol), **2a** (280 mg, 2 mmol) and $InCl_3$ (22 mg, 0.1 mmol) in nitrobenzene (5 cm^3) was stirred under nitrogen at 160 °C for 3 h. After cooling, the mixture was poured into aqueous potassium carbonate and extracted with dichloromethane. Analysis by GLC and GLC–MS confirmed formation of **4a** (226 mg) and **5a** (46 mg) along with a trace amount of **6a**. The products **4a** and **5a** were also isolated by column chromatography on silica gel using hexane–dichloromethane as eluent. 6-Methoxy-2-naphthyl phenyl ketone **4a** was a solid, m.p. 82–84 °C (lit.,[7] 87 °C); *m/z* 262 (M^+); δ_H 3.96 (3 H, s), 7.19–7.26 (2 H, m), 7.49–7.53 (2 H, m), 7.61 (1 H, dd, *J* 7.3, 7.3), 7.80–7.85 (4 H, m), 7.94 (1 H, dd, *J* 1.5, 8.3) and 8.21 (1 H, s). 7-Methoxy-1-naphthyl phenyl ketone **5a** was a solid, m.p. 86.5–87.5 °C; *m/z* 262 (M^+); δ_H 3.82 (3 H, s), 7.19–7.22 (1 H, m), 7.34–7.38 (1 H, m), 7.45–7.49 (2 H, m), 7.57–7.62 (3 H, m), 7.81 (1 H, d, *J* 9.3), 7.85–7.87 (2 H, m) and 7.93 (1 H, d, *J* 7.8). An authentic sample of **5a** was also prepared by the reaction with 7-methoxy-1-naphthylmagnesium iodide[14] with benzonitrile. The m.p., GLC retention time and ^1H NMR spectrum were completely identical with those of the isolated sample. Identification of 3-methoxy-2-naphthyl phenyl ketone **6a** was made by comparison with an authentic sample prepared by the published procedure[15] using GLC and GLC–MS, m.p. 67–68 °C; *m/z* 262 (M^+); δ_H 3.84 (3 H, s), 7.23 (1 H, s), 7.37–7.46 (3 H, m), 7.50–7.59 (2 H, m) and 7.78–7.86 (5 H, m).

Products.—2-Methoxy-1-naphthyl phenyl ketone **3a**; m.p. 122–124 °C (lit.,[7] 125 °C); *m/z* 262 (M^+); δ_H 3.82 (3 H, s), 7.33–7.44 (5 H, m), 7.50–7.58 (2 H, m), 7.83–7.86 (3 H, m) and 7.95 (1 H, d, *J* 8.8).

6-Methoxy-2-naphthyl 4-methoxyphenyl ketone **4b**; m.p. 144.5–146 °C (Found: C, 78.1; H, 5.5. $C_{19}H_{16}O_3$ requires C, 78.06; H, 5.52%); *m/z* 292 (M^+); δ_H 3.90 (3 H, s), 3.95 (3 H, s), 6.98 (2 H, d, *J* 8.3) 7.19–7.21 (2 H, m), 7.77–7.81 (2 H, m), 7.86–7.89 (3 H, m) and 8.17 (1 H s).

4-Bromophenyl 6-methoxy-2-naphthyl ketone **4c**; m.p. 194–195 °C (Found: C, 63.3; H, 3.8. $C_{18}H_{13}BrO_2$ requires C, 63.36; H, 3.84%); *m/z* 340, 342 (M^+); δ_H 3.96 (3 H, s), 7.18–7.23 (2 H, m), 7.63–7.73 (4 H, m), 7.79–7.83 (2 H, m), 7.90 (1 H, dd, *J* 2.0, 8.8) and 8.16 (1 H, s).

Benzyl 6-methoxy-2-naphthyl ketone **4d**; m.p. 113–115 °C (Found: C, 82.4; H, 5.8. $C_{19}H_{16}O_2$ requires C, 82.58; H, 5.84%); *m/z* 292 (M^+); δ_H 3.93 (3 H, s), 4.38 (2 H, s), 7.13 (1 H, d, *J* 2.4), 7.19 (1 H, dd, *J* 2.4, 6.8), 7.23–7.26 (1 H, m), 7.31–7.33 (4 H, m), 7.74 (1 H, d, *J* 8.8), 7.83 (1 H, d, *J* 8.8), 8.03 (1 H, dd, *J* 2.0, 8.8) and 8.47 (1 H, s).

Hexyl 6-methoxy-2-naphthyl ketone **4e**; m.p. 66.5–67 °C (lit.,[16] 68–69 °C); *m/z* 264 (M^+); δ_H 0.90 (3 H, t, *J* 7.3), 1.32–1.37 (4 H, m), 1.40–1.45 (2 H, m), 1.78 (2 H, tt, *J* 7.3, 7.3), 3.06 (2 H, t, *J* 7.3), 3.95 (3 H, s), 7.20 (1 H, dd, *J* 2.5, 8.9), 7.76 (1 H, d, *J* 8.6), 7.85 (1 H, d, *J* 9.0), 8.01 (1 H, dd, *J* 1.7, 8.6) and 8.40 (1 H, s).

2-Methoxy-1-naphthyl methyl ketone **3f**; m.p. 54.5–55 °C (lit.,[17] 57–58 °C); *m/z* 200 (M^+); δ_H 2.65 (3 H, s), 3.97 (3 H, s), 7.28 (1 H, d, *J* 8.8), 7.34–7.38 (1 H, m), 7.45–7.49 (1 H, m), 7.76 (1 H, d, *J* 8.3), 7.78 (1 H, d, *J* 7.8) and 7.88 (1 H, d, *J* 9.3).

6-Methoxy-2-naphthyl methyl ketone **4f**; m.p. 105–106 °C (lit.,[9] 106.5 °C); *m/z* 200 (M^+); δ_H 2.70 (3 H, s), 3.95 (3 H, s), 7.15 (1 H, d, *J* 2.4), 7.20 (1 H, dd, *J* 2.4, 8.8), 7.76 (1 H, d, *J* 8.3), 7.85 (1 H, d, *J* 8.8), 8.00 (1 H, dd, *J* 1.5, 8.3) and 8.39 (1 H, s).

4-Bromophenyl 7-methoxy-1-naphthyl ketone **5c**; m.p. 101–102.5 °C (Found: C, 63.3; H, 3.8. $C_{18}H_{13}BrO_2$ requires C, 63.36; H, 3.84%); *m/z* 340, 342 (M^+); δ_H 3.84 (3 H, s), 7.21 (1 H, dd, *J* 8.8, 2.4), 7.36 (1 H, dd, *J* 7.3, 8.3), 7.54–7.63 (4 H, m), 7.71–7.74 (2 H, m), 7.81 (1 H, d, *J* 8.8) and 7.94 (1 H, d, *J* 8.3). While 1-acyl-7-methoxynaphthalenes **5b**,**d**,**e** were not completely purified

and were obtained as oils (the purity of each determined by GLC was >85%), their spectral data were satisfactorily consistent with the structures: **5b**; *m/z* 292 (M^+); δ_H 3.79 (3 H, s), 3.85 (3 H, s), 6.91–6.94 (2 H, m), 7.17 (1 H, dd, *J* 2.4, 8.8), 7.32–7.37 (1 H, m), 7.46 (1 H, d, *J* 2.4), 7.52–7.54 (1 H, m), 7.78 (1 H, d, *J* 9.3) and 7.80–7.90 (3 H, m). **5d**; *m/z* 292 (M^+); δ_H 3.89 (3 H, s), 4.40 (2 H, s), 7.14–7.19 (2 H, m), 7.24–7.37 (5 H, m), 7.74 (1 H, d, *J* 8.8), 7.91 (1 H, d, *J* 7.8), 8.06 (1 H, d, *J* 6.8) and 8.22 (1 H, d, *J* 2.4). **5e**; *m/z* 264 (M^+); δ_H 0.89 (3 H, t, *J* 7.3), 1.25–1.35 (4 H, m), 1.39–1.45 (2 H, m), 1.79 (2 H, tt, *J* 7.3, 7.3), 3.06 (2 H, t, *J* 7.3), 3.94 (3 H, s), 7.19 (1 H, dd, *J* 2.5, 6.4), 7.34–7.36 (1 H, m), 7.76 (1 H, d, *J* 8.9), 7.90–7.93 (2 H, m) and 8.19 (1 H, d, *J* 2.3).

6-Ethoxy-2-naphthyl phenyl ketone **8**; m.p. 85.5–86.6 °C (Found: C, 82.6; H, 5.7. $C_{19}H_{16}O_2$ requires C, 82.58; H, 5.84%); *m/z* 276 (M^+); δ_H 1.50 (3 H, t, *J* 7.3), 4.18 (2 H, q, *J* 7.3), 7.16–7.21 (2 H, m), 7.48–7.52 (2 H, m), 7.58–7.60 (1 H, m), 7.78–7.85 (4 H, m), 7.92 (1 H, dd, *J* 2.0, 8.8) and 8.20 (1 H, s).

7-Ethoxy-1-naphthyl phenyl ketone **9**; m.p. 63.5–65 °C (Found: C, 82.65; H, 5.8. $C_{19}H_{16}O_2$ requires C, 82.58; H, 5.84%); *m/z* 276 (M^+); δ_H 1.40 (3 H, t, *J* 7.3), 4.04 (2 H, q, *J* 7.3), 7.19 (1 H, dd, *J* 2.4, 9.3), 7.32–7.36 (1 H, m), 7.44–7.48 (2 H, m), 7.56–7.61 (3 H, m), 7.80 (1 H, d, *J* 9.3), 7.84–7.87 (2 H, m) and 7.92 (1 H, d, *J* 8.3).

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