4,8-bisallyl-2,6-dimethylnaphthalene-1,5-diyl diacetate

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Short Note

4,8-Bisallyl-2,6-dimethylnaphthalene-1,5-diyl Diacetate

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Abstract: 4,8-Diallyl-2,6-dimethylnaphthalene-1,5-diyl diacetate (**1**) which is a highly substituted naphthalene derivative has been synthesized in two steps starting from 2,6-dimethyl-1,5-naphthalenediol (**3**) using a modified Claisen-rearrangement.

Keywords: 1,2,4,5,6,8-hexasubstituted naphthalene; Claisen-rearrangement

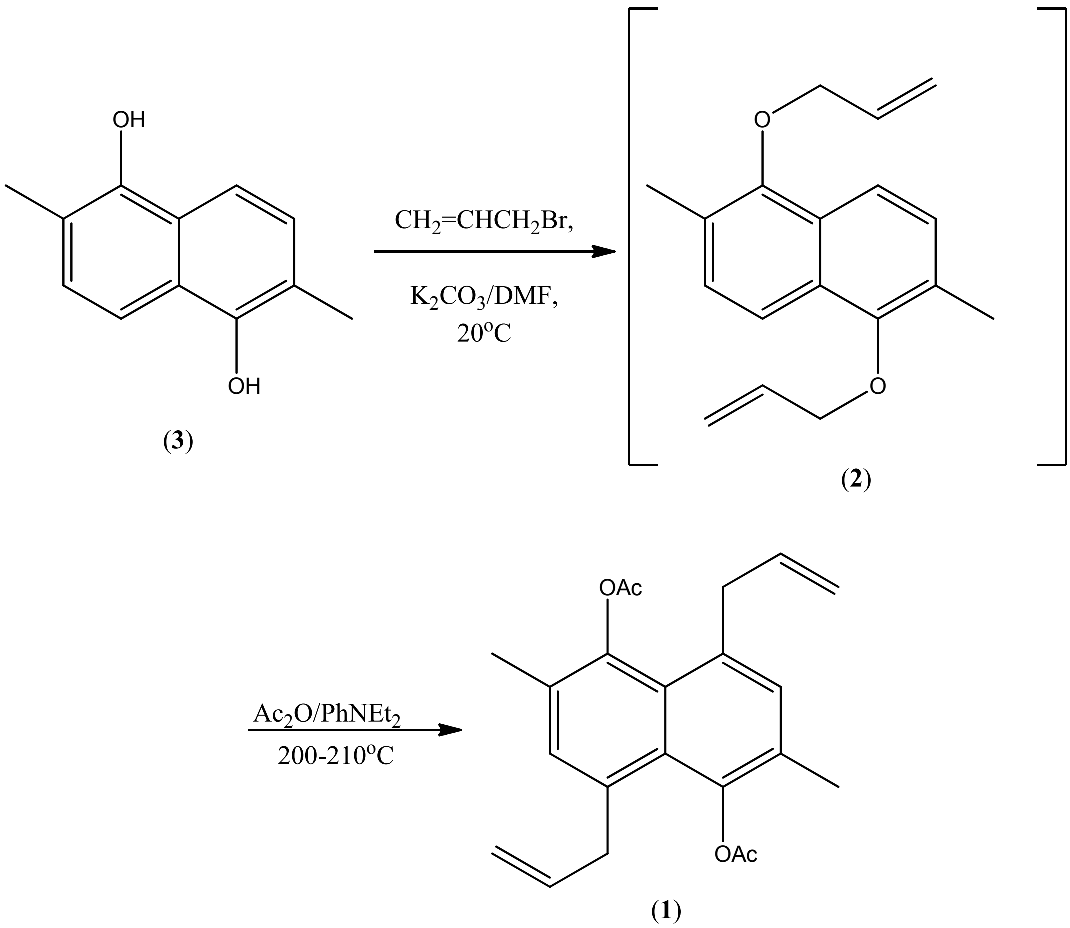
Peri-substituted aromatic compounds [1] such as 1,4,5,8-tetrasubstituted napthalenes are notoriously difficult to synthesize due to the short distance between the peri-positions and in compounds such as 1,4,5,8-tetramethyl naphthalene the methyl groups are interlocking giving rise to restricted rotation [2]. Peri-strain also affects the reactivity of the compounds as for example seen in 4,8-dibromo-1,5-dimethoxynaphthalene, which isomerizes to 2,7-dibromo-1,5-dimethoxy- and finally 2,6-dibromo-1,5-dimethoxynaphthalene upon even short heating in acetic acid [3].

1,4,5,8-tetrasubstituted naphthalenes can serve as staring materials for the synthesis of pyrenes and heterocyclic pyrenes such as dioxapyrenes, which are interesting compounds for conducting radical cation salts. We [4–7] and other groups [8–11] have previously reported different methodologies for the synthesis of 1,6-dioxa- and 1,6-dithiapyrenes from naphthalene derivatives and while the 1,6-dithiapyrenes can be synthesized from 1,5-disubstituted naphthalenes through an acid catalyzed ring closure, the synthesis of 1,6-dioxapyrenes requires either 1,2,5,6-tetrasubstituted naphthalenes or 1,4,5,8-tetrasubstituted napthalenes as intermediates.

The Claisen-rearrangement is an efficient method for introducing substitutents ortho to a phenol via the allyl aryl ether, however if the ortho-positions are blocked, the product is the corresponding 4-allyl substituted compound. [12] This led us to consider the double Claisen-rearrangement of 2,6-disubsubstituted bis allyl ethers of 1,5-naphthalenediols as a synthetic route to *bis*perisubstituted naphthols for subsequent uses for the synthesis of 1,6-dioxapyrenes.

2,6-Dimethyl-1,5-naphthalenediol (**3**) [4] was alkylated with allyl bromide in DMF with K_2CO_3 as the base to give the crude bisallyl ether (**2**), which was subjected to a modified Claisen-rearrangement [13] by reflux in a mixture of *N*,*N*-diethylaniline and acetic anhydride (Scheme 1). Under these conditions, the highly air sensitive tetrasubstituted naphthalenediol is immediately protected by acetylation to give a stable product, that can be purified without any special precautions.

Scheme 1. The synthesis of 4,8-Bisallyl-2,6-dimethylnaphthalene-1,5-diyl Diacetate.



4,8-Bisallyl-2,6-dimethylnaphthalene-1,5-diyl diacetate (**1**)

2,6-Dimethyl-1,5-dihydroxynaphthalene (**3**) [4] (10.2 g; 0.05 mol) and allyl bromide (10 mL; 14 g; 0.12 mol) was added to a degassed suspension of dry K_2CO_3 (0.15 mol) in DMF (50 mL). The mixture was stirred at 20 °C under N_2 overnight. The reaction mixture was poured into water (500 mL) and extracted with diethyl ether (100 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude bis(allyl ether) was dissolved in a mixture of *N*,*N*-diethyl aniline (50 mL) and acetic anhydride (20 mL) and refluxed under N_2 for 3 days (200–210 °C). The product separated upon cooling to room temperature was isolated by filtration, washed with petroleums ether (Bp. 35 °C) until free of *N*,*N*-diethyl aniline and acetic acid and air dried to give (**1**) as an off-white powder.

Yield: 9.6 g (55%).

An analytical sample was crystallized from EtOH. Mp. 166–168 °C.

Calcd. for $C_{22}H_{24}O_4$, C, 74.98; H, 6.86. Found: C, 74.56; H, 6.70.

^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.08 (s, 2 H); 6.07 (m; 2H); 5.03 (m; 2H); 4.92 (m; 2H); 3.78 (m, 4H); 2.30 (s, 6H); 2.13 (s, 6H).

^{13}C-NMR (125 MHz; $CDCl_3$): δ 168.9; 143.9; 137.7; 132.5; 132.1; 127.4; 126.9; 116.2; 40.3; 21.5; 16.7.

Acknowledgments

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Conflict of Interest

The authors declare no conflict of interest.

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