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

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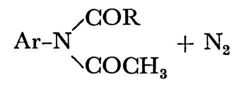
Synopsis. Reactions of arenediazonium tetrafluoroborates (ArN_2BF_4), acetonitrile and sodium carboxylates (RCOONa) gave *N*-acyl acetanilides ($ArN(COR)COCH_3$) in moderate to good yields (Ar=Ph, $2\text{-}MeC_6H_4$, $3\text{-}MeC_6H_4$, $4\text{-}MeC_6H_4$, $2,6\text{-}(Me)_2C_6H_3$; R=Et, *i*-Pr, *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.

$$ArN_2BF_4 + RCOONa + CH_3CN \longrightarrow$$



$$Ar\text{-}N\begin{matrix}\diagup COR\\ \diagdown COCH_3\end{matrix} + N_2 \qquad (1)$$

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
$2\text{-}MeC_6H_4$	Et	71
$3\text{-}MeC_6H_4$	Et	58
$4\text{-}MeC_6H_4$	Et	32
$2,6\text{-}(Me)_2C_6H_3$	Et	78
$2,6\text{-}(Me)_2C_6H_3$	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.

$$ArN_2BF_4 + CH_2{=}CHCN + EtCOONa$$
$$\longrightarrow ArN(COEt)COCH{=}CH_2 + ArNHCOCH{=}CH_2 \qquad (2)$$
$$\begin{array}{rll} Ar{=}Ph: & 0\% & 72\% \\ 2,6\text{-}(Me)_2C_6H_3: & 49 & 0 \end{array}$$

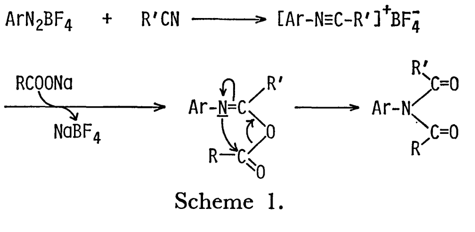
$$ArN_2BF_4 + PhCN + EtCOONa$$
$$\longrightarrow ArN(COEt)COPh + ArNHCOPh \qquad (3)$$
$$\begin{array}{rll} Ar{=}Ph: & 6\% & 2\% \\ 2,6\text{-}(Me)_2C_6H_3: & 25 & 39 \end{array}$$

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 $4\text{-}NO_2C_6H_4N_2BF_4$ or $4\text{-}BrC_6H_4N_2BF_4$, 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.

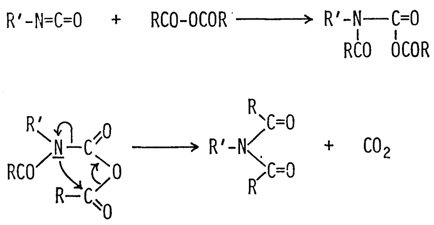
$$ArN_2BF_4 + RCOONa \longrightarrow ArN_2OCOR \longrightarrow$$
$$Ar\cdot + N_2 + RCOO\cdot \xrightarrow{CH_3CN} ArH \qquad (4)$$

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) δ=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) δ=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) δ=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) δ=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) δ=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) δ=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) δ=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) δ=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) δ=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) δ=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 ($CDCl_3$) δ=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) δ=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).