# A Claisen rearrangement route to novel electron-rich perylene dyes

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## Abstract

A combined tandem Friedel-Crafts annulation/Claisen rearrangement strategy was developed for the preparation of tetrasubstituted perylenes. Diallyloxyoctahydroperylene was prepared from commercially available 1,2,3,4-tetrahydronaphth-1,5-diol and oxidized with chloranil to the perylene analogue. Claisen rearrangement followed to the novel 2,8-diallylperylene-3,9-diol, which was acylated *in situ* to the corresponding dioctanoyl ester. These results show that allyloxyperylene undergoes Claisen rearrangement efficiently, while partially hydrogenated analogue generates multiple products under identical conditions.

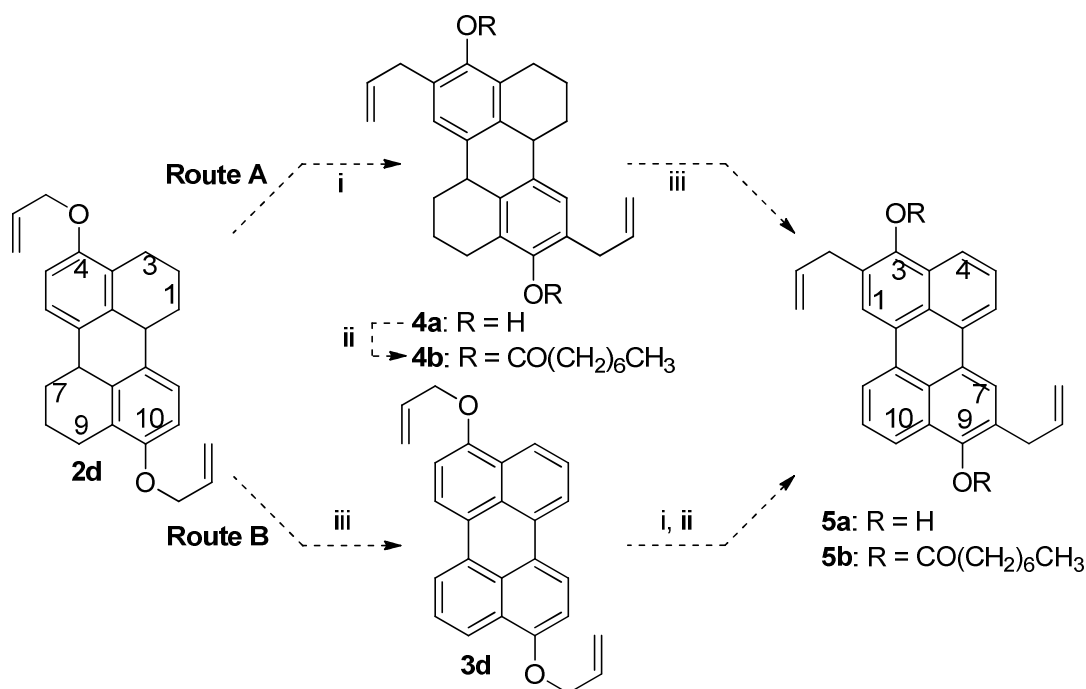**Keywords:** Perylene, Claisen rearrangement, aromatization, polycyclic aromatic hydrocarbon

## Introduction

Emerging dye applications in photovoltaics and photonics are prompting vigorous effort to increase the accessibility of novel perylene analogues.[1] Perylenes bearing electron-donating substitutents are attractive as organic dyes for solar cells due to predicted stability of the radical cations generated upon photoelectron emission.[2] Most novel perylenes are prepared via functionalization of commercially available perylene diimides,[3] which in turn are obtained upon oxidative coupling of the corresponding naphthalene imides. Stepwise coupling of halonaphthalenes followed by oxidative annulation has also been reported but is less common.[4] Our laboratory recently disclosed a novel route to 3,9-dialkoxyperylenes via Tandem Friedel-Crafts Annulation (TFCA) of tetralin analogues (Scheme 1).[5] Herein, we report an extension of this approach for the preparation of novel, dialkoxyperylenes that bear allyl groups via Claisen rearrangement. The target products bear electron-donating allyl groups, which also provide sites for attachment in novel photonic materials.[6]
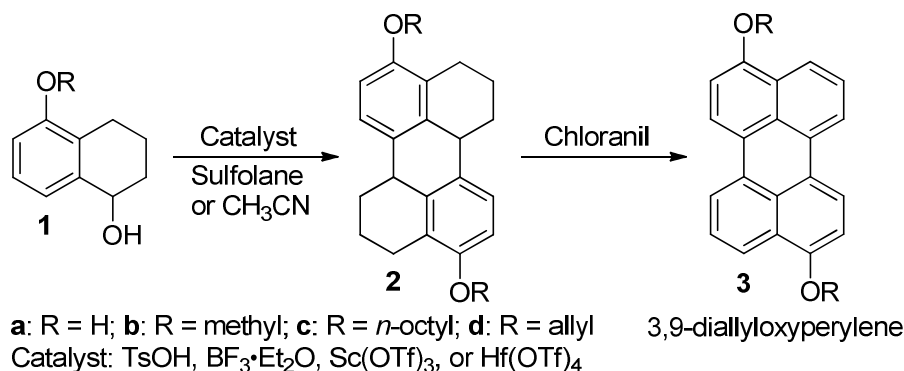
**Scheme 1.** Tandem Friedel-Crafts annulation.

Prior studies demonstrated that 1,2,3,4-tetrahydronaphth-1,5-diol (**1a**: R = H) and corresponding ethers (**1b**: R = $CH_3$ and **1c**: R = $(CH_2)_7CH_3$) are suitable substrates for TFCA, each generating the corresponding octahydroperylene (**2**) in modest to good yields.[5] Allyl ether **1d** (R = allyl),[7] also produced **2d** upon TFCA. Aryl esters of **1** (for example, R = $COCH_3$ or $CO(CH_2)_6CH_3$), however, were resistant to TFCA, presumably due to the reduction of both aryl nucleophilicity and carbocation intermediate stability, limiting the scope of this transformation. We envisaged a modified route to additional dyes in which key intermediate **2d** (R = allyl) is transformed to **5** via sequential Claisen rearrangement and oxidation steps (Scheme 2). Novel product **5a** and its ether (R = alkyl) derivatives are predicted to be easily elaborated to perylenes that are electronically activated toward photoemission.[8] Conversion from known **2d** to **5b** was planned via Claisen rearrangement followed by oxidation (Route A) or the reverse sequence (Route B). The former requires the preparation of acylated octahydroperylene intermediate **4b** *en route* to **5b** to avoid phenolic oxidation to quinones.[5,8] In the present work, we examined feasibility of both synthetic avenues to **5**.

Conditions:  i) 190 °C/neat (Route A) or 180 °C/Me₂PEG (Route B);
ii) CH₃(CH₂)₆COCl/pyridine/0 °C to RT; iii) chloranil/toluene/RT

**Scheme 2.** Proposed routes to 2,8-diallyl-3,9-diacyloxyperylene.


## Results and Discussion

Phenolic allylation of 1,2,3,4-tetrahydronaphth-1,5-diol occurred smoothly in refluxing acetone (allyl bromide, $K_2CO_3$, acetone) to provide **1d** (R = allyl; 90%). The physical and spectral properties of **1d**, which had not been previously disclosed, are consistent with expectations. Tandem Friedel-Crafts annulation of **1d** (acetonitrile, $BF_3 \cdot OEt_2$, 0 °C, 2 h) gave the corresponding octahydroperylene **2d** in improved yield (60%) compared to the established protocol.[5] The product from this transformation, which precipitated during the reaction, was obtained in high purity, enabling its direct use in subsequent synthetic steps.

Efforts to implement Route A commenced upon examination of the thermal Claisen rearrangement of **2d** to **4a** under conditions established in this laboratory for the rearrangement of allyloxybenzene. Thus, solvent-free heating of solid **2d** (190 °C, 10 h) gave a black solid that exhibited loss of ^{1}H NMR signal at 4.8 ppm (allyloxy methylene of **2d**) and concurrent emergence of a complex multiplet between 3.0–3.5 ppm, both suggesting Claisen rearrangement. However, multiple doublets in the 7.8–8.0 ppm region of ^{1}H NMR were consistent with oxidation of the polycyclic core to the corresponding anthracenyl or perylenyl products. The spectrum was further complicated by the presence of multiple vinyl signals indicating multiple

products. Because each of these products consists of similar $R_f$ value in TLC, no further studies were conducted on this pathway to avoid difficult purification steps.

To investigate the feasibility of Route B, chloranil oxidation of **2d** (4 equiv, toluene, room temperature) was examined. *This transformation and others producing analogues with fully aromatized perylene cores were protected from ambient light to avoid photodegradation.* An aliquot of the incomplete reaction was strongly fluorescent and exhibited new signals at 7.8 to 8.0 ppm in ^{1}H NMR, suggesting the partial oxidation of **2d** to the anthracenyl derivative. Continued exposure of the sample to chloranil (60 h total) induced clean conversion to **3d** (Scheme 2), as indicated by the expected aromatic resonances given in ^{1}H NMR spectrum. The product, which precipitated in the reaction milieu, was filtered, washed with acetonitrile/MeOH (1:1), and dried under vacuum to give a greenish yellow solid in good yield (72%). Product **3d** was poorly soluble in available NMR solvents ($CDCl_3$, acetone-$d_6$, acetonitrile-$d_3$, DMSO-$d_6$, THF-$d_8$, benzene-$d_6$), precluding the collection of ^{13}C NMR data.[5]

Thermal Claisen rearrangement of **3d** under solvent-free conditions (150 °C; 4 h) gave a darkened product that was shown to be mainly unreacted substrate by ^{1}H NMR. At higher temperature (180 °C) the product was extensively decomposed. Since the Claisen rearrangement of structurally similar 1-allyloxynaphthalene proceeds at 150 °C (2 h, 98% conversion), the failure of the rearrangement of **3d** at this temperature likely results from inhibition caused by the solid physical state of the perylene core.[9] Thermal rearrangement of **3d** in 1,2-dichlorobenzene at 150 °C gave degraded product as determined by ^{1}H NMR. Heating **3d** in a minimum amount of polyethylene glycol dimethyl ether (2 h, 180 °C) gave targeted product **5a** contaminated with unidentified byproducts. Several attempts made to produce clean **5a** were unsuccessful, possibly due to facile product oxidation. To facilitate isolation and purification of a derivative of **5**, the Claisen rearrangement was followed by acylation *in situ* ($ClCO(CH_2)_6CH_3$, pyridine, 0 °C to rt), which gave **5b** in good yield after chromatography (56% yield). Product **5b** exhibited the expected spectroscopic signals including UV/vis profile with the typical perylene absorbance pattern.[8]

These findings establish a pathway for novel, electron-rich diallyldihydroxyperylene and its diester.[10] The products support potential sites for ligation or chemical modification *en route* to novel photoactive materials, which are under investigation in our laboratory and those of collaborators.


## Conclusions

Tetrasubstituted, electron-rich perylene analogues **5a** and **5b** were prepared in 4 and 5 steps, respectively from commercially available 1,2,3,4-tetrahydronaphth-1,5-diol in good overall efficiency. The present sequence generates electron rich perylene cores that support olefinic and alkoxy groups, which may be employed for subsequent tethering to materials for photonic applications.

## Experimental Section

**General.** Melting points were measured on a Mel-Temp apparatus. Proton NMR and $^{13}$C NMR spectra were recorded at 500 MHz and 125 MHz (Varian INOVA), respectively, in CDCl$_3$ at 25 °C unless otherwise noted. Chemical shift values are reported in ppm with TMS as reference at 0.00 ppm for proton and CDCl$_3$ carbon residue at 77.0 ppm for $^{13}$C spectra. Spin-spin coupling constants (*J*) are given in Hz. Mass (Finnigan LCQ DUO) and FT-IR (Bruker Vector 22) spectra were recorded using APCI and ATR technology, respectively, unless otherwise noted. Kieselgel 60F$_{254}$ silica gel TLC plates were used with ethyl acetate and hexanes as solvents for monitoring reaction progress. All necessary chemicals were purchased in 98% or better purities and used without purification.

**5-Allyloxy-1,2,3,4-tetrahydronaphthalen-1-ol (1d).** A mixture of 1,2,3,4-tetrahydronaphth-1,5-diol **1a** (2.00 g, 12 mmol), K$_2$CO$_3$ (1.60 g, 48 mmol), and allyl bromide (1.00 mL, 12 mmol) in acetone was refluxed 24 h under N$_2$. The reaction mixture was extractively processed with ethyl acetate/water, and the organic layer was dried over Na$_2$SO$_4$, evaporated *in vacuo*, and chromatographed (silica gel, ethyl acetate/hexanes 1:3) to provide **1d** as a white amorphous solid in good yield, 1.62 g (90%), mp 56–57 °C; $^1$H NMR (CDCl$_3$, 500 MHz): δ$_H$ 1.75–1.84 (m, 2H), 1.87–1.99 (m, 2H), 2.58–2.65 (m, 1H), 2.80–2.86 (m, 1H), 4.56 (d, *J* 2.5 Hz, 2H), 4.80 (s, 1H), 5.30 (dd, *J* 2.0 Hz, 7.5 Hz, 1 H), 5.45 (dd, *J* 3 Hz, 10 Hz, 1H), 6.04–6.12 (m, 1H), 6.76 (d, *J* 10 Hz, 1H), 7.09 (d, *J* 5 Hz, 1H), 7.19 (t, *J* 8 Hz, 9 Hz, 1H). $^{13}$C NMR (CDCl$_3$, 125 MHz): δ$_C$ 18.3 (dd), 23.3 (d), 31.9 (d), 68.3 (d), 68.9 (t), 110.1 (d), 117.2 (d), 120.9 (d), 126.6 (dd), 133.7 (m), 140.2 (s), 156.2 (s). IR (ν$_{max}$, cm$^{-1}$): 665, 773, 885, 966, 1232, 1633, 1675, 2784, 2856, 2976, 3018, 3352. MS (*m/z*): 371.5 (M$_2^+$-2H$_2$O-H, 69), 227.5 (M+Na$^+$, 30), 204.4 (M$^+$, 30), 187.4 (M$^+$-OH, 100). HRMS calcd for C$_{13}$H$_{16}$O$_2$ (MH$^+$): 204.1150. Found: 204.1102.

**4,10-Diallyloxy-1,2,3,6b,7,8,9,12b-octahydroperylene (2d).** Allyl aryl ether **1d** (173 mg, 0.85 mmol) in acetonitrile (5 mL) was cooled to ice bath temperature, treated with BF$_3$•Et$_2$O (0.5 mL) by fast dropwise addition, and the mixture was stirred for 2 h at 0 °C.[7] An off-white solid was collected by filtration, triturated with acetone, and dried under vacuum. The solid (**2d**) was of sufficient purity for direct use in the succeeding oxidation, 80 mg (60%), mp 185–188 °C; $^1$H NMR (CDCl$_3$, 500 MHz): δ$_H$ 1.51 (tt, *J* 12.2 Hz, 8.3 Hz, 2H), 1.69–1.79 (m, 2H), 2.00–2.10 (m, 2H), 2.53 (dt, *J* 16.1 Hz, 7.8 Hz, 2H), 2.51–2.58 (m, 2H), 3.15 (ddd, *J* 16.1 Hz, 6.8 Hz, 5.4 Hz, 2H), 3.73 (dd, *J* 11.7 Hz, 4.4 Hz, 2H), 4.51–4.59 (m, two ABX patterns, 4H), 5.27 (dq, *J* 10.8 Hz, 1.5 Hz, 2H), 5.44 (dq, *J* 17.1 Hz, 1.5 Hz, 2H), 6.95 (ddt, *J* 17.1 Hz, 10.8 Hz, 5.4 Hz, 2H), 6.82 (d, *J* 7.8 Hz, 2H), 7.23 (d, *J* 8.3 Hz, 2H). $^{13}$C NMR (CDCl$_3$, 125 MHz): δ$_C$ 20.9 (t), 21.2 (t), 29.9 (t), 36.1 (d), 69.3 (t), 110.1 (d), 116.9 (dd), 124.5 (d), 126.7 (s), 128.2 (s), 133.9 (d), 136.9 (s), 153.5 (s). IR (ν$_{max}$, cm$^{-1}$): 675, 775, 874, 925, 1294, 1414, 1651, 1666, 2792, 2877, 2991, 3005, 3020. MS (*m/z*): 373.2 (MH$^+$, 60), 372.3 (M$^+$, 45), 332.3 (MH$^+$-CH$_2$CH:CH$_2$, 42), 331.4 (M$^+$-CH$_2$CH:CH$_2$, 100), 289.6 (MH$^+$-2CH$_3$CH:CH$_2$, 15). HRMS Calcd for C$_{26}$H$_{28}$O$_2$ (M$^+$): 372.2089. Found: 372.2085.

**3,9-Diallyloxyperylene (3d).** A mixture of **2d** (0.44 g, 2.5 mmol) and chloranil (2.45 g, 10 mmol) in toluene/acetonitrile (11:1) was heated at 45 °C for 20 h under $N_2$. The resultant solid was filtered and washed sequentially with acetonitrile and methanol to generate **3d** as a greenish yellow solid in good yield, 0.32 g (72%), mp 226–228 °C; $^1$H NMR (CDCl$_3$, 500 MHz): $\delta_H$ 4.78 (d, $J$ 6 Hz, 4H), 5.35 (d, $J$ 5 Hz, 2H), 5.43 (d, $J$ 10 Hz, 2H), 6.11–6.20 (m, 2H), 6.81 (d, $J$ 4 Hz, 2H), 7.41 (t, $J$ 2, 3 Hz, 2H), 8.10 (m, 4H). IR ($\nu_{max}$, cm$^{-1}$): 785, 802, 915, 1080, 1249, 1447, 1581, 2862, 2897, 3062. MS (*m/z*): 365.2 (MH$^+$, 46), 323.3 (M$^+$-CH$_2$CH:CH$_2$, 100), 282.5 (M$^+$-2CH$_2$CH:CH$_2$, 29). HRMS Calcd for C$_{26}$H$_{20}$O$_2$ (M$^+$): 364.1463. Found: 364.1478.

**2,8-Diallyl-3,9-dioctanoyloxyperylene (5b).** Diallyloxyperylene **3d** (0.100 g, 0.30 mmol) was dissolved in polyethylene-glycol dimethyl ether (1.0 mL) and heated at 180 °C for 2 h under $N_2$ while stirring. The mixture was removed from heat, cooled to ice bath temperature, and pyridine (2 mL) and octanoyl chloride (0.21 mL, 1.2 mmol) were added with agitation. After overnight stirring the sample was taken up in toluene (2 × 5 mL) and the combined organic layers were washed sequentially with brine and NaHCO$_3$ solution to obtain a greenish yellow solution. The solution was then dried over Na$_2$SO$_4$, evaporated *in vacuo*, and chromatographed (silica gel; solvent gradient: 3–97% ethyl acetate in toluene) to obtain pure **5b** as an amorphous yellow solid, 100 mg (62%), mp 105–110 °C; $^1$H NMR (CDCl$_3$, 500 MHz): $\delta_H$ 0.91 (t, $J$ 8 Hz, 6H), 1.26–1.42 (m, 12H), 1.42–1.48 (m, 4H), 1.84–1.93 (m, 4H), 2.68–2.81 (m, 4H), 3.42–3.50 (m, 4H), 5.24 (t, $J$ 5 Hz, 10 Hz, 4H), 5.98–6.05 (m, 2H), 7.48–7.59 (m, 2H), 7.60 (d, $J$ 5 Hz, 2H), 8.10 (s, 2H), 8.20 (d, $J$ 5 Hz, 2H). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta_C$ 14.3 (t), 22.8 (q), 25.3 (q), 29.2 (q), 29.5 (q), 31.9 (q), 34.4 (t), 35.2 (d), 117.0 (t), 120.4 (d), 121.0 (t), 122.4 (d), 127.4 (s), 128.4 (t), 128.6 (s), 129.2 (s), 129.3 (s), 131.1 (s), 135.8 (q), 144.4 (s), 172.3 (s). IR ($\nu_{max}$, cm$^{-1}$): 762, 906, 1138, 1596, 1615, 1639, 1748, 2850, 2917, 3051. MS (*m/z*): 617.0 (MH$^+$, 5), 491.1 (MH$^+$-COC$_7$H$_{14}$, 47), 450.2 (MH$^+$-(COC$_7$H$_{14}$+CH$_2$CH:CH$_2$), 21), 365.4 (MH$^+$-2COC$_7$H$_{14}$, 44), 364.5 (M$^+$-2COC$_7$H$_{14}$, 100), 324.6 (MH$^+$-(2COC$_7$H$_{14}$+CH$_2$CH:CH$_2$), 35). HRMS Calcd for C$_{42}$H$_{49}$O$_4$ (MH$^+$): 617.3625. Found: 617.3599.

## Acknowledgements

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