# Reaction of Arenediazonium Salts with Nitriles in the Presence of Sodium Carboxylates. A Convenient Synthesis of Unsymmetrical *N*-Aryl Acyclic Imides

Kiyoshi KIKUKAWA,* Kiyoshi KONO, Fumio WADA, and Tsutomu MATSUDA

*Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812*

(Received May 8, 1982)

**Synopsis.** Reactions of arenediazonium tetrafluoroborates ($ArN_2BF_4$), acetonitrile and sodium carboxylates (RCOONa) gave *N*-acyl acetanilides ($ArN(COR)COCH_3$) in moderate to good yields (Ar=Ph, 2-$MeC_6H_4$, 3-$MeC_6H_4$, 4-$MeC_6H_4$, 2,6-$(Me)_2C_6H_3$; R=Et, *i*-Pr, *t*-Bu, Ph). Acrylonitrile and benzonitrile could be used in the reaction instead of acetonitrile.

Acetonitrile has been used as a favorable solvent in the palladium-catalyzed reactions of arenediazonium salts ($ArN_2X$).[1] However, in the presence of sodium acetate, a base frequently used in the palladium-catalyzed reactions, some $ArN_2X$ rapidly decomposed in acetonitrile to give intractable tarry materials. In the course of the studies to clarify this side reaction, the interesting reaction of $ArN_2BF_4$ with sodium carboxylates (RCOONa) and nitriles (R'CN) to produce unsymmetrical *N*-aryl acyclic imides is observed.

## Results and Discussion

Addition of $ArN_2BF_4$ to a suspension of RCOONa in $CH_3CN$ at 60—80 °C caused immediate gas evolution, giving unsymmetrical *N*-aryl acyclic imides (*N*-acyl acetanilides (Eq. 1)). Typical results are summarized in Table 1. Various sodium carboxylates could be used effectively and gave the corresponding *N*-aryl imides. Formation of any symmetrical imides could not be observed under the present reaction conditions. It is noticeable that better yields are obtained in the reactants with bulky groups, such as pivalate, 2-methyl- or 2,6-dimethylbenzenediazonium salt.

$$ArN_2BF_4 + RCOONa + CH_3CN \longrightarrow Ar\text{-}N(COR)COCH_3 + N_2 \quad (1)$$

Table 1. Preparation of *N*-aryl acyclic imides (*N*-acyl acetamides) by the reaction of $ArN_2BF_4$ with RCOONa in acetonitrile (Eq. 1)[a]

| Ar in $ArN_2BF_4$ | R in RCOONa | Products, yield/%[b] $ArN(COR)COCH_3$ |
|---|---|---|
| Ph | Et | 54 |
| Ph | *i*-Pr | 55 |
| Ph | *t*-Bu | 79 |
| Ph | Ph | 74 |
| 2-$MeC_6H_4$ | Et | 71 |
| 3-$MeC_6H_4$ | Et | 58 |
| 4-$MeC_6H_4$ | Et | 32 |
| 2,6-$(Me)_2C_6H_3$ | Et | 78 |
| 2,6-$(Me)_2C_6H_3$ | Ph | 50 |

a) Reactions were carried out by the addition of of $ArN_2BF_4$ to a suspension of RCOONa in $CH_3CN$ at 60—80 °C. b) Based on $ArN_2BF_4$.

Acrylonitrile and benzonitrile also reacted with $ArN_2BF_4$ and RCOONa to give the *N*-aryl imides and/or *N*-aryl amides (Eqs. 2 and 3). *N*-Arylpropionamides could not be observed under the present conditions.

$$ArN_2BF_4 + CH_2{=}CHCN + EtCOONa \longrightarrow ArN(COEt)COCH{=}CH_2 + ArNHCOCH{=}CH_2 \quad (2)$$

| | | |
|---|---|---|
| Ar=Ph: | 0% | 72% |
| 2,6-$(Me)_2C_6H_3$: | 49 | 0 |

$$ArN_2BF_4 + PhCN + EtCOONa \longrightarrow ArN(COEt)COPh + ArNHCOPh \quad (3)$$

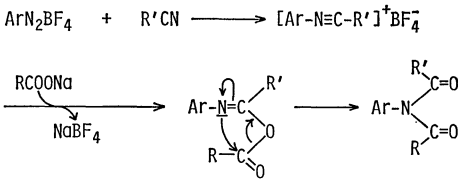
| | | |
|---|---|---|
| Ar=Ph: | 6% | 2% |
| 2,6-$(Me)_2C_6H_3$: | 25 | 39 |

In contrast to the $PhN_2BF_4$ or $(Me)_nC_6H_{5-n}N_2BF_4$, $ArN_2BF_4$ bearing electron-withdrawing groups, such as as 4-$NO_2C_6H_4N_2BF_4$ or 4-$BrC_6H_4N_2BF_4$, gave ArH (*ca.* 20%) along with tarry materials under the present conditions. Sodium acetate is used as a base in the Gomberg-Bachmann reaction of an $ArN_2X$ bearing electron-withdrawing group to produce an aryl radical intermediate.[2] Thus, the formation of the ArH is reasonably understood by the pathway *via* aryl radical shown in Eq. 4.

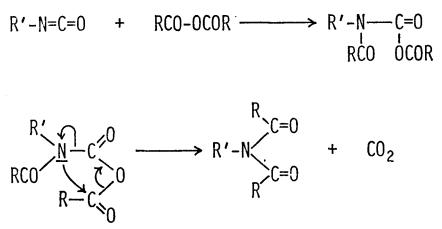
$$ArN_2BF_4 + RCOONa \longrightarrow ArN_2OCOR \longrightarrow Ar\cdot + N_2 + RCOO\cdot \xrightarrow{CH_3CN} ArH \quad (4)$$

Reaction of $(Me)_nC_6H_{5-n}N_2BF_4$ with nitriles has been known to give *N*-aryl nitrilium tetrafluoroborates, $[Ar\text{–}N{\equiv}C\text{–}R]^+BF_4^-$.[3] Since the present reaction favorably proceeds with $(Me)_nC_6H_{5-n}N_2BF_4$, the *N*-aryl nitrilium salt might be an intermediate. Thus, the following scheme could explain the formation of *N*-aryl acyclic imides (Scheme 1). The similar pathway has been proposed for the reaction of isocyanate and acid anhydride to form an acyclic imides (Scheme 2).[4]

Unsymmetrical (mixed) imides are conventionally obtained through acylation of amides with acid anhydrides or acid chlorides.[4,5] But sometimes symmetri-




Scheme 1.



Scheme 2.

cal imides were obtained because the reaction required drastic conditions.

The present reaction provides a convenient route to unsymmetrical *N*-acyl imides, especially *N*-acyl acetanilides.

## Experimental

*Materials.* Sodium carboxylates were used as received or obtained by neutralization of the corresponding acids. Nitriles were distilled before use. Arenediazonium tetrafluoroborates were prepared by the ordinary method[6] and stored at −20 °C.

*General Procedure.* To a suspension of RCOONa (40 mmol) in a R'CN (40 ml) held at 60—80 °C was added an $ArN_2BF_4$ (20 mmol) slowly. The addition of $ArN_2BF_4$ caused exothermic reaction with gas evolution. After the addition, the mixture was stirred for 0.5 h at 60—80 °C. After removal of solids ($NaBF_4$ and excess RCOONa), excess R'CN was evaporated (or distilled) off under reduced pressure. The residue was extracted with hot (≈50 °C) hexane. After evaporation of hexane, the residue was distilled or recrystallized from benzene (or hexane–ether) to give *N*-aryl imides. The extraction with hexane served to seperate the imides from amides, since the latter remained as insoluble solid. The structure of the imides was confirmed by IR, NMR, and elemental analysis. The C=O stretching of the imides was observed near 1700 $cm^{-1}$ and was easily distinguishable from that of amides appeared near 1650 $cm^{-1}$.

*PhN(COEt)COMe*: Bp 107 °C/3 mmHg (1 mmHg= 133.322 Pa), IR (neat) 1710 $cm^{-1}$, NMR ($CCl_4$) $\delta$=1.00 (t), 2.38 (q) ($J$=7.2 Hz, EtCO), 2.18 (s) (MeCO). Found: C, 69.25; H, 6.94; N, 7.32%. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.33%. *PhN(CO-i-Pr)COMe*: Mp 44.5—48.5 °C, IR (neat) 1695, 1715 $cm^{-1}$, NMR ($CCl_4$) $\delta$=1.07 (d), 2.91 (hep) ($J$=6.4 Hz, *i*-PrCO), 2.21 (s) (MeCO), Found: C, 70.14; H, 7.33; N, 7.02%. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82%. *PhN(CO-t-Bu)COMe*: Mp 66.5—67.0 °C, IR (Nujol) 1690 $cm^{-1}$, NMR ($CCl_4$) $\delta$=1.15 (s) (*t*-BuCO), 2.00 (s) (MeCO), Found: C, 71.06; H, 7.79; N, 6.33%. Calcd for $C_{13}H_{17}NO_2$: C, 71.20; H, 7.82; N, 6.39%. *PhN(COPh)COMe*: Mp 68.2—68.7 °C, IR (Nujol) 1690 $cm^{-1}$, NMR ($CCl_4$) $\delta$=2.32 (s) (MeCO), Found: C, 75.15; H, 5.55; N, 5.85%. Calcd for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.47; N, 5.85%. *PhN(COEt)COPh*: Mp 62.3—66.5 °C, IR (Nujol) 1670, 1710 $cm^{-1}$, NMR ($CCl_4$) $\delta$=1.13 (t), 2.60 (q) ($J$=7.0 Hz, EtCO), Found: C, 76.05; H, 6.03; N, 5.59%. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53%. *2-MeC$_6$H$_4$N(COEt)COMe*: Bp 80—81 °C/ 0.2 mmHg, IR (neat) 1710 $cm^{-1}$, NMR ($CCl_4$) $\delta$=1.01 (t), 2.34 and 2.37 (two q) ($J$=7.1 Hz, EtCO), 2.04 (s) (MeCO), 2.17 (s) (Me–Ar), Found: C, 70.05; H, 7.34; N, 7.10%. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82%. *3-MeC$_6$H$_4$N(COEt)COMe*: Bp 78—80 °C/0.09 mmHg, IR (neat) 1715 $cm^{-1}$, NMR ($CCl_4$) $\delta$=1.08 (t), 2.48 (q) ($J$= 7.2 Hz, EtCO), 2.32 (s), 2.37 (s) (MeCO and MeAr), Found: C, 70.15; H, 7.51; N, 6.78%. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.35; N, 6.82%. *4-MeC$_6$H$_4$N(COEt)COMe*: Bp 127 °C/4 mmHg, IR (neat) 1710 $cm^{-1}$, NMR ($CCl_4$) $\delta$= 1.00 (t), 2.38 (q) ($J$=6.8 Hz, EtCO), 2.17 (s), 2.26 (s) (MeCO and MeAr), 6.82 (d), 7.08 (d) ($J$=8.0 Hz, Ar), Found: C, 70.21; H, 7.47; N, 7.12%. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.35; N, 6.82%. *2,6-(Me)$_2$C$_6$H$_3$N(COEt)-COMe*: Bp 87—90 °C/1 mmHg, IR (neat) 1710 $cm^{-1}$, NMR ($CCl_4$) $\delta$=1.01 (t), 2.32 (q) ($J$=7.2 Hz, EtCO), 2.00 (s) (MeAr), 2.11 (s) (MeCO), 6.97 (s) (Ar), Found: C, 71.29; H, 7.85; N, 6.33%. Calcd for $C_{13}H_{17}NO_2$: C, 71.20; H, 7.82; N, 6.39%. *2,6-(Me)$_2$C$_6$H$_3$N(COPh)COMe*: Bp ≈120 °C/0.5 mmHg (Kugelrohr distillation), IR (neat) 1685, 1710 $cm^{-1}$, NMR ($CCl_4$) $\delta$=2.18 (s) (MeCO), 2.20 (s) (MeAr), Found: C, 76.48; H, 6.46; N, 5.20%. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24%. *2,6-(Me)$_2$C$_6$H$_3$N(COEt)-COCH=CH$_2$*: Bp ≈120 °C/3 mmHg (Kugelrohr distillation), IR (neat) 1695, 1710 $cm^{-1}$, NMR ($CDCl_3$) $\delta$=1.10 (t), 2.68 (q) ($J$=7.0 Hz, EtCO), 2.02 (s) (MeAr), 5.48 (d-d) ($J_{gem}$= 4.0, $J_{cis}$=7.9 Hz, trans HC=C–CO), 6.22 (d) (C=CH–CO), 6.25 (d) (cis HC=C–CO) (These latter two chemical shifts are too close for observing $J_{trans}$), 7.02 (s) (MeAr), Found: C, 72.88; H, 7.50; N, 5.87%. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06%. *2,6-(Me)$_2$C$_6$H$_3$N(COEt)COPh*: Bp ≈120 °C/0.3 mmHg (Kugelrohr distillation), IR (neat) 1685, 1715 $cm^{-1}$, NMR ($CCl_4$) $\delta$=1.10 (t) 2.30 (q) ($J$= 7.0 Hz, EtCO), 2.21 (s) (MeAr), Found: C, 77.45; H, 6.92; N, 5.22%. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.80; N, 4.98%.

## References

1) K. Kikukawa, K. Nagira, F. Wada, and T. Matsuda, *Tetrahedron*, **37**, 31 (1981); K. Nagira, K. Kikukawa, F. Wada, and T. Matsuda, *J. Org. Chem.*, **45**, 2365 (1980); K. Kikukawa, K. Kono, K. Nagira, F. Wada, and T. Matsuda, *ibid.*, **46**, 4413 (1981).

2) O. C. Dermer and M. T. Edmison, *Chem. Rev.*, **57**, 77 (1957).

3) H. Meerwein, P. Laasch, R. Mersch, and J. Spille, *Chem. Ber.*, **89**, 209 (1956).

4) D. Davidson and H. Skouronek, *J. Am. Chem. Soc.*, **80**, 376 (1958).

5) C. D. Hurd and A. G. Prapas, *J. Org. Chem.*, **24**, 388 (1959).

6) A. Roe, *Org. React.*, **5**, 193 (1949).