Journal of Organic Chemistry

2024, 89, 4, 2764–2770 Publication Date: January 25, 2024 https://pubs.acs.org/doi/10.1021/acs.joc.3c02002

Bay-Substitution of Perylene Bisimides with Bidentate Nucleophiles: The Case of Aryloxide Anions

Carlos J. Rivas, Leandro D. Mena, María T. Baumgartner, Liliana B. Jimenez

Universidad Nacional de Córdoba. Facultad de Ciencias Químicas. Departamento de Química Orgánica, Haya de la Torre y Medina Allende , Ciudad Universitaria . Córdoba , X5000HUA , Argentina

Consejo Nacional de Investigaciones Científicas y Técnicas. Instituto de Investigaciones en Fisicoquímica de Córdoba. Haya de la Torre s/n, Ciudad Universitaria. Córdoba, X5000HUA, Argentina

Correspondencia: Liliana B. Jimenez, ljimenez@unc.edu.ar

Abstract

In this study, we delve into the regioselectivity of nucleophilic reactions involving brominated perylene bisimides (PBIs) and various bidentate aryloxide anions, previously associated with an $S_{RN}1$ mechanism. We present herein a new perspective, suggesting that a single-electron-transfer aromatic nucleophilic substitution (SeT-S_NAr) mechanism is a more plausible scenario. Our study reveals the favorable impact of photostimulation on reaction yields, making our method a convenient approach for accessing *O*-arylated PBIs.



Este Artículo se encuentra embargado hasta el día 26 de enero 2025

En el siguiente enlace puede consultar Supporting Information: https://pubs.acs.org/doi/10.1021/acs.joc.3c02002?goto=supporting-info

Table of Contents

1. Experimental information p SI-3

1.1. Figure S1: Spectrum of lamps used for photoinduced reactions.

1.2. Synthesis of nonan-5-amine, N,N'-Bis(5-nonyl)-perylene-3,4,9,10-bis(dicarboximide) (PBI), N,N'-Bis-(5-nonyl)-1-bromoperylene-3,4,9,10-bis(dicarboximide) (1), (allyloxy)benzene, 2-allylphenol and N,N'-Bis(5-nonyl)-1-(2-allyl)phenoxyperylene-3,4,9,10-bis(dicarboximide).

1.3. Large scale synthesis of N,N'-Bis(5-nonyl)-1-phenoxyperylene-3,4:9,10-bis(dicarboximide) 1.4. Table S1.

2. Formation of radical anion with different bases p SI-8

2.a.1 - Br-PBI (1) + KOtBu

2.a.2 - Normalized UV-Visible spectra of Br-PBI (1), PBI and 1+KOtBu (dark for 24 h)

2.b.1 - Br-PBI (1) + K2CO3

2.b.2 - Pictures of substrate 1 in K2CO3/DMSO (N2) at different times and temperatures

2.b.3 - Normalized UV-Visible spectra of 1, PBI and 1+K2CO3

2.b.4 - TLC of 1, PBI, 1+KOtBu (24h, dark) (A) and 1+K2CO3 (hv =1h) (B).

2.b.5 - UV-Spectra of the formation of radical anion of Br-PBI+K2CO3+2,6 DTBP in DMSO at 120 °C.

2.b.6 - UV-Spectra of the formation of radical anion of Br-PBI+K2CO3+2-naphthol in DMSO at 40 °C, and photoinduced reaction.

2.b.7 - UV-Spectra of Br-PBI and Br-PDI+K2CO3+2-naphthol in DMSO.

3. Spectroscopic characterization of products p SI-13

3.a. UV-visible spectra of the radical anion of *O*-products

3.b. UV-visible spectra of the anions of *C*-products

4. NMR Spectra p SI-16

1H NMR of Nonan-5-amine.

1H NMR of (allyloxy)benzene and 1H NMR of 2-allylphenol.

1H-NMR and FT-IR. N,N'-Bis(5-nonyl) perylene-3,4,9,10-bis(dicarboximide), PBI.

1H-, 13C{1H}-, 2D-NMR and FT-IR. N,N'-Bis(5-nonyl)-1-bromoperylene-3,4,9,10-bis(dicarboximide) (1)

1H-, 13C{1H}-, 2D-NMR, FT-IR and HRMS. N,N'-Bis(5-nonyl)-1-naphtoxyperylene-3,4,9,10-bis(dicarboximide)

1H-, 13C{1H}-, 2D-NMR, FT-IR and HRMS. N,N'-Bis(5-nonyl)-1-phenoxyperylene-3,4:9,10-bis(dicarboximide)

1H-, 13C{1H}-, 2D-NMR, FT-IR and HRMS. N,N'-Bis(5-nonyl)-1-p-tert-butylphenoxyperylene-3,4,9,10-bis(dicarboximide)

1H-NMR, FT-IR and HRMS. N,N'-Bis-(5-nonyl)-1-(4-hydroxy-3,5-di-tert-butylphenyl)-perylene-3,4,9,10-bis(dicarboximide)

1H-, 13C-{1H}, 2D-NMR, FT-IR and HRMS. N,N'-Bis-(5-nonyl)-1-(9-phenanthroxy)perylene-3,4:9,10-bis(dicarboximide)

1H-, 13C-{1H}, 2D-NMR, FT-IR and HRMS. N,N'-Bis(5-nonyl)-1-(9-hydroxyphenanthryl)perylene-3,4:9,10-bis(dicarboximide).

1H- and 13C{1H}-NMR. N,N'-Bis(5-nonyl)-1-(2-allyl)phenoxyperylene-3,4,9,10-bis(dicarboximide). SI-2

5. Computational details p SI-70

6. Mechanism proposed for the case of the "clock" nucleophile 2-allylphenoxide. p SI-93

7. References p SI-93