Question, Query and Relevant Response: Pick any two

Sandy Lawson

Director R&D,

MDL Information Systems GmbH

And in Future Years?

MDL Information Systems GmbH

- Ask Etna, Vesuvius, Mauna Loa, Pele´..
- Thank you for your attention.

From: The Beilstein File :The Quiet (R)evolution (San Diego May 2001)

The Quest in Question

MDL Information Systems GmbH

- Use of Chemical Information services is largely research driven
- Research is largely driven by the search for the Unknown
- The Known is largely accessible, and largely the starting basis for the quest
- Therefore there is usually a hidden subjective context relationship between question and query

Relevant Response

MDL Information Systems GmbH

- The relevance of the response of any ordered set of data is strongly dependent on the externally superimposed context of the ordering system (Garbage in, Garbage out).
- Therefore, secondary indexing data are subject to a heterogeneous series of internal conventions, each homogeneous in nature. (That's life in a pluralistic marketplace)
- The query is a map of the question context onto the order of the underlying data (What I Mean as opposed to What I Say)
- Primary source data, although subject to external conventions, is naturally heterogeneous (Just Say It)

Question and Relevant Response

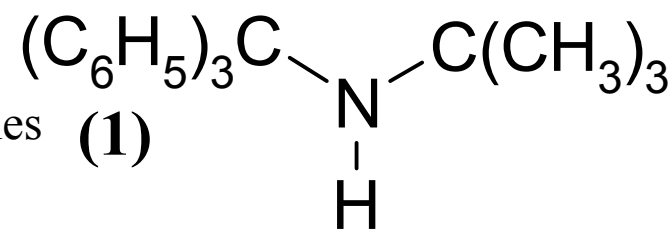
MDL Information Systems GmbH

- It is not merely an issue of a universal set of standards for querying (In one way or another this has dominated the discussion for 20 years..). The best approach here is a Natural Language Analyzer, operating on source as well as query. This is a separate subject (Reading Machines).
- In a non-monopolistic environment it is more an issue of moving the issue of “Query Formulation” out of the central focus of attention. This is the subject of this talk.

The Distance between the Quest and the Relevant Response: one example

MDL Information Systems GmbH

Sterically shielded secondary N-tritylamines and N-tritylamide bases, readily available and useful synthetic reagents



(1)

"It was astonishing to us that N-trityl derivatives of t-alkylamines apparently have never been reported." (Corey, 2000)

(Nobel Prize 1990: "for his development of the theory and methodology of organic synthesis")

Melting Point 1-2 of 2

94.5 ethanol Brander; Recl.Trav.Chim.Pays-Bas; 37; 1918; 71.

90 - 91 methanol Busch-Petersen, Jakob; Corey, E. J.; Tetrahedron Lett.; 41; 15; 2000; 2515 .

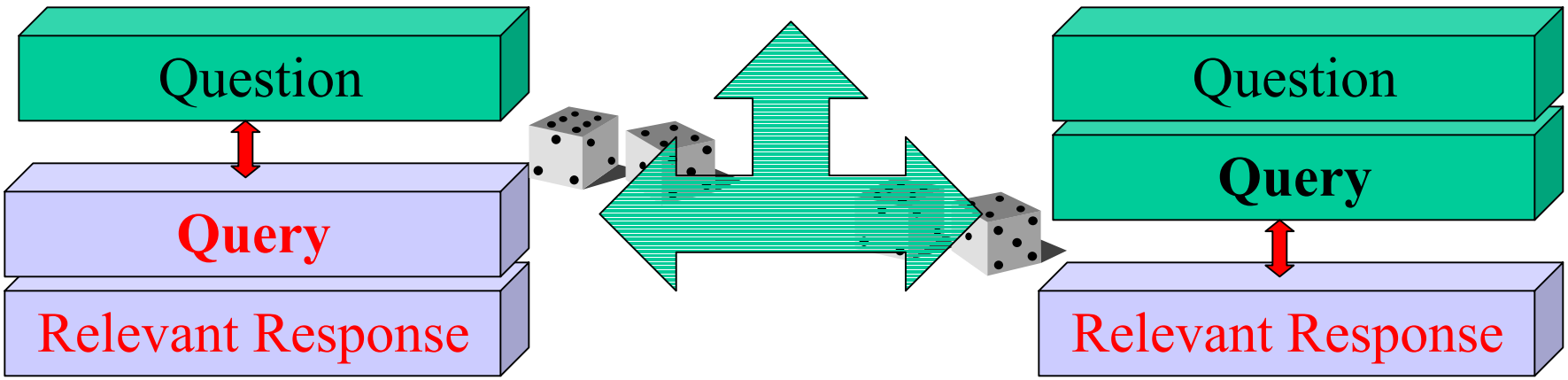
Prep. Brander; Recl.Trav.Chim.Pays-Bas; 37; 1918; 71.; Buckus et al.; J.Org.Chem.USSR (Engl.Transl.); 4; 1968; 1073; Zh.Org.Khim.; 4; 1968; 1113; Maender; Janzen; J.Org.Chem.; 34; 1969; 4072

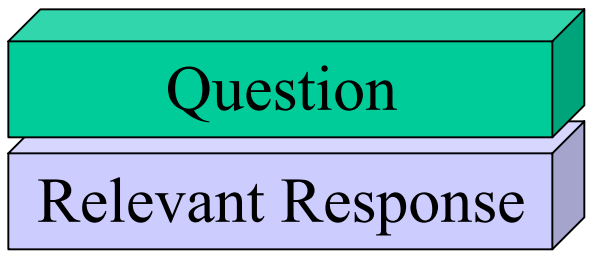
Ammonium Ion :Arnett, Edward M.; Venimadhavan, Sampath; J.Org.Chem.; 56; 8; 1991; 2742.
Nitroxide radical (ESR) : Maender; Janzen; J.Org.Chem.; 34; 1969; 4072.

Pick Any Two

MDL Information Systems GmbH

Natural Language Interface

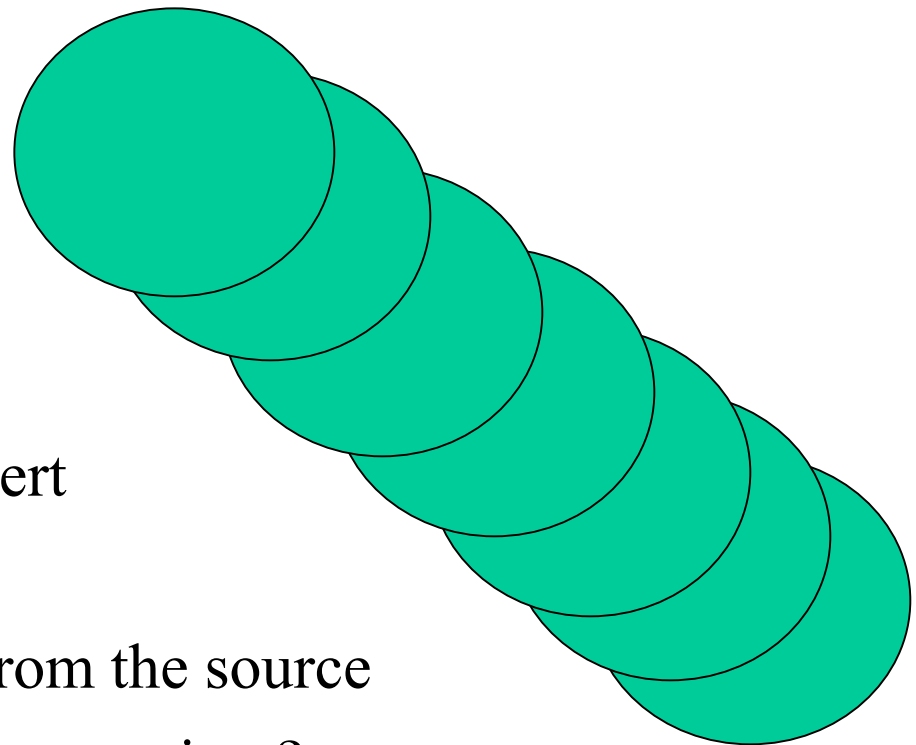




Point & Click

Pre- CrossFire, Pre-SciFinder: User, Expert Intermediary, Index and Source

MDL Information Systems GmbH



The underlying question

How I say it to the expert

How it is heard by the expert

How it is formulated by the expert

How it is heard by the database

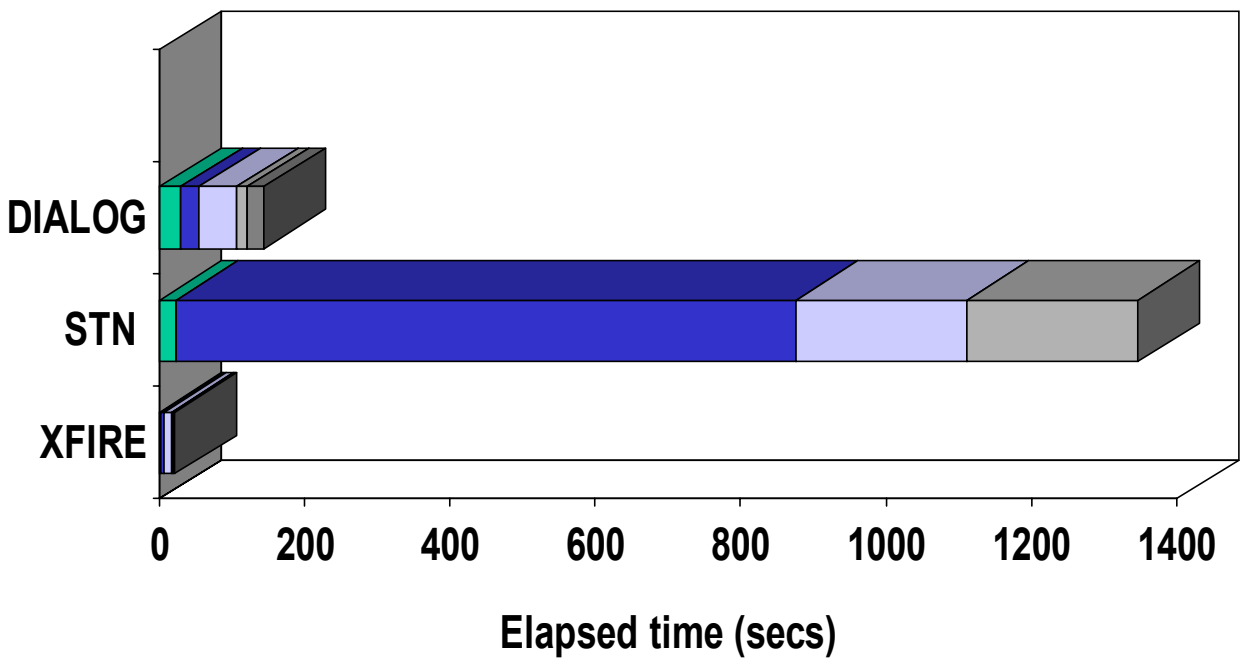
What the database understood from the source

How relevant is the source to the question ?

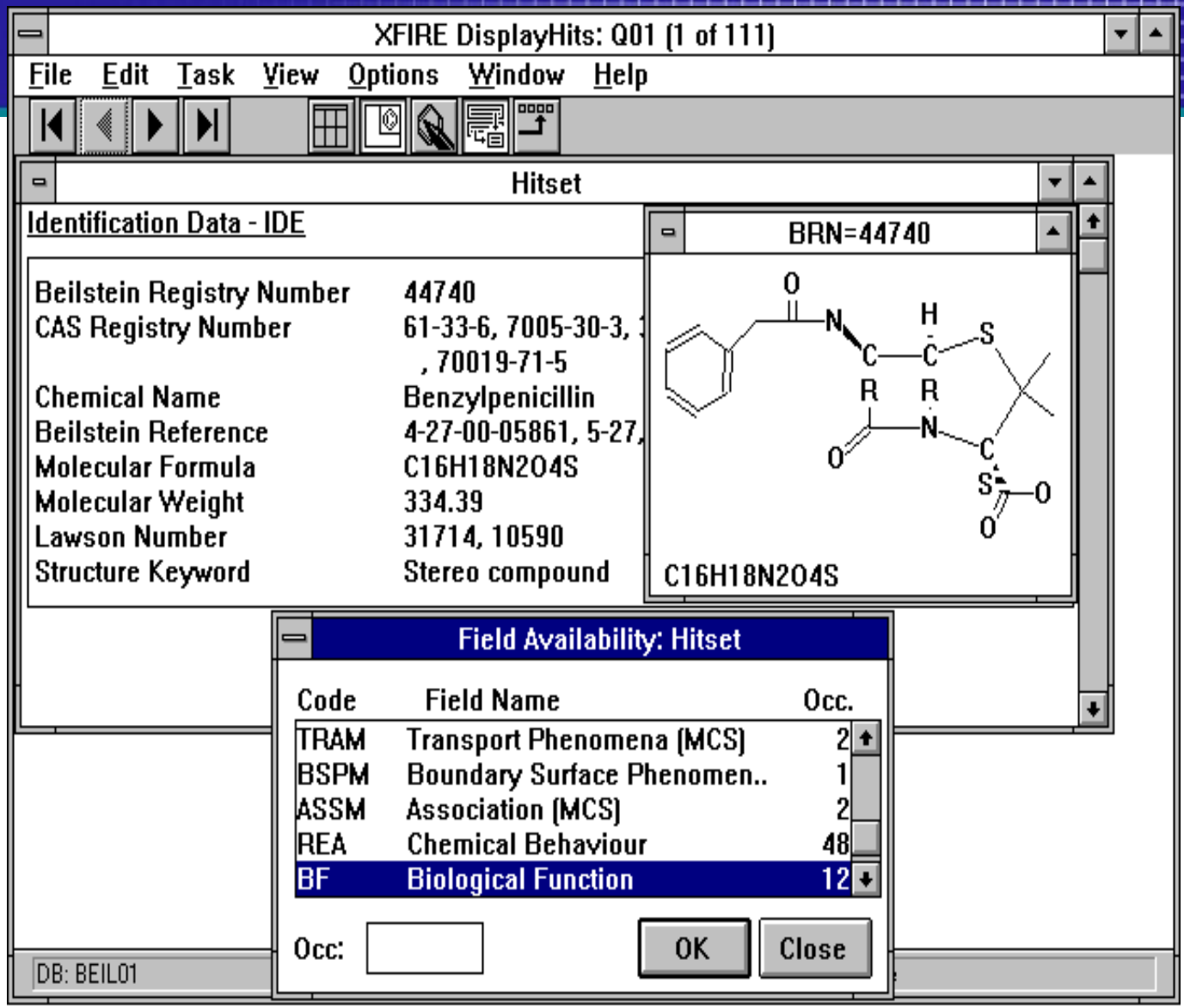
Efficiency = $(95\%^{7} = 63\% \; .. \; 85\%^{7} = 23\%) / (\text{cost} * \text{time})$

XFIRE is Fast

MDL Information Systems GmbH



From: Electronic Publishing: The Coming Storm (Munich 1994)



From: Electronic Publishing: The Coming Storm (Munich 1994)

CrossFire 1.0, 2.0

MDL Information Systems GmbH

The underlying question

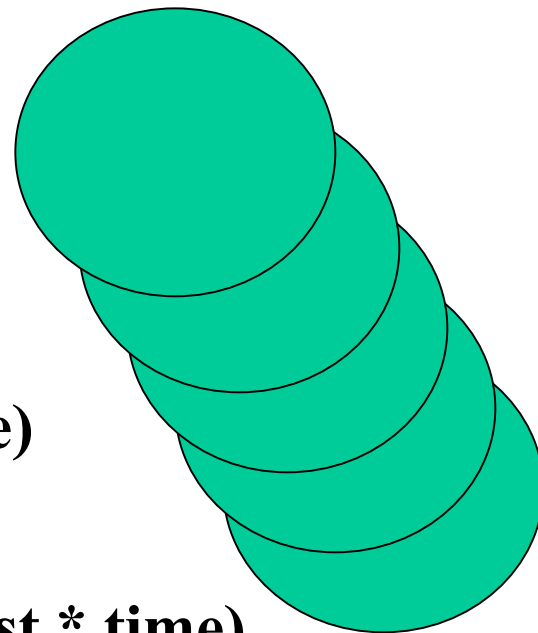
How it is formulated by the user

How it is heard by the database

(What the database understood from the source)

How relevant is the source to the question ?

Efficiency= (95% ^{5} = 77% .. 85% ^{5} = 44%) / (* **cost * time)**



2nd-Generation

MDL Information Systems GmbH

Display Hits - Q01:BS9703AB hit 3 of 3

File Edit Task View Options Window Help

Q01:BS9703AB hit 3 of 3

Title A Convenient Semisynthetic Route to Hypericin

Abstract A semisynthetic route to produce hypericin was established using Cortex frangulae as the starting point. The emodin isolated from it easily and in good yield was reduced to emodin anthrone by means of SnCl2. The latter was reacted via a known oxidative dimerization and photocyclization reaction into hypericin. Keywords: Emodin; Emodin anthrone;

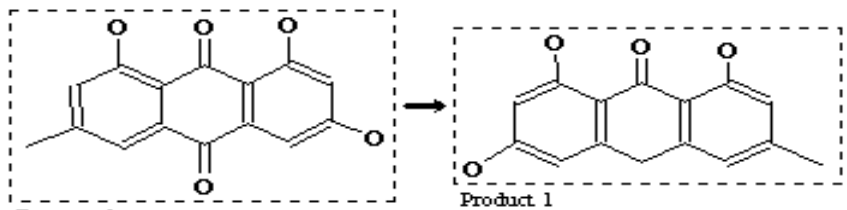
CrossFire

1997188:BS9703AB hit 1 of 1

Reagent	$SnCl_2*2\ H_2O$,
Solvent	acetic acid
Time	5 hour(s)
Yield	88. (BRN=21
Other conditions	Heating

Ref. 1 5756860; Journal; Falk, H.; Me
Monatsh.Chem.; EN; 124; 3; 1

Hit = 1



For Help, press F1 | idle | USER | Citation

SciFinder

MDL Information Systems GmbH

The underlying question

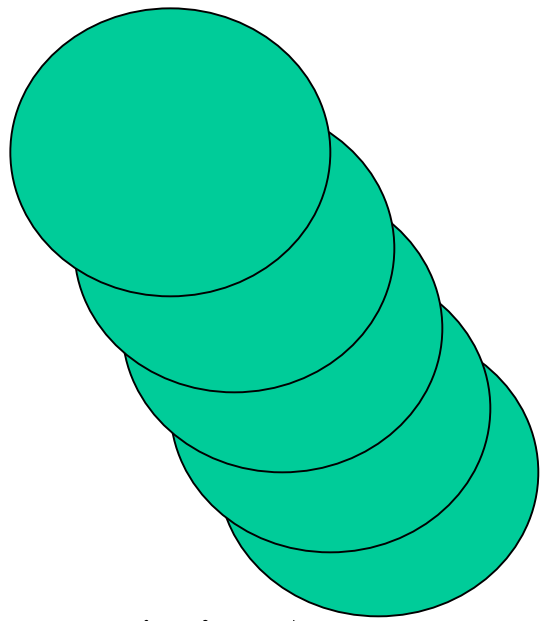
(How it is formulated by the user)

(How it is heard by the database)

What the database understood from the source

How relevant is the source to the question ?

Efficiency= (95%^{5} = 77% .. 85%^{5} = 44%) / (* **cost** * time)



Documents... Reactions... Compounds...

MDL Information Systems GmbH

Language
Title

Abstract

Substance 1 of 5

Beilstein Registry I
CAS Registry Num
Chemical Name

For Help, press F1

Display Hits - [3871664:BS9803AB hit 1 of 1]

File Edit Task View Options Window Help

Reaction

Reaction ID
Reactant BRN

Product BRN

Reaction Details

Reaction Classification
Solvent
Temperature

Ref. 1 *5844541*; Jo
Susanne; AI
GE; 326; 9;

For Help, press F1

Display Hits - [Q02:BS9803AB hit 2 of 143]

File Edit Task View Options Window Help

Reaction ID *3871664*
Reactant BRN 94993 *ent*-4,5α-epox
6631865 $C_8H_{13}NO_2$
Product BRN *6628554* $C_{18}H_{21}NO_3$*

Ref. 1 *5844541*; Journal; Knabe, Joachim;
Ger.); GE; 326; 9; 1993; 551-558;

Optical Rotatory Power 1 of 2

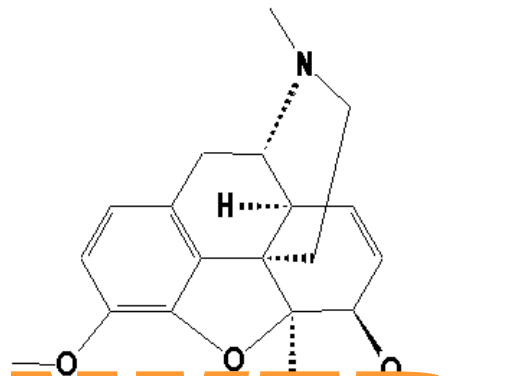
Type <alpha>

Optical Rotatory Power 2 of 2

Type <alpha>
Concentration 0.693
Solvent ethanol

For Help, press F1 | idle | USER | Substance

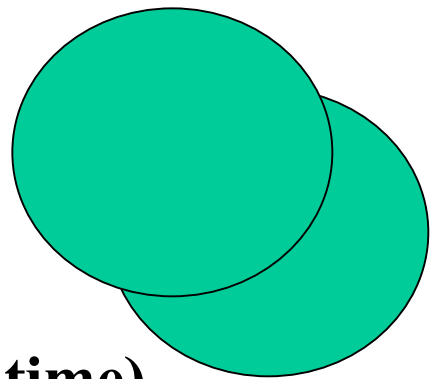
Q02: Hit 2



HYPERLINKED

CrossFire 3.0 onwards: Defined Hyperlink Technology (Index)

MDL Information Systems GmbH



The underlying question

How relevant is the source to the question ?

Efficiency= (95% ^{2} = 90% .. 85% ^{2} = 72%) / (cost *** time)**

CrossFire Web - Microsoft Internet Explorer

MDL Information Systems

CrossFire Web VERSION 1.0

QUERIES | RESULTS | REPORTS | RXN SCHEMES

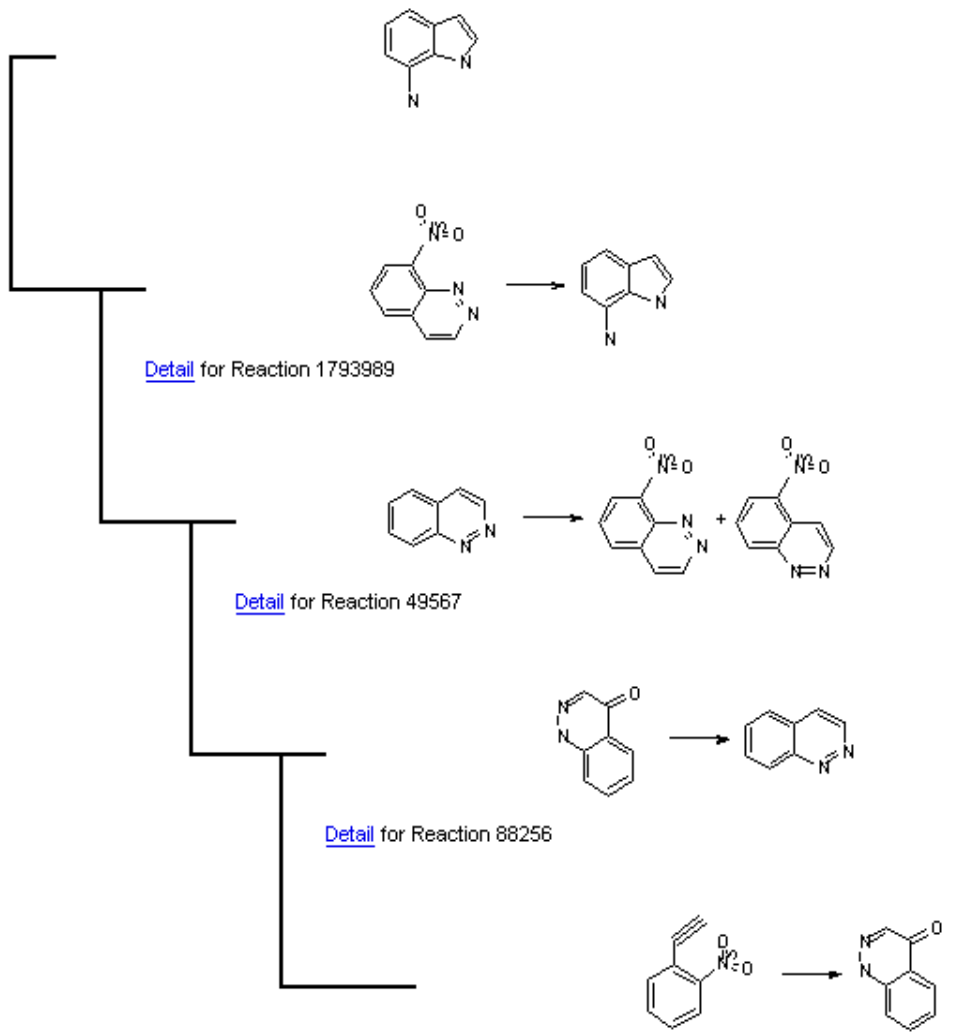
COPY TO REPORT | PAGE SETUP | PRINT | SAVE | REFINE QUERY | NEW QUERY | HELP | LOGOUT

Find in Rxn Tree: Next

Rxn Tree | History

- Substance 471787
  - Reaction 1793989
    - Substance 144633
      - Reaction 49567
        - Substance 109227
          - Reaction 74124
          - Reaction 88256
            - Substance 118882
              - Reaction 156820
              - Reaction 172932
              - Reaction 289131
                - Substance 194
              - Reaction 579583
              - Reaction 3055476
          - Reaction 134389

Synthetic Scheme for Substance 471787



Detail for Reaction 1793989

Detail for Reaction 49567

Detail for Reaction 88256

Detail for Reaction 289131

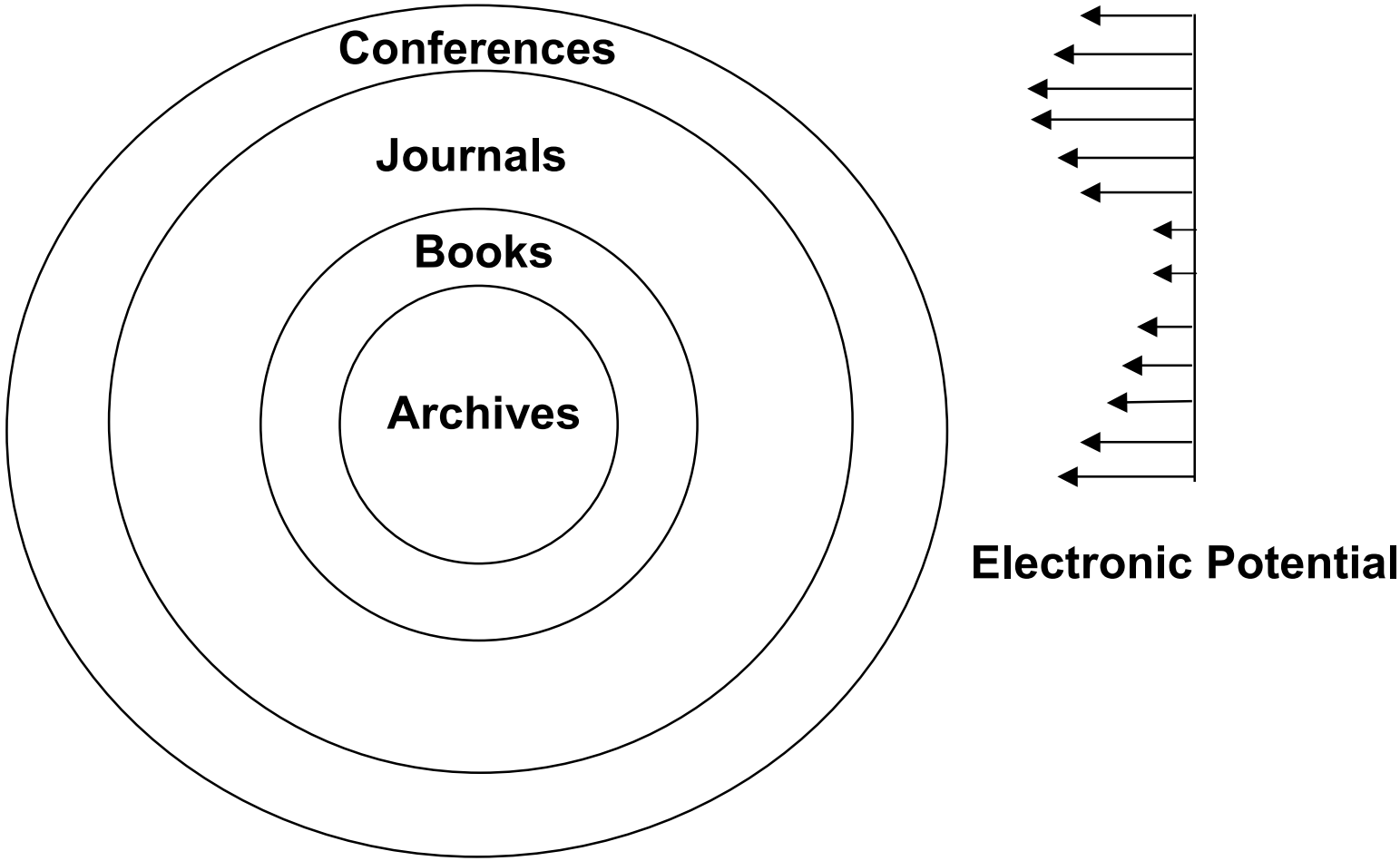
Electronic Publishing.. The Coming Storm

MDL Information Systems GmbH

- Primary Services
  - Conferences — Growth area
  - Journals — Storm Clouds
  - Books — Well. .maybe
- Secondary Services
  - Indexing — Second Spring
  - Database Mining — Growth area

From: Electronic Publishing: The Coming Storm (Munich 1994)

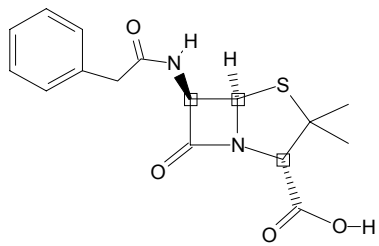
The Tree-trunk Model of Chemical Information



From: Electronic Publishing: The Coming Storm (Munich 1994)

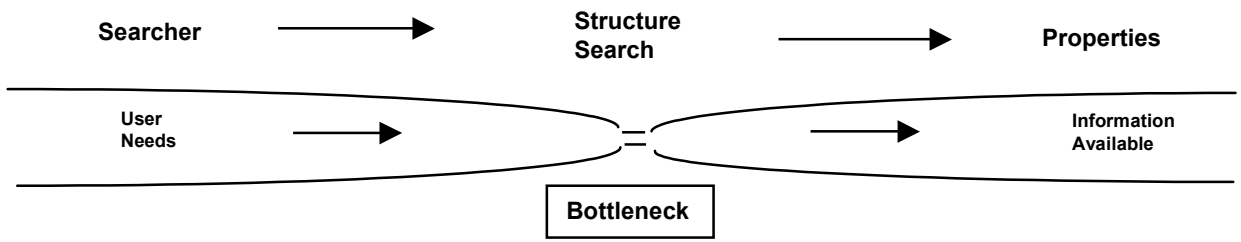
The Structure IS the Property

MDL Information Systems GmbH



Physical properties..
Biological action..
Acid / base behaviour
Toxicology..
Lipophilicity..
Reactivity..

etc..



From: Electronic Publishing: The Coming Storm (Munich 1994)

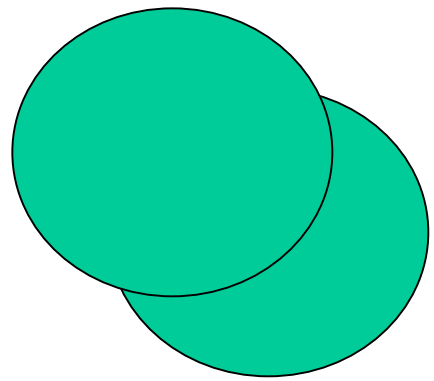
Defined Hyperlink Technology (Source)

MDL Information Systems GmbH

(How relevant is the source to the question?)

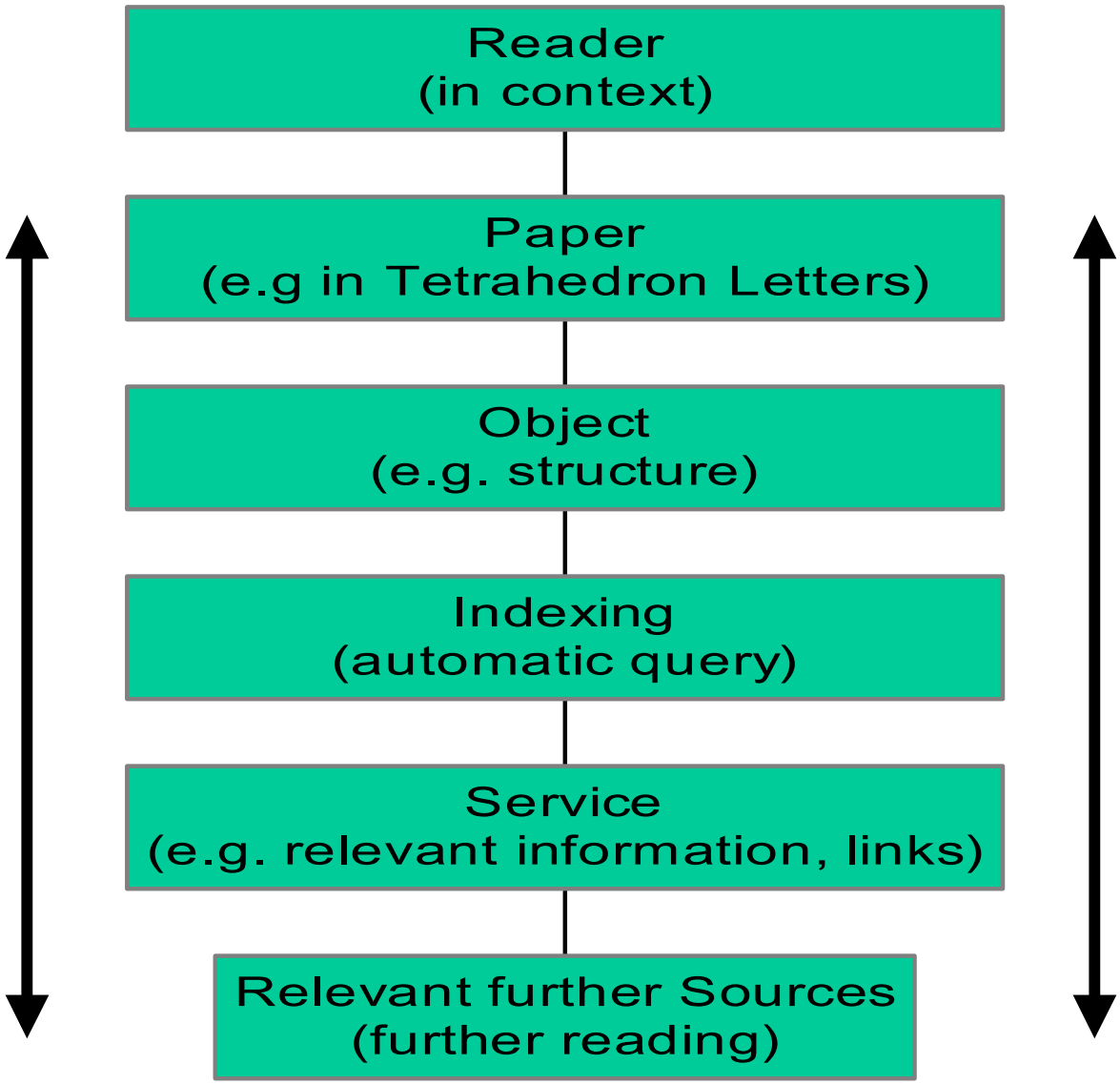
The underlying question

Efficiency= (95% ¨ 85%) / (cost *** time)**



Something Old, Something New..

MDL Information Systems GmbH



Search for hetero-Diels-Alder reactions

MDL Information Systems GmbH

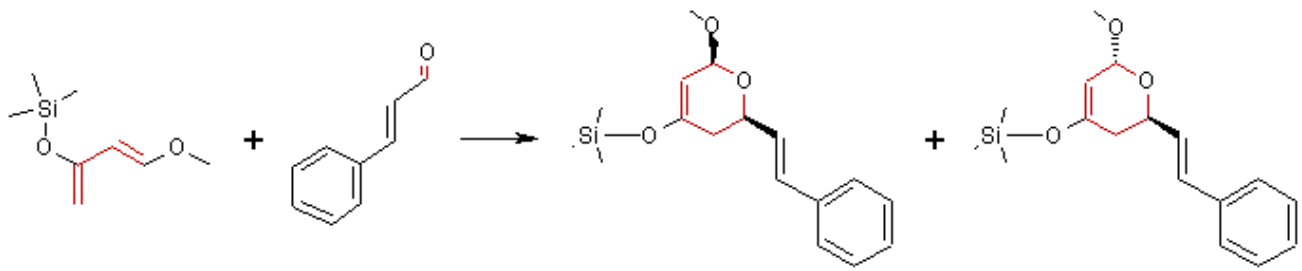
Forms | Query | Browse | Update <RXN> 7 of 20

Summary | Reference | Reagents | Conditions | Table

ChemInform RX 1992 - 1996 | RXN 7 of 20 | Variation 1 of 1 | Path A | Step 1 OF 2

Cluster # | Item # | Value:

REGNO: 235389



REFNO: 9433054

Variation	Literature Reference	Reagents	% Yield
1	VAN DE WEGHE, P.; COLLIN, J.; Tetrahedron Lett [TELEAY] 1994, 35 (16), 2545-2548.	SmI2 (cat.) CH2Cl2	84.3 13.7

BROAD	MEDIUM	NARROW
292719508717176	330789623257863	360076379380431
292719508717176	330789623257863	360076379380431

Table of Contents

- CAC
- COFGT
- EROS

Select a Search Page:

All licensed iMRW publications
CAC only
COFGT only

Select a Search Page:

All licensed iMRW publications
CAC only
COFGT only
EROS only

iMRW - integrated Major Reference Works

Search Results - Related reactions in All Licensed iMRW Publications

Return to Previous Results

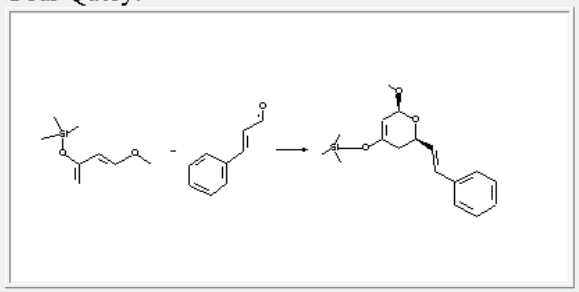
Return to Previous Results from All Licensed iMRW Publications

Return to Product Selection

New Query

Hints and Tips

Your Query:

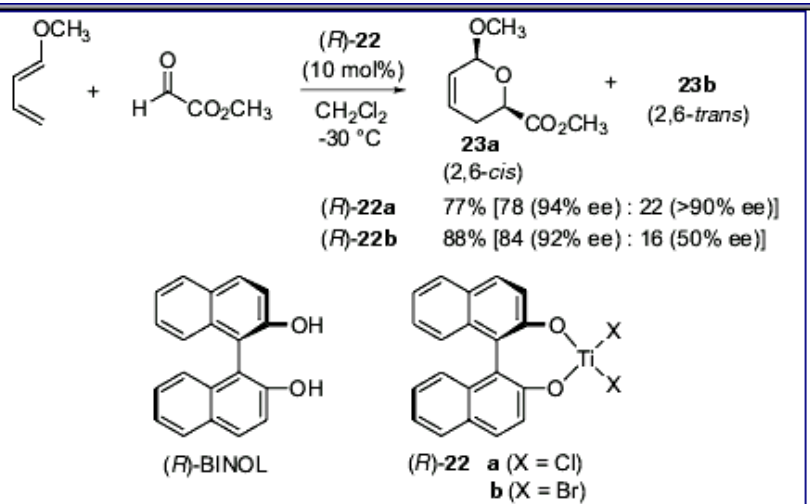


The related reactions are grouped in categories named Broad, Medium and Narrow. These classifications are made on the basis of the reaction centers of your reaction of interest, shown above. Click Hints and Tips for more information.

- **CAC**
  Broad: 30 Hits Medium: 4 Hits Narrow: 0 Hits
- **COFGT**
  Broad: 11 Hits Medium: 0 Hits Narrow: 0 Hits
- **EROS**
  Broad: 68 Hits Medium: 10 Hits Narrow: 1 Hit

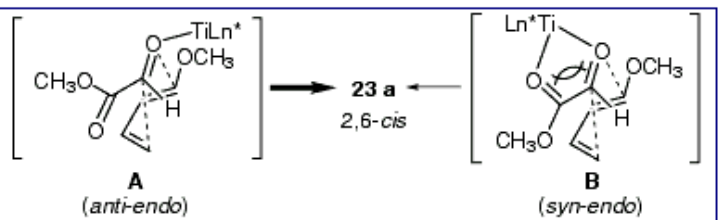
Groups from which examples were taken

Information for related reactions in CAC



Scheme 11

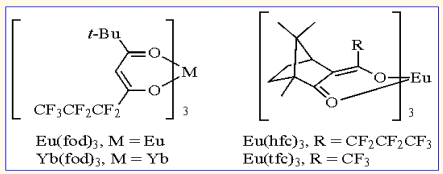
The observed *cis*-selectivity provides a mechanistic insight into the state of complexation between glyoxylate and the chiral titanium catalyst. Of the two transition states leading to the *cis*-product, the *syn-endo* transition state **B** should be less favorable because of the steric repulsion in the sterically demanding titanium complex. Thus, the titanium catalyst should be complexed in an *anti* fashion and then the reaction proceeds through an *endo*-orientation (Structure 2).



Structure 2

Information from EROS

Lanthanide Shift Reagents



$Eu(fod)_3$, M = Eu
$Yb(fod)_3$, M = Yb

$Eu(hfc)_3$, R = $CF_2CF_2CF_3$
$Eu(tfc)_3$, R = CF_3

($Eu(fod)_3$)

(mild Lewis acids capable of catalyzing a variety of synthetic transformations)

Alternate Names: $Eu(fod)_3$ = tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium; $Yb(fod)_3$ = tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)ytterbium; $Eu(hfc)_3$ = tris[3-(heptafluoropropylhydroxymethylene)-(+ or -)-camphorato]europium; $Eu(tfc)_3$ = tris[3-(trifluoromethylhydroxymethylene)-(+ or -)-camphorato]europium.

Physical Data: $Eu(fod)_3$: mp 203-207 °C; $Yb(fod)_3$: mp 108-111 °C; $Eu(hfc)_2$: mp 156-158 °C; $Eu(tfc)_3$: mp 195-198 °C.

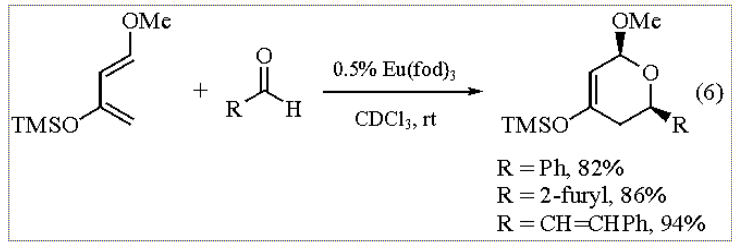
Solubility: generally sol in a wide variety of organic solvents; commonly used in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$.

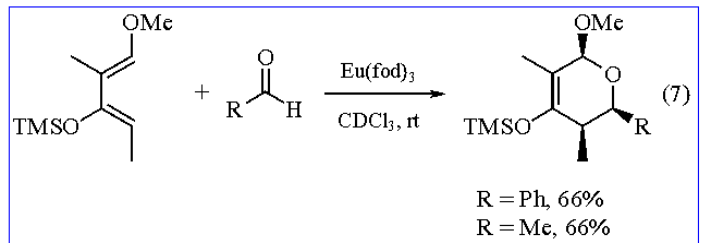
Form Supplied in: hygroscopic solids; commercially available. *Drying:* if necessary, they can be dried and stored over P_2O_5.

Purification: can generally be used directly without purification. Occasionally contain insoluble material which can be removed by filtration of a solution of the reagent through a millipore filter or a plug of cotton or glass wool. Insoluble material can also be separated and removed by centrifugation.

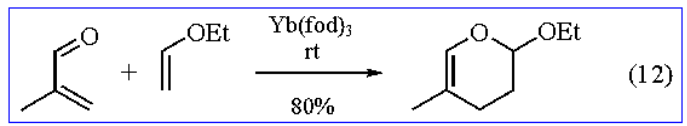
Handling, Storage, and Precautions: though hygroscopic, they can be handled for short periods of time in the presence of air without deleterious effect. In general, the use of glove bags or dry boxes is

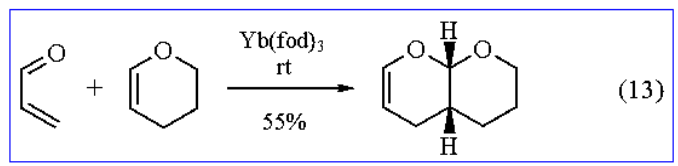
The lanthanide shift reagent catalyzed Diels-Alder cycloaddition reaction of oxygenated dienes with aldehydes has been extensively investigated. $Eu(fod)_3$ effectively catalyzes this reaction at room temperature and, in many cases, allows the relatively unstable silyl enol ether intermediates to be isolated (eqs 6-11).[3,8-10]





Enol ethers undergo [4 + 2] cycloaddition with α,β-unsaturated aldehydes in the presence of catalytic amounts of lanthanide shift reagents to give dihydropyran derivatives (eqs 12 and 13).[11]





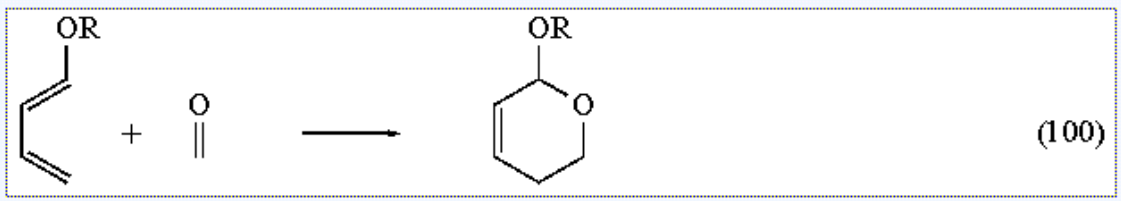
Lanthanide shift reagents catalyze the addition of silyl enol ethers to aldehydes.[4,12] The yield and diastereoselectivity obtained with lanthanide shift reagents are often better than those observed with more conventional catalysts (eq 14).

Information from COFGT

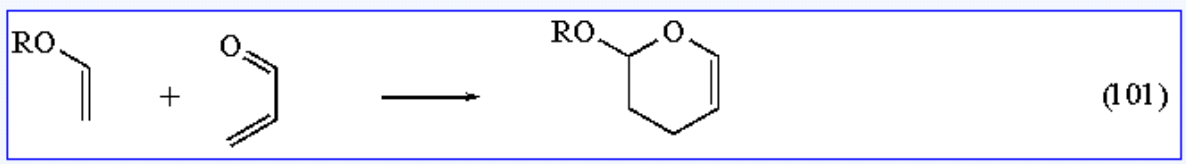
MDL Information Systems GmbH

4.04.3.3.4 By hetero Diels-Alder reactions

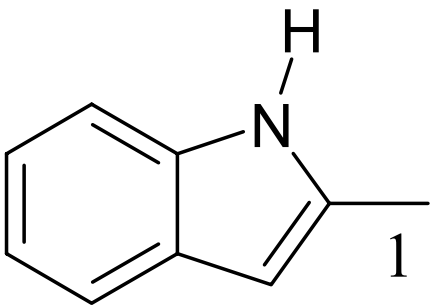
The hetero Diels-Alder cycloaddition is a useful method for the preparation of 2-alkoxypyran derivatives which has been widely exploited in natural-product synthesis. Two modes of reaction are possible and have been studied. Cycloaddition of an alkoxy-substituted diene with an aldehyde as the dienophile has been most widely studied (Equation (100)). Alternatively, an inverse electron demand, Diels-Alder reaction between an enol ether and an α,β-unsaturated carbonyl derivative provides pyran derivatives (Equation (101)). Both types of reactions may occur under thermal conditions, but they are generally carried out with Lewis acid catalysis or under high pressure. Numerous examples have appeared in the literature, and reviews should be consulted for further details [362] [486] [493] [494].

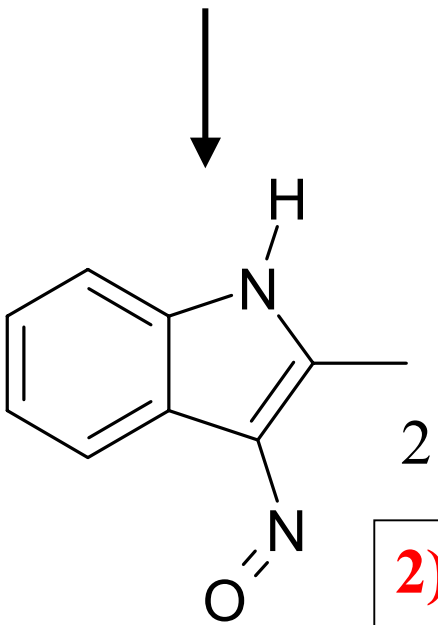


(100)



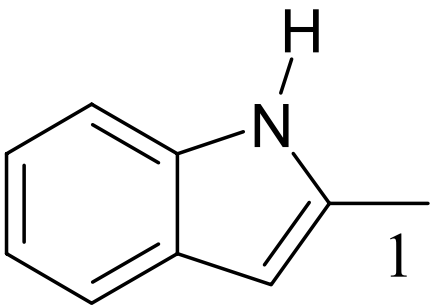
(101)





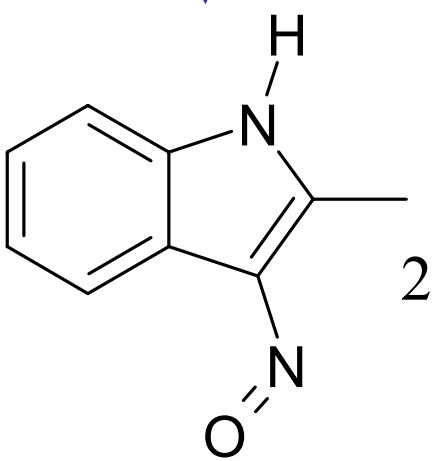
- **The Mechanism of the Nitrosation of Indoles**
  By John Doe
  Summary : The kinetics of nitrosation of several alkyl-indoles in dilute HClO4 at room temperature are reported.
- **Discussion.** Indoles are known to be very prone to electrophilic substition in the five membered ring. (Ref. 1). In the case of aromatic nitrosation, the products depend on the presence or absence of substitution on the ring nitrogen. (Ref. 2). Etc..
- **Experimental**. 2-methyl-indole (5g) was dissolved in glacial acetic acid (200 ml) .. Etc..
- **References.**
  1) Peter Grimes, JACS..
  2) John Smith, TETRAHEDRON..

2) Even after indexing, it is not enough to rely on Querying (a passive method), the paper itself should be alive with Point & Click access.



(Beilstein)

Related reactions



(Beilstein)

- **The Mechanism of the Nitr** oe
  S The kinetics of nitrosation of several alkyl-indoles in dilute HClO4 at room temperature are reported.
- **Discussion.** Indoles are known t one to electrophilic substition in the five ring. (Ref. 1). In the case of aromatic nitrosation, the ucts depend on the presence titution on the ring nitrogen. (R
- **Experimental**. 2-methyl-indole 1 (5g) was dissolved in glacial acetic acid (200 ml) .. Etc..
- **References.**
  1) Peter Grimes, JACS..
  2) John Smith, TETRAHEDRON..

Secrets

Related Papers

Review

Dymond

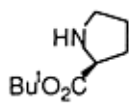
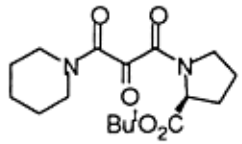
Litlink

4) Electronic articles update their hyperlinks in step with the publication of new papers.

We now report a further method for forming the tricarbonyl array starting from oxalic acid mono amides which are readily available by monoacylation of an amine such as piperidine with dimethyl oxalate or by treatment of the amine with the acid chloride of oxalic acid monomethyl ester. Hydrolysis of the ester with LiOH yields the corresponding carboxylic acid **1** (~98%).

To form the oxomalondiamides, the monoamide **1** was transformed to the acid chloride and then coupled with the cyano ylide in the presence of BSA to form the diacyl cyano ylide **2**. [3] Oxidation of **2** yielded a labile triacyl nitrile **3** which was trapped by nucleophiles to give products **4** [4] (Table 1). [5]

Table 1 Coupling of tricarbonyl intermediate **3** with various nucleophiles[a]

Entry	NuH	Products (**4**)	Yield, %
a			89

And in Future Years?

MDL
Information Systems GmbH

All the best for Guenter and the Team..

And thank you for
your attention today!