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An effective synthesis of *N*,*N*-dimethylamides from carboxylic acids and a new route from *N*,*N*-dimethylamides to 1,2-diaryl-1,2-diketones

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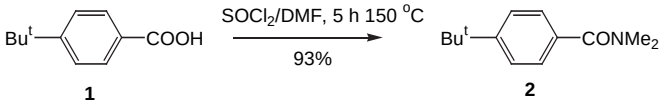
ABSTRACT

Carboxylic acids were heated at 150 °C in DMF in the presence of 1.25 equiv of thionyl chloride to give corresponding *N*,*N*-dimethylamides in good yields. Tandem chlorination and amidation reactions occurred in the one-pot procedure. Dicarboxylic acids needed prolonged reaction time to produce bisamides in good yields. Some benzamides were efficiently converted into corresponding 1,2-diaryl-1,2-diketones (benzils) under acyloin condensation conditions in the presence of 4,4′-di-*tert*-butylbiphenyl (DBB) in THF. Ultrasonic irradiation effectively accelerates the reaction, but it is not critical. However, the presence of DBB is fatal to the reaction. Although a few synthetic methods for benzils from benzoic acids have been reported so far, this method is one of the most convenient and highly reproducible procedures.

1. Introduction

N,*N*-Dialkylamides are versatile synthetic building blocks. For example, reactions of organolithiums or Grignard reagents with *N*,*N*-dimethylformamide (DMF) afforded corresponding aldehydes upon acidic hydrolysis.[1] A key point of this reaction is that intermediacy formed *N*,*N*-dimethylaminoalkoxides are stable under the basic condition to interrupt further reaction. By using this feature, *N*,*N*-dialkylcarbamates and *N*,*N*-dialkylamides are employed for the synthesis of symmetric and asymmetric ketones, respectively.[1] Previously we reported another synthetic utility of aminoalkoxides; quenching them with cyclopentadiene in place of acidic hydrolysis furnished 6-mono- or 6,6-disubstituted pentafulvenes in moderate to high yields.[2,3]

N,*N*-Dimethylbenzamide is readily prepared by heating commercially available benzoyl chloride at 150 °C in DMF for 4 h.[4] However, most acid chlorides need to be prepared from corresponding carboxylic acids by using chlorination reagents such as thionyl chloride. The Vilsmeier complex generated from *N*,*N*-dimethylformamide (DMF) and thionyl chloride is known as a good reagent for chlorination of carboxylic acids.[5] In general, the chlorination was carried out at 80–85 °C for 2.5 h in DMF. In this case, DMF served as a solvent. If the resulting reaction mixture is subsequently heated at 150 °C, the amidation should occur in one flask. Actually, a DMF solution of 4-*tert*-butylbenzoic acid (**1**) was heated with thionyl chloride at 150 °C for 5 h to afford *N*,*N*-dimethyl-4-*tert*-butylbenzamide (**2**)[6] in 93% upon a usual aqueous work-up (Scheme 1). Then, we examined the amidation of various carboxylic acids under the one-pot conditions.



1 **2**

Scheme 1. One-pot synthesis of **2** from **1**.

Karaman and Fry reported that treatment of aryl carboxylic acids with lithium in the presence of 4,4′-di-*tert*-butylbiphenyl (DBB) in THF under ultrasonic irradiation furnished corresponding 1,2-diarylethane-1,2-diones (benzils) in good yields through the acyloin type reaction mechanism.[7] However, the reactions were not highly reproducible,[8] and they required impractically long irradiation time (17 h–5 days). When the analogous procedure using *N*,*N*-dimethylamides **2** was examined, the metal reduction

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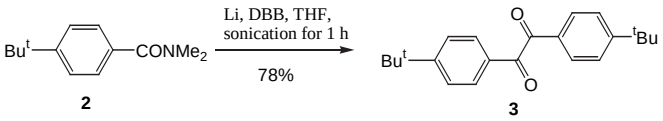
underwent smoothly and rapidly (1 h), and the yield of **3** went up to 78% (Scheme 2). Despite two-step procedures, thus, we can establish a new and effective route from benzoic acids to benzils.[9] Here we report some details of the procedures.



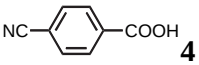
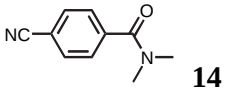
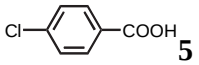
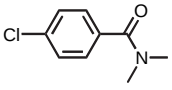
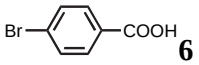
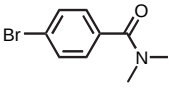
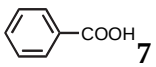
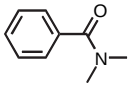
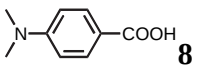
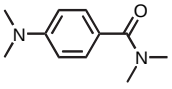
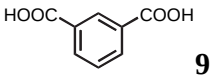
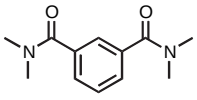
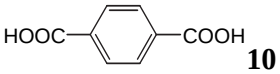
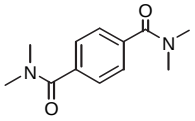
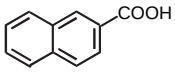
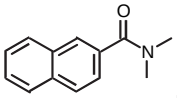
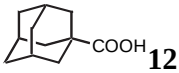
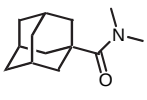
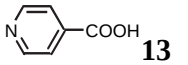
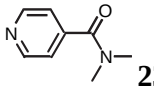
Scheme 2. Alkali metal deduction of **2** to **3**.

2. Results and discussion

2.1. One-pot synthesis of *N*,*N*-dimethylamides

The results of the amidation are summarized in Table 1. The reaction of benzoic acid derivatives **4**–**7** except *p*-dimethylamino-benzoic acid (**8**) smoothly underwent to afford corresponding *N*,*N*-dimethylamides **14**–**17** (run 1–4). The yield of **18** from **8** was relatively low, although **8** disappeared and no other isolable products were obtained. Polymerization would occur under the conditions (run 5). The amination reaction of *iso*- and tere-phthalic acids (**9**) and (**10**) were examined under the conditions. The yields of phthalamides **19** and **20** are relatively low (<30%) probably due to poor solubility of the acids in DMF. When the reaction times were prolonged, the yields went up to 71% yields, respectively (run

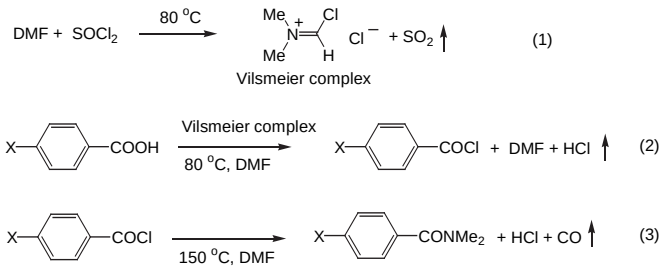
Table 1
One-pot synthesis of *N*,*N*-dimethylamides **14**–**23** from carboxylic acids **4**–**13**

Run	Substrate	Product	Ref.	Yeild %
1	 **4**	 **14**	10	73
2	 **5**	 **15**	11	64
3	 **6**	 **16**	10	82
4	 **7**	 **17**	6	68
5	 **8**	 **18**	10	34
6[a]	 **9**	 **19**	12	71
7[b]	 **10**	 **20**	13	71
8	 **11**	 **21**	6	89
9	 **12**	 **22**	14	71
10	 **13**	 **23**	15	42

[a] The reaction was carried out for 24 h.
[b] The reaction was carried out for 15 h.

6 and 7). The reactions of 2-naphthalenecarboxylic acid (**11**) and 1-adamantanecarboxylic acid (**12**) successfully produced dimethylamides **21** and **22** in good yields (run 8 and 9). On the other hand, the yield of *N*,*N*-dimethylisonicotinamide (**23**) was not so high because of high water solubility of **23** (run 10). This procedure cannot avoid aqueous quenching and neutralization in aqueous media to isolate **23** from the reaction mixture. Thus, the result pointed out a disadvantage of this procedure.

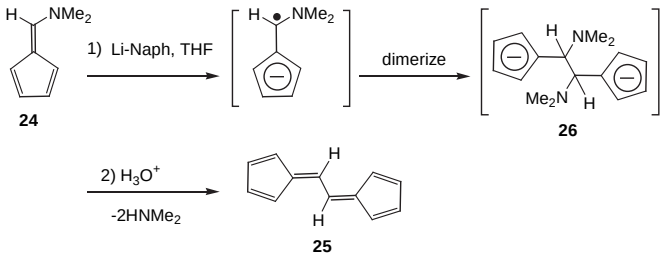
A proposed mechanism of the amination was shown in Scheme 3. First, the Vilsmeier complex generated from DMF and thionyl chloride at 80 °C in DMF. Second, the Vilsmeier complex acted as a reagent for chlorination of benzoic acids.[5] Third, the amino transfer reaction between benzoyl chlorides and DMF would occur at 150 °C.[4] Decomposition of DMF should occur under the conditions. But, the participation of free dimethylamine in this reaction would be negligible because of the low boiling point (5 °C).



Scheme 3. A proposed mechanism of the one-pot amination.

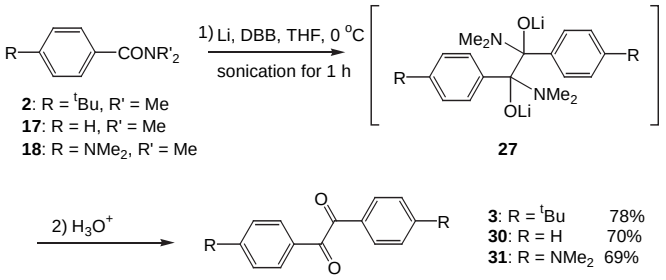
2.2. Metal reduction of *N*,*N*-dimethylamides

Previously, we have reported that metal reduction of 6-*N*,*N*-dimethylaminopentafulvene **24** with lithium naphthalene afforded 6,6-bifulvenyl **25** in good yield (Scheme 4).[16] This reaction mechanism is analogous to that of acyloin condensation. But, the intermediacy formed biscyclopentadienide ion **26** does not undergo the elimination of dimethylamino groups. The fulvene π-systems eventually regenerate upon an aqueous work-up. Low elimination ability of dimethylamino group is a key point of the reaction to maintain the highly reductive pentafulvene skeleton. Analogous to the mechanism, metal reduction of *N*,*N*-dimethylamides should produce the bis-aminoalkoxide **27** as an intermediate via radical coupling of initially formed ketyl radical. Since the elimination of dimethylamino groups of **27** would not occur under the condition, further reduction similar to the acyloin condensation should be prevented. So, we examined the metal reduction of *N*,*N*-dimethyl-4-*tert*-butylbenzamide **2** (Scheme 5).



Scheme 4. Reaction mechanism of metal reduction of 6-*N*,*N*-dimethylaminopentafulvene **24**.

Table 2 summarized the reaction conditions and yields of 1,2-bis(4-*tert*-butylphenyl)ethane-1,2-dione (**3**).[17] At first, we employed naphthalene (15 mol %) as an electron transfer reagent (run 1). This



Scheme 5. A new route for benzils, **3**, **30**, and **31**.

case, **2** recovered in 76% upon usual aqueous work up, while naphthalene consumed completely. Thus, naphthalene is not suitable for this purpose. In the presence of DBB (run 2), the solution immediately turned to yellow after starting ultrasonic irradiation, which indicated that the reaction started off. The color of the solution changed to yellow, red, purple, and black within the first 30 min. A TLC monitoring indicated that the starting material disappeared completely upon 1 h irradiation. The sonication accelerates the reaction well, but it is not critical, because all the starting material consumed upon simply stirring for 3 h at room temperature to yield **3** in 68% yield (run 4). However, the presence of DBB is critical. When a THF solution of **2** was stirred with lithium for 20 h, the reaction did not start at all (run 5). Ultrasonic irradiation for 12 h provided **3** in 32% yield with considerable amount of recovery (run 6).

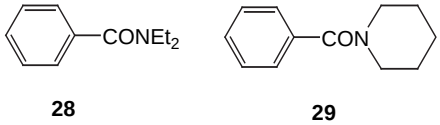
Table 2
Reactions of **2** with lithium under the conditions

Run	Additive	Conditions	Yields of **3** (%)
1	Naphthalene	Sonicated for 1.0 h	0[a]
2	DBB	Sonicated for 0.5 h	73
3	DBB	Sonicated for 1 h	78
4	DBB	Stirred for 3 h	68
5	None	Stirred for 20 h,	0
6	None	Sonicated for 12 h	32[b]

[a] Starting material recovered in 76%.
[b] Starting material recovered in 29%.

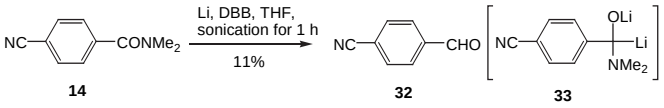
To search the scope and limitation of the reaction, we have examined the reaction of several benzamides. The reductions of *N*,*N*-diethylbenzamide **28** and *N*-benzoylpiperidine **29** (Scheme 6) were examined under same conditions of run 3 in Table 2. Both cases provided benzil **30** in low yields (10–15%) with considerable amount of recovery. The results indicate that the presence of bulky substituents hampered a rapid progress of this reaction. Thus, the dimethylamino group is suitable for this reaction. The reactions of *N*,*N*-dimethylbenzamides **17** and **18**, smoothly proceeded to give benzil **30** and its derivative **31**[18] in good yields, respectively. On the other hand, 4-cyanobenzamide **14** bearing an electron withdrawing group furnished 4-cyanobenzaldehyde **32**[19] in 11%. The metal reduction would form corresponding dianion **33** due to the electron withdrawing property of cyano group. An

Chart. 1



Scheme 6.

acidic work-up resulted in the elimination of dimethylamine to yield aldehyde **32** (Scheme 7).



14 32 33

Scheme 7. Alkali metal reduction of **14** to form **32** via corresponding dianion **33**.

4-Chloro- and 4-bromo-benzamides, **15**, and **16**, underwent reductive dehalogenation to produce benzil **30** in 13 and 64% yields, respectively. Since the starting materials were not recovered, polymerization would take place as a competitive reaction. Bis (dimethylamides) **19** and **20** are sparingly soluble in THF. Then, even upon 8 h irradiation, no reaction occurred at all. On the other hand, the metal reduction of 2-naphthylcarbamide **21** readily occurred even without DBB. Upon 30 min irradiation, all starting material disappeared, and unidentified products were obtained alone. When the reaction was quenched after 5 min irradiation, desired 1,2-bis(2-naphthyl)ethane-1,2-dione (**34**)[20] was yielded in 18% together with 65% of recovery. Over reduction should occur under the condition. Isonicotinic amide **22** and adamantanecarbamide **23** were recovered unchangedly, probably due to high LUMO energy of these compounds.

3. Conclusion

A new and efficient synthetic procedure for *N*,*N*-dimethylamides from corresponding carboxylic acids were established. Chlorination and amidation of carboxylic acid subsequently occured in one-pot manner. Various monocarboxylic acids involving an aliphatic carboxylic acid afforded corresponding *N*,*N*-dimethylamides in good yields. On the other hand, dicarboxylic acids needed prolonged reaction times to gain sufficient yields. Moreover, *p*-alkyl and *p*-dimethylaminobenzamides can be converted into corresponding 1,2-diaryl-1,2-diketones (benzils) by an alkali metal reduction in the presence of 4,4′-di-*tert*-butylbiphenyl (DBB) in THF. Ultrasonic irradiation effectively accelerates the reaction. Although various synthetic methods for 1,2-diaryl-1,2-diketones have been reported so far, this method is one of the simplest and highly economic procedures. On the other hand, the reactions of *p*-chloro- and *p*-bromobenzamides underwent reductive dehalogenation to afford benzyl upon an aqueous work-up. The reactions of *iso*- and tere-phthalic bisamides, isonicotinamide, and adamantanecarbamide did not take place. Low solubility and/or relatively high reduction potentials of these compounds would prevent the reaction progress.

4. Experimental

4.1. General

All the reactions dealing with air or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of nitrogen. Air- and moisture-sensitive liquids and solutions were transferred via syringe. Analytical thin-layer chromatography was performed using glass plates pre-coated with Merck Art. 7730 Kieselgel 60G F-254. Thin layer chromatography plates were visualized by exposure to ultraviolet light (UV). Organic solutions were concentrated by rotary evaporation at ca. 15 Torr using a diaphragm pump. Column chromatography was performed with Merck Kiesel-gel 60 and Merck Art. 1097 Alminiumoxid 90 (Aktivitatss fufe II–III).

All reagents were purchased from Tokyo Kasei Co., Nakarai Tesc., Wako Co. and other commercial suppliers and were used as supplied unless otherwise stated. Granular lithium (granule 99.9+%) was purchased from Aldrich Co.. THF was distilled from sodium/benzophenone at 760 Torr under a nitrogen atmosphere before used. *N*,*N*-Diethylbenzamide **28** and *N*-benzoylpiperidine **29** were prepared from benzoyl chloride and corresponding amines as reported.[21]

^{1}H NMR spectra (tetramethylsilane; 0 ppm as an internal standard) were recorded on JEOL lambda-500, JEOL JNM-GSX-400, and JEOL EX-270 apparatus. The chemical shifts are given in parts per million. IR spectra were obtained from JASCO FTIR-460K2 spectrometer. Ultrasonic irradiations were performed with BRANSON 5200 Ultrasonic Cleaner.

4.2. General procedure for preparation of *N*,*N*-dimethylamides

A solution of 4-*tert*-butylbenzoic acid **1** (356 mg, 2.0 mmol) and thionyl chloride (0.18 mL, 2.5 mmol) in dry DMF (20 mL) was heated at 150 °C under N_2 and stirred for 5 h. The color of the solution gradually turned to dark red. The resulting solution was cooled to room temperature and quenched with water (30 mL). The reaction mixture was extracted with ethyl acetate (100 mL) twice. The combined organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. The filtrate was evaporated, and the residue was charge on silica gel column chromatography (30 g) to give dimethylamide **2** (388 mg) from a hexane/ethyl acetate (1:1) elution in 93% yield. The yields of products **14**–**23** were listed in Table 1. Their physical and spectral data were consistent with the reported ones.

*4.2.1. N,N-Dimethyl-4-tert-butylbenzamide (**2**)*[10]. Colorless crystals: mp 84–85 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.38 (d, J=8.5 Hz, 2H), 7.33 (d, J=8.5 Hz, 2H), 3.02 (br s, 3H), 3.00 (br s, 3H), 1.30 (s, 9H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 171.74, 152.65, 133.35, 126.90, 125.14, 39.64, 35.30, 34.70, 31.16; IR (KBr) ν 2964s, 1624s, 1491m, 1388s, 1266m, 1113m, 1079m, 855m, 771m, 716m, 580m, 505m cm^{-1}.

*4.2.2. N,N-Dimethyl-4-cyanobenzamide **14***[6]. Yield (73%). Colorless solid; mp 99–100 °C; bp 180–190 °C (10 mmHg; Kugelrohr distillation); ^{1}H NMR (270 MHz, $CDCl_3$) δ/ppm 7.74–7.71 (m, *AA*′′BB′′, 2H), 7.55–7.52 (m, AA′*BB*′, 2H), 3.13 (s, 3H), 2.96 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.32, 140.69, 132.23, 127.69, 118.10, 112.97 39.21, 35.15; IR (KBr) ν 2939w, 2230m, 1636s, 1483m, 1491m, 1400s, 1267m, 1082m, 853m, 762m cm^{-1}; MS (EI) m/z (rel intensity) 174 (M^+, 29), 173 [$(M-1)^+$, 59], 130 ([$(M+H)-NMe_2$]$^+$, 100).

*4.2.3. N,N-Dimethyl-4-chlorobenzamide **15***[11]. Yield (64%). Colorless solid; 56–57 °C; bp 160–170 °C (10 mmHg; Kugelrohr distillation); ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm 7.41–7.34 (m, 4H), 3.10 (s, 3H), 3.07 (s, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 170.47, 135.52, 134.66, 128.62, 128.59, 39.53, 35.38; IR (KBr) ν 3049w, 2932w, 1624s, 1481m, 1394s, 1090s, 850s, 758m, 556m cm^{-1}; MS (EI) m/z (rel intensity) 184 [(M (^{37}Cl)$-1)^+$, 8], 185 [M (^{35}Cl)$^+$, 14],184 [(M (^{35}Cl)$-1)^+$, 43], 141 ([M (^{37}Cl)$-NMe_2$]$^+$, 28), 139 ([M (^{35}Cl)$-NMe_2$]$^+$, 100).

*4.2.4. N,N-Dimethyl-4-bromobenzamide **16***[10]. Yield (82%). Colorless solid; 76–77 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm 7.55–7.53 (m, *AA*′′BB′′, 2H), 7.31–7.29 (m, AA′*BB*′, 2H), 3.10 (s, 3H), 2.98 (s, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 170.48, 135.11, 131.55, 128.82, 123.77, 39.53, 35.39; IR (KBr) ν 3045w, 2932w, 1622s, 1479m, 1394s, 1084m, 846m, 756m cm^{-1}; MS (EI) m/z (rel intensity) 229 [M (^{81}Br)$^+$, 19], 228 [(M (^{81}Br)$-1)^+$, 55], 227 [M (^{79}Br)$^+$, 21], 226 [(M (^{79}Br)$-1)^+$, 55], 185 ([M (^{81}Br)$-NMe_2$]$^+$, 98), 183 ([M (^{79}Br)$-NMe_2$]$^+$, 100).

*4.2.5. N,N-Dimethylbanzamide **17***[6]. Yield (52%). Colorless solid; 40 °C; bp 160–170 °C (10 mmHg; Kugelrohr distillation); ^{1}H NMR (270 MHz, $CDCl_3$) δ/ppm 7.46–7.36 (m, 5H), 3.10 (s, 3H), 2.97 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 171.29, 136.25, 129.33, 128.17,

126.87, 39.35, 35.08; IR (KBr) ν 2935w, 1631s, 1578m, 1506m, 1483m, 1447m, 1396s, 1265m, 1085m, 1074m, 791m, 716m, 700m, 638m cm^{-1}; MS (EI) *m*/*z* (rel intensity) 149 (M^+, 23), 148 [$(M-1)^+$, 49], 105 ([$M-NMe_2$]$^+$, 100).

4.2.6. N,N-Dimethyl-4-dimethylaminobenzamide ***18***[10]. Yield (34%). Colorless solid; 89–90 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm 7.39–7.36 (m, *AA*″BB″, 2H), 6.68–6.65 (m, AA′*BB*′, 2H), 3.07 (s, 6H), 2.99 (s, 6H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 172.06, 151.25, 129.19, 122.94, 110.97, 40.13, 38.53; IR (KBr) ν 2903w, 1611s, 1495m, 1385s, 1367s, 1269m, 1232m, 1188m, 1172m, 1083m, 1066m, 845m, 822m, 765m cm^{-1}; MS (EI) *m*/*z* (rel intensity) 192 (M^+, 37), 148 ([$M-NMe_2$]$^+$, 100).

4.2.7. N,N,N′,N′-Tetramethylisophthalamide ***19***[12]. Yield (71%). Colorless crystals: mp 92–93 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.46 (br s, 4H), 3.11 (br s, 6H), 2.97 (br s, 6H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 170.66, 136.35, 128.45, 128.03, 125.48, 39.43, 35.24; IR (KBr) ν 2935m, 1627s, 1502m, 1397s, 1256m, 1203w, 1074m, 920w, 823m, 740m, 636m cm^{-1}; MS (EI) *m*/*z* (rel intensity) 220 (M^+, 25), 176 ([$M-NMe_2$]$^+$, 100).

4.2.8. N,N,N′,N′-Tetramethylterephthalamide ***20***[13]. Yield (71%). Colorless crystals: mp 145–146 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.45 (s, 4H), 3.12 (br s, 6H), 2.97 (br s, 6H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 170.60, 137.20, 126.87, 39.23, 35.08; IR (KBr) ν 2935m, 1630s, 1526m, 1478m, 1400s, 1266m, 1228w, 1088m, 858m, 736m, 599m cm^{-1}; MS (EI) *m*/*z* (rel intensity) 220 (M^+, 29), 176 ([$M-NMe_2$]$^+$, 100).

4.2.9. N,N-Dimethyl-2-naphthcarbamide ***21***[6]. Yield (89%). Colorless solid; 82–83 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm 7.91–7.84 (m, 4H), 7.55–7.50 (m, 3H), 3.16 (s, 3H), 3.03 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ/ppm 171.65, 133.66, 133.61, 132.68, 128.40, 128.20, 127.80, 127.00, 126.86, 126.64, 125.48, 39.43, 35.24; IR (KBr) ν 3026 w, 2935w, 1616s, 1572m, 1501s, 1468m, 1410s, 1276m, 1259m, 1182m, 1126m, 1076s, 872m, 824s, 779m, 761s cm^{-1}; MS (EI) *m*/*z* (rel intensity) 199 (M^+, 399), 155 ([$M-NMe_2$]$^+$, 100) 127 ([$M-CONMe_2$]$^+$, 84).

4.2.10. N,N-Dimethyl-1-adamantanecarboxamide ***22***[14]. Yield (71%). Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm 3.07 (s, 6H), 2.02 (m, 9H), 1.69 (m, 6H); IR (KBr) ν 2901s, 2848m, 1614s, 1497m, 1452m, 1383s, 1163m, 1057m, 650m cm^{-1}; MS (EI) *m*/*z* (rel intensity) 207 (M^+, 29), 135 ([$M-CONMe_2$]$^+$, 100).

4.2.11. N,N-Dimethyl-isonicotincarboxamide ***23***[15]. Yield (42%). Colorless solid; 57–58 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ/ppm 8.70–8.68 (m, *AA*″BB″, 2H), 7.31–7.29 (m, AA′*BB*′, 2H), 3.13 (br s, 3H), 2.95 (br s, 3H).

4.3. General procedure for alkali metal reduction of *N,N*-dialkylamides

In a 50 ml of two-necked round-bottomed flask equipped with a N_2 balloon and a rubber septum was charged with *N,N*-dimethyl-4-*tert*-butylbanzamide **2** (417 mg, 2.03 mmol), 4,4′-di-*t*ert-butylbiphenyl (89 mg, 0.33 mmol), granuler lithium (ALDRICH, granule 99.9+%, 74 mg, 10.7 mmol), and a stirrer bar. The flask was purged with N_2, and THF (10 ml) was added via syringe. The solution was sonicated in an ice-water bath. The color of the solution gradually changed yellow, brown and black for 45 min. Upon 1 h irradiation, the reaction mixture was poured into an ice-cold hydrochloric acid (50 ml). The mixture was extracted with ethyl acetate (50 ml). The organic layer was separated, washed with water and brine, and dried over anhydrous Na_2SO_4. Upon evaporation of the solvent, the residue was charged with a column chromatography (silica gel, 30 g) to give **3** from a hexane/CH_2Cl_2 elution as yellow solid; 254 mg (78%). The spectral data of **3**, **28**–**32**, and **34** were consistent with the reported ones.

4.3.1. N,N-Diethylbanzamide ***28***[22]. ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm 7.40–7.34 (m, 5H), 3.55 (br s, 2H), 3.25 (br s, 2H), 1.25 (br s, 3H), 1.10 (br s, 3H); IR (KBr) ν 2974w, 1630s, 1429m, 1288m, 706m cm^{-1}; MS (EI) *m*/*z* (rel intensity) 177 (M^+, 21), 176 [$(M-1)^+$, 42], 105 ([$M-N(C_2H_5)_2$]$^+$, 100).

4.3.2. N-Benzoylpiperidine ***29***[23]. ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm 7.39 (m, 5H), 3.71 (br s, 2H), 3.34 (br s, 2H), 1.68–1.51 (m, 6H); IR (KBr) ν 2937w, 2856w, 1634s, 1434m, 1277m, 1111m, 1001m, 708m cm^{-1}; MS (EI) *m*/*z* (rel intensity) 189 (M^+, 38), 188 [$(M-1)^+$, 99], 105 ([$M-N(CH_2)_5$]$^+$, 100).

4.3.3. 1,2-Di(4-tert-butylphenyl)ethane-1,2-dione ***3***[17]. Yellow solid; 104–104.5 °C; ^{1}H NMR (270 MHz, $CDCl_3$); δ/ppm 7.93–7.88 (m, *AA*″BB″, 4H), 7.53–7.49 (m, AA′*BB*′, 4H), 1.34 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm 31.05, 35.44, 125.90, 129.81, 130.56, 158.75, 194.35; IR (KBr, ν/cm^{-1}) 3056 (w), 3037 (w), 2961 (s), 2904 (m), 2870 (m), 1682 (s), 1661 (s), 1602 (s), 1566 (m), 1475 (m), 1410 (m), 1394 (w), 1224 (s), 1178 (s), 1108 (s), 1026 (w), 896 (s), 852 (s), 773 (m); MS (EI) m/*z* (rel intensity) 322 [M^+, 1], 161 (100), 146 (9), 118 (15).

4.3.4. 1,2-Diphenylethane-1,2-dione (benzil) ***30***[9a]. Yield (14% from **15**, 64% from **16**, 70% from **17**, 13% from **28**, and 10% from **29**). Yellow solid; 94–95 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ/ppm 7.97 (m, *AA*″BB′C, 4H), 7.65 (m, AA′BB″*C*, 2H), 7.52 (AA′*BB*′C, 4H).

4.3.5. 1,2-Bis(4-N,N-dimethlyaminophenyl)ethane-1,2-dione ***31***[18]. Yield (69%). Yellow solid; 202–203 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ/ppm 7.88–7.82 (m, *AA*″BB′, 4H), 7.68–7.62 (m, AA′*BB*′, 4H), 3.06 (s, 12H).

4.3.6. 4-Cyanobenzaldehyde ***32***[19]. Yield (11%). Yellow solid; 99–100 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ/ppm 10.10 (s, 1H), 8.01–7.98 (m, *AA*″BB′, 2H), 7.86–7.83 (m, AA′*BB*′, 2H).

4.3.7. 1,2-Di(2-naphthyl)ethane-1,2-dione ***34***[20]. Yield (18%) together with 48% of recovery, **21**. Yellow solid; 156–157 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ/ppm 8.46 (s, 1H), 8.15 (dd, J=8.9, 1.6 Hz, 1H), 8.00–7.89 (m, 3H), 7.65 (dt, J=7.6, 1.3 Hz, 1H), 7.55 (dt, J=7.3, 1.3 Hz, 1H).

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Supplementary data

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