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NOVEL TRANSFORMATION OF ARENEDIAZONIUM SALTS TO ACID ANHYDRIDES UNDER PALLADIUM CATALYSIS

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Palladium catalyzed reaction of arenediazonium salts, carbon monoxide and sodium carboxylates gave mixed anhydrides, which in turn could be converted to aromatic acid anhydrides in good yields.

Recently we reported a convenient carboxylation of arenediazonium salts(**1**) with carbon monoxide in the presence of $Pd(OAc)_2$ and sodium carboxylates(**2**).[1] In the carboxylation an initial product was supposed to be a mixed acid anhydride in which one of the acyl groups came from **1** and another from **2**. Here, a novel preparation of mixed acid anhydrides from **1**, carbon monoxide and **2** is described.

The reaction was carried out with 10 mmol of **1**, 15 mmol of **2**, 0.1-0.2 mmol of $Pd(OAc)_2$ and 9 kg/cm^2 of carbon monoxide in acetonitrile (60 ml) at r.t. for 0.5 h (eq. 1). Since **1** react with **2** spontaneously at r.t. in acetonitrile to form tarry materials in the absence of carbon monoxide, **1** must be added to the reaction mixture after the introduction of carbon monoxide. From the filtrate of the reaction mixture acetonitrile was evaporated off at 0 °C under reduced pressure. The residue was extracted several times with hexane at 30 °C when NaOAc was used. The products (**3**) crystallized out on cooling the hexane extracts or were obtained by removal of hexane under reduced pressure. When PhCOONa was used, the residue was washed successively by small amounts of acetonitrile, water and petroleum ether at 0 °C, and dried under reduced pressure. Typical results are summarized in Table I. The contamination of the products with acids or other acid anhydrides was proved to be negligible by IR and NMR measurements except for **3** (Ar=Ph), which includes 12% of $(PhCO\text{-})_2O$ estimated by NMR. Further purification of the mixed anhydrides was difficult because of their facile disproportionation by heat.

$$\underset{\mathbf{1}}{ArN_2BF_4} + CO + \underset{\mathbf{2}}{RCOONa} + Pd(OAc)_2 \xrightarrow[25\text{-}30\ ^\circ C,\ 0.5\ h]{CH_3CN} \underset{\substack{\mathbf{3}\ (R=CH_3)\\ \mathbf{4}\ (R=Ph)}}{ArCOOCOR} \tag{1}$$

The facile disproportionation provides a convenient route to homo acid

Table I. Synthesis of Mixed Acid Anhydrides and Acid Anhydrides[a]

Product (Ar)	Yield,[b] %	mp, °C (lit)	IR,[c] $\nu_{C=O}$, cm^{-1}
3 (Ph)	83	liquid	1738, 1810
3 (4-Me-C_6H_4)	68	liquid	1736, 1809
3 (4-Br-C_6H_4)	83	27	1735, 1810
3 (4-I-C_6H_4)	68	65.0-66.0	1727, 1796
3 (4-NO_2-C_6H_4)	65	71.7-73.6	1736, 1802
4 (4-Br-C_6H_4)	59	82.3-83.3(82-83)[d]	1725, 1785
4 (4-NO_2-C_6H_4)	42	122.5-124(130-130.5)[d]	1728, 1788
4 (1-naphthyl)	45	85.3-86.8(89.5-90.3)[d]	1708, 1772
5 (Ph)	72	42.9-43.5(42)[e]	1714, 1779
5 (4-Me-C_6H_4)	64	93-94(95)[e]	1715, 1778
5 (4-Br-C_6H_4)	67	219.4-220.6(205-209)[e]	1725, 1789
5 (4-I-C_6H_4)	65	237-237.4(229)[e]	1725, 1789
5 (4-NO_2-C_6H_4)	64	188.7-190(195-195.5)[e]	1730, 1794

a) The structure of 3 and 4 was confirmed by IR and NMR, and that of 5 by comparison of IR with authentic samples. b) Isolated yields based on 1 used. c) Neat or nujol mull. d) J. M. Zeavin and A. M. Fisher, *J. Am. Chem. Soc.*, 54, 3738 (1932). e) Cited from "*Beilsteins Handbuch der Organischen Chemie*".

anhydrides.[2] Heating of 3 at 100-120 °C under reduced pressure gave aromatic carboxylic acid anhydrides (5) in good yields (eq. 2). The overall yields from arenediazonium salts are shown in Table I.

$$\underset{3}{\text{ArCOOCOCH}_3} \xrightarrow{100\text{-}120\ ^\circ\text{C}} \underset{5\ (81\text{-}98\%)}{(\text{ArCO-})_2\text{O}} + \text{Ac}_2\text{O} \qquad (2)$$

In view of availability of various arylamines and the mild reaction conditions the present procedure would provide a useful synthetic method for aromatic carboxylic acid anhydrides.

References

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