4,8-bisallyl-2,6-dimethylnaphthalene-1,5-diyldiacetate

Christensen, Jørn Bolstad; Sørensen, Jeanett N.; Schaumburg, Kjeld; Bechgaard, Klaus

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Short Note

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

Jørn B. Christensen *, Jeanett N. Sørensen, Kjeld Schaumburg and Klaus Bechgaard

Department of Chemistry, University of Copenhagen, Thorvaldsensvej 40, DK-1871 Frederiksberg C, Denmark

* Author to whom correspondence should be addressed; E-Mail: jbc@chem.ku.dk.

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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 naphthalenes 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-dioxapa- and 1,6-dithiapryrenes from naphthalene derivatives and while the 1,6-dithiapryrenes 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 naphthalenes 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-disubstituted 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 K₂CO₃ 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-diyli Diacetate.

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

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$_3$): $\delta$ 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$_3$): $\delta$ 168.9; 143.9; 137.7; 132.5; 132.1; 127.4; 126.9; 116.2; 40.3; 21.5; 16.7.

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Conflict of Interest

The authors declare no conflict of interest.

References


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