A New and Convenient Synthesis of 2,2′-Biphenyldicarboxylic Acids and 2-Cyano-2′-biphenylcarboxylic Acids

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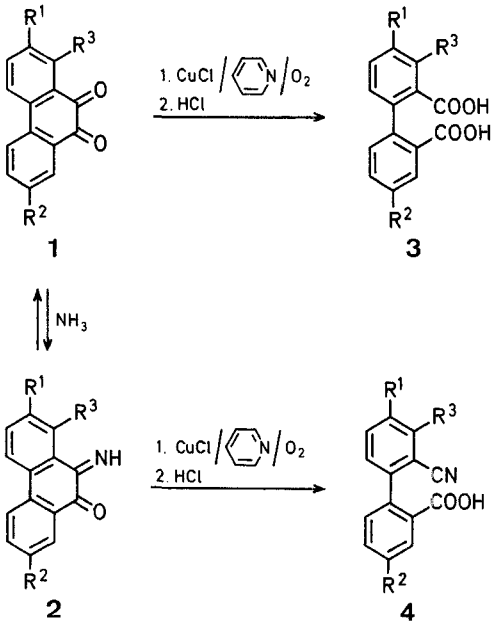
We have previously shown that copper(I) halides in pyridine are capable of oxygenating 9,10-phenanthrenequinone with oxygen to give well characterised biphenatocopper(II) complexes[1]. In a similar reaction with 9,10-phenanthrenequinone-monoimines, 2-cyano-2′-biphenylcarboxylatocopper(II) complexes are formed[2]. After acidification the free acids could be isolated.

In an extension of our studies, we searched for an alternative, new, laboratory-scale preparation of biphenic acids, under mild conditions which would be superior to already known methods of coupling[3] or oxidation by chromic acid[4], potassium permanganate[5], or hydrogen peroxide[6], giving higher



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yields and better selectivity, and a new oxidative method for the preparation of 2-cyano-2′-biphenylcarboxylic acids instead of starting from 9,10-phenanthrenequinone monoximes[7].

9,10-Phenanthrenequinones **1** and their monoimines **2** with different functionalities are easily oxygenated by copper(I) chloride in pyridine with cleavage of the C-9—C-10 bond and transformation of the functional groups >C=NH and >C=O to —C≡N and —COOH groups, respectively, to give the products **3** and **4**.

The monoimines **2**, can be prepared *in situ* from the quinones **1** with ammonia and then oxygenated. The oxygenation is selective, no lactonisation was observed. Alkyl and nitro groups as well as halogens on the ring are unaffected but amino and hydroxy groups interfere with the reaction. The new method is simple and the products **3** and **4** were obtained in good to excellent yields (Table).

Table. Compounds **3** and **4** prepared

Product No.	R^1	R^2	R^3	Yield [%]	m.p. [°C] (solvent)	Molecular formula[a] or Lit. m.p. [°C]
3a	H	H	H	95	230–232° (AcOH)	228–229°[2]
3b	O_2N	H	H	93	214–216° (AcOH)	220–221°[8]
3c	Br	H	H	100	241–245° (AcOH)	238–239°[9]
3d	Br	Br	H	100	277–279° (AcOH)	277–278°[10]
3e	*t*-C_4H_9	*t*-C_4H_9	H	96	301–304° (AcOH)	$C_{22}H_{26}O_4$ (354.4)
3f	H	*i*-C_3H_7	CH_3	82	181–183° (C_2H_5OH)	188–189.5°[11]
4a	H	H	H	85	174° (C_2H_5OH)	173°[12]
4b	H	Br	H	74	172–175° (AcOH)	$C_{14}H_8BrNO_2$ (302.1)
4c	Br	Br	H	76	189–191° (AcOH)	$C_{14}H_7Br_2NO_2$ (381.0)
4d	O_2N	H	H	87	190–192° (AcOH)	194–195°[12]
4e	O_2N	O_2N	H	68	218–220° (AcOH)	217–218°[12]
4f	*t*-C_4H_9	*t*-C_4H_9	H	85	261–263° (AcOH)	$C_{22}H_{25}NO_2$ (335.4)

[a] All products were characterized by microanalyses (C ±0.70, H ±0.50, N ±0.30), I.R., U.V., mass, and ^{1}H-N.M.R. spectrometry.

2,2′-Biphenyldicarboxylic Acids 3 or 2-Cyano-2′-biphenylcarboxylic Acids 4; General Procedure:

A mixture of 9,10-phenanthrenequinone **1** (10 mmol) or 9,10-phenanthrenequinone-monoimine **2** (10 mmol; which can be prepared alternatively *in situ* by bubbling ammonia for 10 min through the solution of the quinone **1**) and copper(I) chloride (1.0 g, 10 mmol) in pyridine (40 ml) is stirred under oxygen until gas consumption ceases (usually 6 h). The solvent is then evaporated in vacuum and the dry residue extracted with ether (150 ml) after acidification with diluted hydrochloric acid. The ether extracts are dried with anhydrous magnesium sulfate, the ether pumped off, and the residues recrystallised from acetic acid and ethanol to give the pure acids **3** or **4**.

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