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Catalytic Action of Azolium Salts. III.[1] Aroylation of *N*-Phenylbenzimidoyl Chlorides with Aromatic Aldehydes in the Presence of 1,3-Dimethylimidazolium Iodide

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N-Phenylbenzimidoyl chlorides 10, 11, 12, 13, and 14 were aroylated with aromatic aldehydes 9 in the presence of a catalytic amount of 1,3-dimethylimidazolium iodide (1) to afford N-(α-aroylbenzylidene)anilines 15, 16, 17, 18, and 19. Treatment of the resulting N-(α-aroylbenzylidene)anilines (15—19) with diluted hydrochloric acid (HCl) produced the benzils 20, 21, 22, 23, and 24 in excellent yields.

Keywords 1,3-dimethylimidazolium iodide; catalytic aroylation; aromatic aldehyde; *N*-(α-aroylbenzylidene)aniline; *N*-phenylbenzimidoyl chloride; benzil; hydrolysis

In the previous paper,[1] we reported that 1,3-dimethylbenzimidazolium iodide (**2**)[2] is an effective catalyst for the preparation of the 4-aroylquinazolines **6**, **7**, and **8** by treatment of the 4-chloroquinazoline **3**, **4**, and **5** with aromatic aldehydes **9** and sodium hydride (NaH) in tetrahydrofuran (THF), as shown in Chart 1. The reaction pathway may be as follows: the aroylation using aromatic aldehydes **9** proceeds through the formation of the key intermediate B-2 *via* the ylide A generated by expulsion of the C^2 hydrogen of **2**. The important intermediate B-2 is equivalent to the aroyl anion ($Ar\bar{C}=O$). Utilization of B-2 for the preparation of aroyl compounds by nucleophilic reaction is a useful method in organic synthesis. It can also be considered that as the structure of 1,3-dimethylimidazolium iodide (**1**)[3] is analogous to **2**, the imidazolium salt **1** acts as a catalyst for nucleophilic aroylation. We therefore tried to extend the new aroylation reaction to the *N*-phenylbenzimidoyl chlorides, whose structures are an open-chain form of the 4-chloroquinazoline ring, and found that the aroylation in the presence of **1** proceeded, resulting in the formation of the *N*-(α-aroylbenzylidene)anilines.

In the present paper, we describe the aroylations of *N*-phenylbenzimidoyl chloride (**10**),[4] *N*-phenyl-*m*-chlorobenzimidoyl chloride (**11**),[5] *N*-phenyl-*p*-chlorobenzimidoyl chloride (**12**),[6] *N*-phenyl-*p*-methoxybenzimidoyl chloride (**13**),[4] and *N*-phenyl-*p*-nitrobenzimidoyl chloride (**14**)[4] with aromatic aldehydes **9** in the presence of **1** as a useful method for the synthesis of the *N*-(α-aroylbenzylidene)anilines, as well as the hydrolysis of the resulting aroyl derivatives for the preparation of benzils.

N-Phenylbenzimidoyl chlorides used in this paper were easily obtained by chlorination of benzanilides according to the reported procedures.[4—6] When a mixture of *N*-phenylbenzimidoyl chloride (**10**), benzaldehyde (**9a**), and NaH was refluxed in THF for 1 h in the presence of a catalytic amount of **1** (1 : 0.33 molar ratio of **10** to **1**), the chlorine atom of **10** was replaced with a benzoyl group, and *N*-(α-benzoylbenzylidene)aniline (**15a**) was obtained in 94% yield. On the other hand, an attempt to conduct the above reaction in the absence of **1** failed, and the benzanilide was obtained in 65% yield. Furthermore, the above reaction in the presence of **1** (1 : 0.1 molar ratio of **10** to **1**) gave the aroylated compound **15a** in 87% yield. These results suggested that the imidazolium salt **1** acts as a catalyst in the aroylation. In order to examine the generality of this nucleophilic aroylation, we carried out the reactions of **10** with various aromatic aldehydes **9** in the presence of **1**. The reaction of **10** with *p*-bromobenzaldehyde (**9b**), *p*-methoxybenzaldehyde (**9c**), *m*-methoxy-

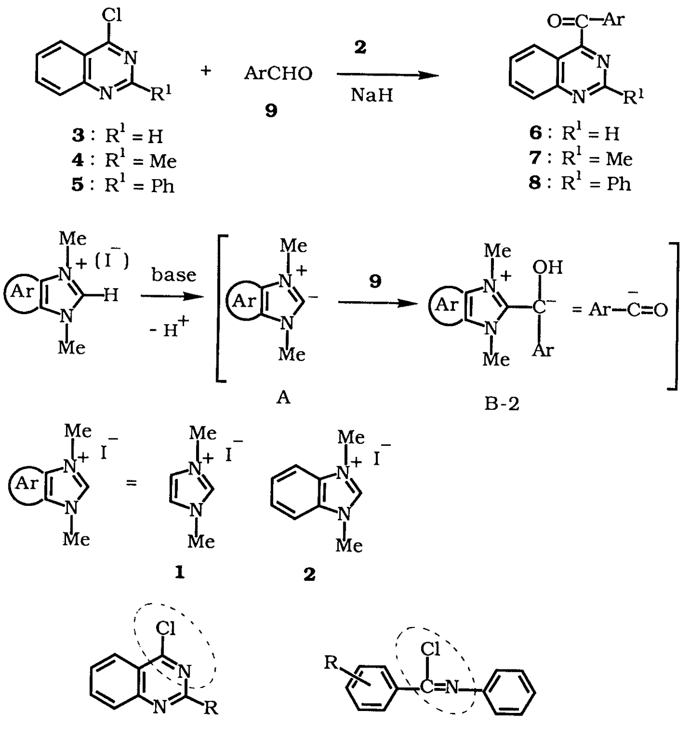


Chart 1

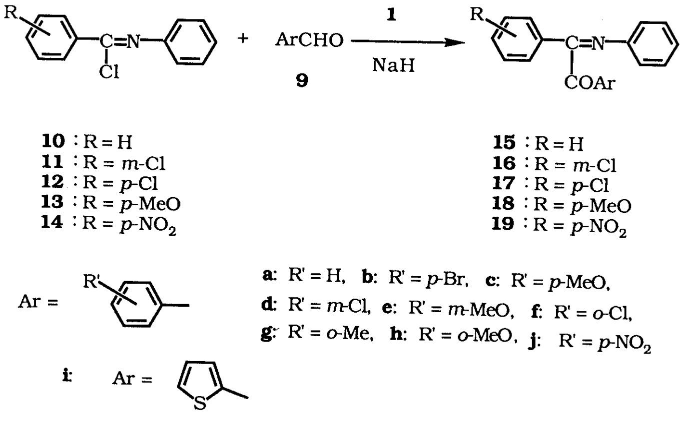


Chart 2

benzaldehyde (**9e**), and 2-thiophenecarboxaldehyde (**9i**) in the presence of **1** in refluxing THF gave the corresponding *N*-(α-aroylbenzylidene)anilines (**15b, 15c, 15e**, and **15i**) in satisfactory yields. The reaction of **10** with **9a** in the presence of **2** gave **15a** in only 1% yield, and benzanilide, a hydrolysis product of **10**, was obtained as the main product (85%).

Next, the above aroylation was extended to **11, 12, 13**, and **14**. When *N*-phenyl-*m*-chlorobenzimidoyl chloride (**11**) was treated with **9a, 9b**, and **9i** in the presence of **1**, the corresponding aroyl compounds **16a, 16b**, and **16i** were formed in good yields. In these cases, the aroylation proceeded at room temperature. The conversion of *N*-phenyl-*p*-chlorobenzimidoyl chloride (**12**) into the corresponding aroyl compounds **17a, 17b, 17c, 17d**, and **17i** was achieved in good yields by treatment with **9a, 9b, 9c**, and *m*-chlorobenzaldehyde (**9d**) in THF catalyzed by **1** at room temperature. The reaction of **12** with *o*-methylbenzaldehyde (**9g**) led to the aroyl compound **17g**, though the yield was low (48%). The low reactivity of *ortho*-substituted benzaldehyde might be caused by steric hindrance by the *ortho*-substituent. The treatment of **13**, which was substituted with a methoxy group at the benzene ring, with **9a, 9b, 9e**, *o*-chlorobenzaldehyde (**9f**), and **9i** in the presence of **1** resulted in aroylation to give the corresponding aroyl compounds **18a, 18b, 18e, 18f**, and **18i**, but the yields were poor. In these cases, the yields were not increased by increasing the reaction time or by using a higher reaction temperature; the low reactivity for the nucleophilic substitution might be caused by the inactivating effect of the methoxy group, which acts as an electron donor to the active carbon of **13**. Nucleophilic aroylation of **13** with *o*-methoxybenzaldehyde (**9h**) failed to afford **18h**. It seemed that aroyl derivatives, which were substituted with electron-donating groups at both benzene rings, could not be obtained or could be obtained only in poor yields. The reaction of **14**, which was substituted with a nitro group on the benzene ring, with **9a, 9b, 9c, 9d, 9g**, and **9i** in the presence of **1** at room temperature gave the corresponding aroyl derivatives **19a, 19b, 19c, 19d, 19g**, and **19i** in excellent yields. Similar treatment of **14** with **9a** using the azolium salt **2** as a catalyst produced **19a**, though in poor yield (4%). The result was similar to that of the reaction of **10** with **9a**.

TABLE I. Aroylation of the Benzimidoyl Chlorides **10**—**14** with Aromatic Aldehydes **9** in the Presence of NaH

Benzimidoyl chloride	Azolium salt	9	Reaction conditions		Product, yield (%)	
			Time (h)	Temp.[a]	Aroyl deriv.	
10	1	**9a**	1	Refl.	**15a**	94
10	2	**9a**	1	Refl.	**15a**	1[b]
10	1	**9b**	1.5	Refl.	**15b**	81
10	1	**9c**	5	Refl.	**15c**	76
10	1	**9e**	5	Refl.	**15e**	65
10	1	**9i**	3	Refl.	**15i**	69
11	1	**9a**	3	R.T.	**16a**	72
11	1	**9b**	2	R.T.	**16b**	84
11	1	**9i**	2	R.T.	**16i**	73
12	1	**9a**	5	R.T.	**17a**	77
12	1	**9b**	3	R.T.	**17b**	78
12	1	**9c**	5	R.T.	**17c**	82
12	1	**9d**	4	R.T.	**17d**	72
12	1	**9g**	4	R.T.	**17g**	48
12	1	**9i**	4	R.T.	**17i**	80
13	1	**9a**	3	Refl.	**18a**	30
13	1	**9b**	5	Refl.	**18b**	26
13	1	**9e**	3	Refl.	**18e**	12
13	1	**9f**	20	Refl.	**18f**	22
13	1	**9h**	28	Refl.	**18h**	—[c]
13	1	**9i**	14	Refl.	**18i**	48
14	1	**9a**	1	R.T.	**19a**	80
14	2	**9a**	1	R.T.	**19a**	4[d]
14	1	**9b**	1	R.T.	**19b**	87
14	1	**9c**	1.5	R.T.	**19c**	89
14	1	**9d**	1	R.T.	**19d**	85
14	1	**9g**	2	R.T.	**19g**	66
14	1	**9i**	1	R.T.	**19i**	87

a) Refl. = reflux, R.T. = room temperature. *b*) Benzanilide was obtained in 85% yield. *c*) *p*-Methoxybenzanilide was obtained in 78% yield. *d*) *p*-Nitrobenzanilide was obtained in 33% yield.

We established a preparative method of *N*-(α-aroylbenzylidene)anilines by the reaction of the *N*-phenylbenzimidoyl chlorides **10**—**14** with aromatic aldehydes **9** in the presence of an azolium salt. Namely, we found that aroylation proceeded in the same way as we had reported for the aroylation of fused diazines.[1,7] The imidazolium salt (**1**) and benzimidazolium salt (**2**) were used as azolium salts, and it was found that their activity as catalysts for

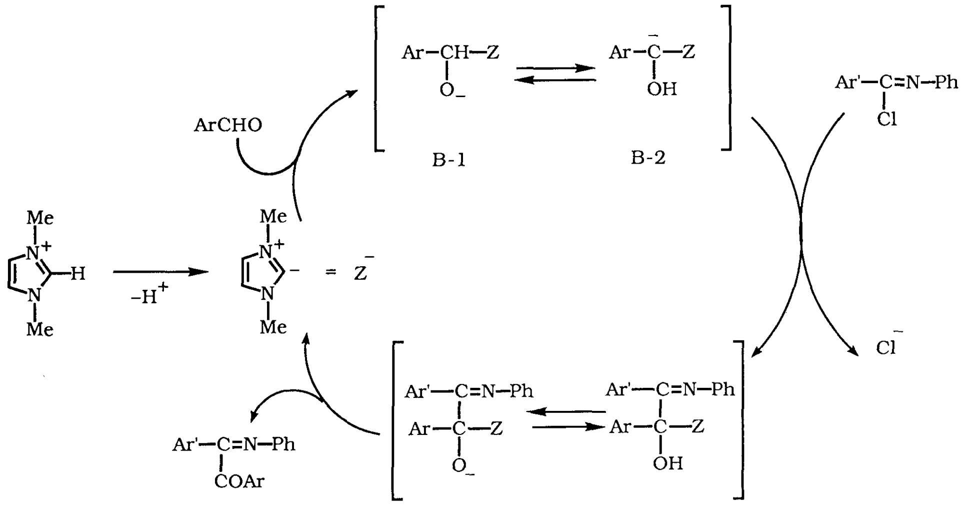
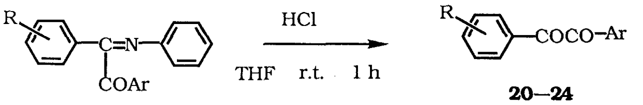


Chart 3

the aroylation of *N*-phenylbenzimidoyl chlorides was pronouncedly different. That is to say, though the aroylation of **10** with **9a** catalyzed by **1** gave the corresponding aroyl compound **15a** in excellent yield (94%), using **2** as a catalyst in the above reaction gave **15a** in only 1% yield. A similar result was observed in the reaction of **14** with **9a**.

As illustrated in Chart 3, the formation of the aroyl derivatives involving the catalytic action of **1** is considered to proceed through a similar process to that reported for the formation of 4-aroylquinazolines.[1] The formation of the aroyl compounds showed that benzimidoyl chloride reacted preferentially with the carbanion B-2 rather than the *O*-anion B-1, as in the case of 4-chloroquinazoline. In the recycling process, 1,3-dimethylimidazolium iodide (**1**) acts as a catalyst.



15—19

20—24

benzil	R	yield (%)	benzil	R	yield (%)
20a	H	98	**22d**	*p*-Cl	80
20b	H	84	**22i**	*p*-Cl	88
20c	H	97	**23a**	*p*-MeO	95
21a	*m*-Cl	98	**23i**	*p*-MeO	78
21b	*m*-Cl	88	**24a**	*p*-NO_2	92
22a	*p*-Cl	90	**24c**	*p*-NO_2	84
22c	*p*-Cl	87	**24g**	*p*-NO_2	90

Chart 4

In order to prepare the benzils, hydrolysis of the *N*-(α-aroylbenzylidene)anilines was carried out, and the benzils **20—24** were obtained by stirring of **15**, **16**, **17**, **18**, and **19** with diluted hydrochloric acid (HCl) at room temperaure for 1 h in good yields. For example, treatment of **15a** with 10% HCl in THF at room temperature for 1 h resulted in hydrolysis to give the benzil (**20a**) in 98% yield. The results are shown in Chart 4. We have thus developed a procedure to obtain benzil derivatives with suitable substituents at both benzene rings in two steps starting from benzimidoyl chlorides. It is well known that benzils having a strongly electron-deficient group, such as a nitro group, on the benzene ring are difficult to prepare. But, using this procedure, we could easily prepare the benzils **20—24** in good yield. Furthermore, 4,4′-dinitrobenzil (**24j**),[13] which has two nitro groups bonded to different benzene rings, was synthesized by catalytic aroylation of *N*-phenyl-*p*-nitrobenzimidoyl chloride (**14**) with 4-nitrobenzaldehyde (**9j**) followed by hydrolysis of the resulting product in 6% overall yield.

The structures of the newly obtained compounds were supported by the elemental analyses or high resolution mass spectra (HRMS), infrared (IR) spectra and proton (^{1}H-) nuclear magnetic resonance (NMR) spectra, as shown in Tables II—IV.

In conclusion, we have established a simple and useful method to prepare benzils with different substituents on the two benzene rings by the catalytic aroylation of

Table II. Melting Points, Mass Spectral Data, and Elemental Analyses for the *N*-(α-Aroylbenzylidene)anilines **15—19**

Compd.	mp (°C)	Formula	Analysis (%) Calcd C	Calcd H	Calcd N	Found C	Found H	Found N	MS *m/z* M^+
15a	108—109 (Yellow prisms)$^{a)}$	$C_{20}H_{15}NO$	84.19	5.30	4.91	83.95	5.13	4.99	285
15b	— (Yellow oil)	$C_{20}H_{14}BrNO$							Calcd: 363.0259 (Found: 363.0248)
15c	76—78 (Yellow plates)$^{a)}$	$C_{21}H_{17}NO_2$	79.98	5.43	4.44	79.99	5.32	4.25	315
15e	109—110 (Yellow prisms)$^{a)}$	$C_{21}H_{17}NO_2$	79.98	5.43	4.44	79.70	5.41	4.50	315
15i	122—123 (Yellow prisms)$^{a)}$	$C_{18}H_{13}NOS$	74.20	4.50	4.81	73.97	4.45	4.89	291
16a	98—100 (Yellowish columns)$^{a)}$	$C_{20}H_{14}ClNO$	75.12	4.41	4.38	75.10	4.20	4.42	319
16b	— (Yellow oil)	$C_{20}H_{13}BrClNO$							Calcd: 396.9870 (Found: 396.9883)
16i	114—115 (Brown needles)$^{a)}$	$C_{18}H_{12}ClNOS$	66.36	3.71	4.30	66.44	3.56	4.17	325
17a	106—107 (Yellow columns)$^{a)}$	$C_{20}H_{14}ClNO$	75.12	4.41	4.38	74.82	4.24	4.08	319
17b	210—212 (Yellow plates)$^{a)}$	$C_{20}H_{13}BrClNO$	60.25	3.29	3.51	60.02	3.20	3.22	397
17c	— (Yellow oil)	$C_{21}H_{16}ClNO_2$							Calcd: 349.0869 (Found: 349.0849)
17d	— (Yellow oil)	$C_{20}H_{13}Cl_2NO$							Calcd: 353.0374 (Found: 353.0378)
17g	141—143 (Yellow scales)$^{a)}$	$C_{21}H_{16}ClNO$	75.56	4.83	4.20	75.40	4.67	4.15	333
17i	85—88 (Yellow scales)$^{a)}$	$C_{18}H_{12}ClNOS$	66.36	3.71	4.30	66.14	3.58	4.14	325
18a	114—116 (Yellow prisms)$^{b)}$	$C_{21}H_{17}NO_2$	79.98	5.43	4.44	79.77	5.31	4.35	315
18b	137—139 (Yellow needles)$^{b)}$	$C_{21}H_{16}BrNO_2$	63.97	4.09	3.55	63.72	4.04	3.41	393
18e	128—130 (Yellow needles)$^{a)}$	$C_{22}H_{19}NO_3$	76.50	5.54	4.06	76.39	5.55	3.91	345
18f	97—98 (Yellow plates)$^{a)}$	$C_{21}H_{16}ClNO_2$	72.10	4.61	4.00	72.10	4.36	3.82	349
18i	126—128 (Brown plates)$^{a)}$	$C_{19}H_{15}NO_2S$	71.01	4.70	4.36	70.91	4.69	4.30	321
19a	136—137 (Yellowish orange prisms)$^{a)}$	$C_{20}H_{14}N_2O_3$	72.72	4.27	8.48	72.51	4.19	8.47	330
19b	184—185 (Yellow plates)$^{a)}$	$C_{20}H_{13}BrN_2O_3$	58.70	3.20	6.85	58.63	3.07	6.85	408
19c	98—100 (Yellow needles)$^{a)}$	$C_{21}H_{16}N_2O_4$	69.99	4.48	7.77	69.79	4.41	7.67	360
19d	122—123 (Yellow plates)$^{a)}$	$C_{20}H_{13}ClN_2O_3$	65.85	3.59	7.68	65.71	3.44	7.58	364
19g	143—144 (Yellow prisms)$^{a)}$	$C_{21}H_{16}N_2O_3$	73.24	4.68	8.13	73.49	4.51	8.08	344
19i	122—123 (Yellow columns)$^{a)}$	$C_{18}H_{12}N_2O_3S$	64.27	3.60	8.33	64.11	3.39	8.30	336

a) Recrystallized from isopropyl ether (IPE). *b*) Recrystallized from MeOH.

TABLE III. IR and ^{1}H-NMR Spectral Data for the *N*-(α-Aroylbenzylidene)anilines **15**—**19**

Compd.	IR ν_{max}^{KBr} cm^{-1}	^{1}H-NMR ($CDCl_3$) δ (ppm)
15a	1660 (CO)	6.67—7.94 (15H, m, aromatic H)
15b	1670 (CO)[j]	6.72—7.80 (12H, m, aromatic H), 7.80—8.14 (2H,[a] m)
15c	1660 (CO)	3.79 (3H, s, OMe), 6.78 (2H,[b] d, *J*=8.6), 6.50—7.57 (8H, m, aromatic H), 7.73 (2H,[c] d, *J*=8.6), 7.57—8.01 (2H,[a] m)
15e	1660 (CO)	3.60 (3H, s, OMe), 6.73—7.70 (12H, m, aromatic H), 7.70—8.09 (2H,[a] m)
15i	1640 (CO)	6.65—7.78 (11H, m, aromatic H), 7.78—8.09 (2H,[a] m)
16a	1665 (CO)	6.73—7.94 (13H, m, aromatic H), 8.00 (1H,[d] br s)
16b	1670 (CO)[j]	6.70—7.84 (12H, m, aromatic H), 7.98 (1H,[d] br s)
16i	1650 (CO)	6.68—7.95 (11H, m, aromatic H), 8.02 (1H,[d] br s)
17a	1670 (CO)	6.72—7.96 (12H, m, aromatic H), 7.85 (2H,[e] d, *J*=8.5)
17b	1670 (CO)	6.75—7.43 (5H, m, N-Ph), 7.41 (2H,[f] d, *J*=8.5), 7.54 (4H,[g] br s), 7.83 (2H,[e] d, *J*=8.5)
17c	1660 (CO)[j]	3.81 (3H, s, OMe), 6.59—7.25 (7H, m, N-Ph and 2H[b]), 7.41 (2H,[f] d, *J*=8.5), 7.74 (2H,[c] d, *J*=9.0), 7.85 (2H,[e] d, *J*=8.5)
17d	1675 (CO)[j]	6.77—8.13 (11H, m, aromatic H), 7.87 (2H,[e] d, *J*=8.5)
17g	1675 (CO)	2.42 (3H, s, Me), 6.67—7.71 (11H, m, aromatic H), 7.87 (2H,[e] d, *J*=8.5)
17i	1635 (CO)	6.50—7.72 (10H, m, aromatic H), 7.86 (2H,[e] d, *J*=8.5)
18a	1665 (CO)	3.85 (3H, s, OMe), 6.61—8.02 (14H, m, aromatic H)
18b	1675 (CO)	3.84 (3H, s, OMe), 6.70—8.12 (13H, m, aromatic H)
18e	1665 (CO)	3.76 (3H, s, OMe), 3.84 (3H, s, OMe), 6.68—7.68 (11H, m, aromatic H), 7.81 (2H,[c] d, *J*=8.5)
18f	1685 (CO)	3.85 (3H, s, OMe), 6.58—7.50 (11H, m, aromatic H), 7.90 (2H,[c] d, *J*=8.5)
18i	1645 (CO)	3.84 (3H, s, OMe), 6.73—7.70 (10H, m, aromatic H), 7.87 (2H,[c] d, *J*=8.5)
19a	1675 (CO), 1515, 1350 (NO_2)	6.77—7.94 (10H, m, aromatic H), 8.04 (2H,[h] d, *J*=8.5), 8.29 (2H,[i] d, *J*=8.5)
19b	1670 (CO), 1515, 1340 (NO_2)	6.76—7.46 (5H, m, N-Ph), 7.54 (4H,[g] br s), 8.05 (2H,[h] d, *J*=8.5), 8.34 (2H,[i] d, *J*=8.5)
19c	1665 (CO), 1515, 1350 (NO_2)	3.82 (3H, s, OMe), 6.72—7.40 (7H, m, aromatic H), 7.72 (2H,[c] d, *J*=9), 8.06 (2H,[h] d, *J*=8.5), 8.29 (2H,[i] d, *J*=8.5)
19d	1665 (CO), 1520, 1350 (NO_2)	6.74—7.85 (9H, m, aromatic H), 8.06 (2H,[h] d, *J*=8.5), 8.34 (2H,[i] d, *J*=8.5)
19g	1665 (CO), 1515, 1350 (NO_2)	2.47 (3H, s, Me), 6.73—7.60 (9H, m, aromatic H), 8.12 (2H,[h] d, *J*=8.5), 8.37 (2H,[i] d, *J*=8.5)
19i	1650 (CO), 1520, 1345 (NO_2)	6.73—7.87 (8H, m, aromatic H), 8.12 (2H,[h] d, *J*=8.5), 8.34 (2H,[i] d, *J*=8.5)

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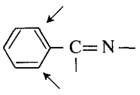

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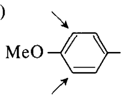

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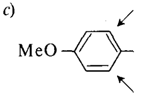

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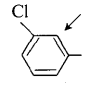

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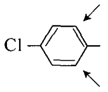

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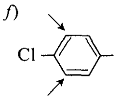

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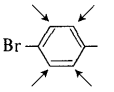

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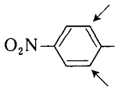

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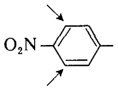


j) ν_{max}^{neat} cm^{-1}

TABLE IV. Melting Points, Mass Spectral Data, and Elemental Analyses for the Benzils **20**—**24**

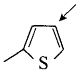
Compd.	mp (°C)	Formula	Analysis (%) Calcd C	Calcd H	Calcd N	Found C	Found H	Found N	MS *m/z* M$^+$
20a	94—96 (lit.[8] 95)	$C_{14}H_{10}O_2$							
20b	84—85 (lit.[9] 86.5)	$C_{14}H_9BrO_2$							
20c	63—65 (lit.[10] 64—65)	$C_{15}H_{12}O_3$							
21a	86—88 (lit.[11] 87—88)	$C_{14}H_9ClO_2$							
21b	131—132[a,c]	$C_{14}H_8BrClO_2$	51.97	2.49		51.96	2.40		322
22a	70—72 (lit.[9] 73)	$C_{14}H_9ClO_2$							
22c	128—129 (lit.[12] 126—128)	$C_{15}H_{11}ClO_3$							
22d	121—122[a,b]	$C_{14}H_8Cl_2O_2$	60.24	2.89		60.21	2.82		278
22i	98—100[a,c]	$C_{12}H_7ClO_2S$	57.49	2.81		57.49	2.88		250
23a	63—65 (lit.[9] 64—65)	$C_{15}H_{12}O_3$							
23i	53—54[a,b]	$C_{13}H_{10}O_3S$	63.40	4.09		63.53	4.08		246
24a	141—142 (lit.[11] 142)	$C_{14}H_9NO_4$							
24c	158—159 (lit.[12] 155—156)	$C_{15}H_{11}NO_5$							
24g	122—123[a,b]	$C_{15}H_{11}NO_4$	66.91	4.12	5.20	66.95	4.17	5.18	269

a) Recrystallized from EtOH. *b)* Yellow needles. *c)* Yellowish brown columns.

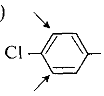
Table V. IR and ^{1}H-NMR Spectral Data for the Benzils **21**—**24**

Compd.	IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}	^{1}H-NMR (CDCl$_3$) δ (ppm)
21b	1660 (CO)	7.38—8.12 (8H, m, aromatic H)
22d	1660 (CO)	7.28—8.07 (8H, m, aromatic H)
22i	1665 (CO), 1640 (CO)	7.09—7.33 (1H,[a] m), 7.47 (2H,[b] d, J=9.0), 7.85 (2H,[c] d, J=3.8), 8.01 (2H,[d] d, J=9.0)
23i	1640 (CO)	3.92 (3H, s, OMe), 7.01 (2H,[e] d, J=9.2), 7.03—7.38 (1H,[a] m), 7.85 (2H,[c] d, J=3.8), 8.07 (2H,[f] d, J=9.2)
24g	1655 (CO), 1525, 1345 (NO$_2$)	2.76 (3H, s, Me), 7.14—7.89 (4H, m, aromatic H), 8.20 (2H,[g] d, J=9.0), 8.43 (2H,[h] d, J=9.0)

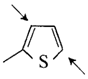
a)



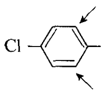
b)



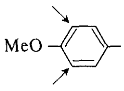
c)



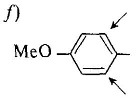
d)



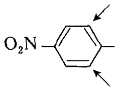
e)



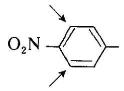
f)



g)



h)



N-phenylbenzimidoyl chlorides with aromatic aldehydes followed by hydrolysis. The imidazolium salt (**1**) is an effective catalyst for this aroylation of *N*-phenylbenzimidoyl chlorides.

Experimental

All melting points are uncorrected. IR absorption spectra were recorded on a Jasco A-102 diffraction grating IR spectrometer. ^{1}H-NMR spectra were measured at 60 MHz on a JEOL PMX60SI NMR spectrometer. Chemical shifts are quoted in parts per million (ppm) with tetramethylsilane (TMS) as an internal standard, and the coupling constants (J) are given in hertz (Hz). The following abbreviations are used: s = singlet, m = multiplet, and br s = broad singlet. Positive mass spectra (MS) and HRMS were recorded on a JEOL JMX-DX303 mass spectrometer by a direct inlet method. Column chromatography was carried out on silica gel (Wakogel C-200). *N*-Phenylbenzimidoyl chlorides **10**,[4] **11**,[5] **12**,[6] **13**,[4] and **14**,[4] and 1,3-dimethylimidazolium iodide (**1**)[3] and 1,3-dimethylbenzimidazolium iodide (**2**)[2] were prepared by the reported procedures.

Reaction of the *N*-Phenylbenzimidoyl Chlorides 10, 11, 12, 13, and 14 with Aromatic Aldehydes 9 in the Presence of NaH Catalyzed by 1,3-Dimethylimidazolium Iodide (1) General Procedure: A stirred solution of a *N*-phenylbenzimidoyl chloride (**10**, **11**, **12**, **13** or **14**, 3.0 mmol), an aromatic aldehyde (**9**, 3.3 mmol) and 1,3-dimethylimidazolium iodide (**1**, 1.0 mmol) in THF (20 ml) was treated with NaH (60% in oil, 3.3 mmol), and then the mixture was stirred under appropriate conditions (the reaction conditions are shown in Table I). The solvent was evaporated off under reduced pressure and ice-water was poured onto the residue. Then the mixture was extracted with ether (100 ml × 2). The organic layer was dried over MgSO$_4$ and concentrated to dryness. The residue was chromatographed on a column of silica gel with CHCl$_3$, which gave the corresponding aroyl compound (yields, recrystallization solvents, melting points and spectral data are shown in Table I—III).

In the reaction of **10** with **9a** in the absence of the catalyst **1**, the fraction eluted with CHCl$_3$ gave benzanilide in 65% (384 mg) yield. In the reaction (1 : 0.1 molar ratio of **10** to **1**) of **10** with **9a** catalyzed by **1** (0.3 mmol), the fraction eluted with CHCl$_3$ gave **15a** in 87% (744 mg) yield. In the the reaction of **10** with **9a** catalyzed by 1,3-dimethylbenzimidazolium iodide (**2**, 1.0 mmol), the fraction eluted with CHCl$_3$ gave **15a** (9 mg, 1%) and benzanilide (500 mg, 85%). In the reaction of **13** with **9h** catalyzed by **1**, the fraction eluted with CHCl$_3$ gave *p*-methoxybenzanilide (530 mg, 78%). In the reaction of **14** with **9a** catalyzed by **2**, the fraction eluted with CHCl$_3$ gave **19a** (42 mg, 4%) and *p*-nitrobenzanilide (236 mg, 33%).

Hydrolysis of *N*-(α-Aroylbenzylidene)anilines 15, 16, 17, 18, and 19 with HCl General Procedure: An *N*-(α-aroylbenzylidene)aniline (**15**—**19**, 100 mg) was dissolved in THF (10 ml) and 10% HCl (1 ml), and the solution was stirred at room temperature for 1 h. The solvent was evaporated off under reduced pressure, and the residue was recrystallized to give the corresponding benzil derivative (yields, recrystallization solvents, melting points and spectral data are shown in Chart 3 and Tables IV and V).

4,4′-Dinitrobenzil[13] Sodium hydride (60% in oil, 3.3 mmol) was added to a solution of *N*-phenyl-*p*-nitrobenzimidoyl chloride (**14**, 3.0 mmol), *p*-nitrobenzaldehyde (**9j**, 3.3 mmol), and **1** (224 mg, 1.0 mmol) in 20 ml of THF, and the solution was stirred at room temperature for 3 h. The reaction mixture was worked up as described above. The first fraction eluted with CHCl$_3$ gave *N*-[α-(4-nitrobenzoyl)-4-nitrobenzylidene]aniline in 7% (83 mg) yield and the second fraction gave *p*-nitrobenzanilide in 52% (380 mg) yield. Treatment of the resulting product with 10% HCl (1 ml) in THF (10 ml) gave 4,4′-dinitrobenzil (**24j**)[13] in 78% (47 mg) yield.

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