Photoinduced Decarbonylative rearrangement of Bicyclo[2.2.2]octenone

Synthesis of the Marasmane skeleton

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Marasmane is a sesquiterpenoid skeleton: fused-5,6,3-tricyclic ring

Many bioactive properties: antibacterial
Synthetic challenge

Price: 164 800 € / 1 g (sigma-aldrich)
Photochemical rearrangement

bicyclo[2.2.2]octenones

Scope of our bicycloocteteneone derivate

Synthesis of MOB: masked-o-benzoquinone

\[ \text{MOB} \]

Diels-Alder

\[ \text{Diels-Alder} \]

25-92 % over two steps
25 examples

\[ \text{R}^2 = \text{H, alkyl, acetal, OMe} \]
\[ \text{R}^3 = \text{H, alkyl, acetal, ester} \]
\[ \text{R}^4 = \text{H, alkyl, vinyl, TMS, EWG} \]
\[ \text{R}^5 = \text{H, OMe} \]

Scope of the reaction

33 – 99 %
18 examples

\[ R^2 = H, Me, \text{acetal}, \]
\[ R^3 = H, Me, \text{acetal, EWG} \]
\[ R^4 = H, \text{alkyl, vinyl, TMS}, \]
\[ R^5 = H, \text{OMe} \]
$R^4$ governed the photoreaction pathway. No EWG tolerated.
Proposed reaction pathway for the decarbonylative 1,3 migration

1,3-acyl migration

Oxa-di-π-methane
Proposed reaction pathway for the decarbonylative 1,3 migration

EWG = Acetyl or CHO

Oxa-di-π-methane

Disclosed a construction of Marasmane skeleton thank to a photochemical rearrangement of bicyclo[2.2.2]octenones

Easily available precursors

Many functional groups are compatibles

This new photoreaction may be useful in synthesis of analogues of the Isovelleral skeleton