BURIED TREASURES:
CASCADES WE HAVEN’T SEEN

R. Robinson,
*J. Chem. Soc.*, 1917, 762
Cascades Articulated

Main Entry: 1cascade
Pronunciation: ("kas-"kAd
Function: noun
Etymology: French, from Italian cascata, from cascare to fall, from (assumed) Vulgar Latin casicare, from Latin casus fall, Date: 1641

1: a steep usually small fall of water; especially : one of a series

2a: something arranged or occurring in a series or in a succession of stages so that each stage derives from or acts upon the product of the preceding <blood clotting involves a biochemical cascade > b: a fall of material (as lace) that hangs in a zigzag line

3: something falling or rushing forth in quantity <a cascade of sound> <a cascade of events>
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1: a steep usually small fall of water; *especially* : one of a series

2a: **something arranged or occurring in a series or in a succession of stages so that each stage derives from or acts upon the product of the preceding** <blood clotting involves a biochemical *cascade*> b: a fall of material (as lace) that hangs in a zigzag line

3: something falling or rushing forth in quantity <a *cascade* of sound> <a *cascade* of events>

4: **One-pot, sequential reactions involving more than one intermediate, preferrably 1) leading to an increase in molecular complexity and 2) without changing reaction conditions**

*see: Chem. Commun., 2003, 551*
Some Inspiration


3 intermediates
Some Inspiration


Some Inspiration

1) H₂, Pd/BaSO₄, quinoline
2) toluene, 100 °C

3 intermediates


2 intermediates


4 intermediates

Dihydropyrididone Synthesis

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*Chem. Pharm. Bull., 1987, 4730*
Dihydropyridone Synthesis

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Degredation to a Cyclohexadiene

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Degredation to a Cyclohexadiene


\[
\text{Br-Br} \xrightarrow{\text{CH}_3\text{Li, Et}_2\text{O}} \text{H} \equiv \text{H}
\]

\[
\text{CH}_3\text{Li} \quad \xrightarrow{} \quad \text{H} \equiv \text{H}
\]

\[
\text{Br-Br} \quad \xrightarrow{\text{CH}_3\text{Li}} \quad \text{Cyclohexadiene}
\]
Degredation to a Cyclohexadiene

Starting Material?
*Angew. Chem. Intern. Ed.*, **1975**, *496*

\[
\begin{align*}
\text{1. CH}_2\text{I}_2, \text{Zn/Cu} \\
\text{2. CHBr}_3 \\
\text{3. MeLi, Et}_2\text{O}
\end{align*}
\]
Starting Material?

1. CH$_2$I$_2$, Zn/Cu
2. CHBr$_3$
3. MeLi, Et$_2$O
Starting Material?
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*Angew. Chem. Intern. Ed.*, **1975**, *496*
Starting Material?
*Angew. Chem. Intern. Ed.,* **1975**, *496*
Synthesis of a Tetrayne
*Tetrahedron Lett., 1976, 2663*
Synthesis of a Tetrayne


\[
\text{AcO}\text{CHCH}_{\ldots}\text{H} \quad \text{BuLi; CuCl} \quad \text{Cu}^+ \text{Cu}_{\ldots}\text{Li}
\]

\[
\text{AcO}\text{CHCH}_{\ldots}\text{Li} \quad \text{Cu}^+ \text{Cu}_{\ldots}\text{Cu}
\]
Synthesis of a Tetrayne

\[
\text{AcO}\equiv\text{H} \xrightarrow{\text{BuLi; CuCl}} \text{[structure image]}
\]

\[
\text{BuLi} \quad \text{AcO}\equiv\text{Li} \xrightarrow{\text{Cu}^+} \quad \text{AcO}\equiv\text{Li} \quad \text{Cu}\quad \text{[structure image]}
\]

\[
\text{[structure image]}
\]
Synthesis of a Tetrayne

Synthesis of a Tetrayne

Complex Polycycle

![Reaction Scheme]
Complex Polycycle

Complex Polycycle


![Chemical reaction diagram](image)
Complex Polycycle

Complex Polycycle Cont...


6 e⁻ disrotatory
Complex Polycycle Cont...

A [3.2.0] Bicycle


![Chemical structures](image)
A [3.2.0] Bicycle


\[
\text{MeO}_2\text{C-} + \text{TMSI, (TMS)_2NH} \rightarrow \text{TBDPSO-} + \text{CO}_2\text{Me}
\]
A [3.2.0] Bicycle

A [3.2.0] Bicycle

A [3.2.0] Bicycle

A [3.2.0] Bicycle

A Hydrindane

Unpublished
A Hydrindane

Unpublished

\[
\text{PhH, } \square
\]
A Hydrindane

Unpublished
Another (the same) Hydrindane

Hoye, T., *Unpublished*
Another (the same) Hydrindane

Hoye, T., Unpublished
Another (the same) Hydrindane

Hoye, T., Unpublished
Summary