Science in 1985

Physics: Klaus von Klitzing
for the discovery of the quantized Hall effect

Chemistry: Herbert A. Hauptman and Jerome Karle
for development of direct methods for the determination of crystal structures

ACIEE in 1985
* 12 issues
** 366 articles

*** Top publishing authors:
H. M. Hoffmann, L. F. Tietze, A. Schmidpeter & ...

Most cited articles in organic chemistry subfield:
Double Asymmetric Synthesis and a New Strategy for Stereoochemical Control in Organic Synthesis
Masamune et al., 24, 1-30 (1048)

Syntheses with Radicals—C-C Bond Formation via Organotin and Organomercury Compounds
Giese, 24, 553-565 (238)

Chiral Compounds Synthesized by Biocatalytic Reductions
Simon et al., 24, 539-553 (222)

Enzymes as Catalysts in Synthetic Organic Chemistry
Wong, 24, 617-638 (408)
Synthesis of 3'-C-Methyl-2'-deoxyribonucleoside with MeMgI


Site-selective tosylation

Bu$_2$SnO

R$_4$N$^+$X, TsCl

Major

in most cases


Ph rings cover the bottom face!

0.3 ppm downfield shift was observed upon acylation of 3-OH important for structure identification

Similar β-face selectivity even without Trt-group

NaBH$_4$

* Chelation? No
* Uracil's steric effect? No


Common method for Trt deprotection: TFA Challenging in SPPS

Selective deprotection of Trt: OTrt vs OTBDMS:

BCl$_3$, DCM, -30 °C then MeOH

J. Org. Chem. 2000, 65, 1, 263-265
Nickel-Catalyzed Cyclodimerization of 2-tButyl- and 2-TMS-1,3 butadien


R

Ni(COD)₂

toluene 60 °C

Head Tail


R= TMS or tBu → Selective [4+2]

Mechanism


\[
\begin{array}{c}
\text{A} \\
\text{B} \\
\text{C} \\
\text{D} \\
\text{E}
\end{array}
\]

\[
\begin{array}{c}
\text{COD} \\
\text{DVCB} \\
\text{VCH} \\
\text{DVCB} \\
\text{DVCB} \\
\text{COD}
\end{array}
\]

Phosphine Ligand effect is dramatic!

Inhibition

Activation

Selectivity of Ni-catalyzed isoprene dimerization versus \( \gamma \)-value of phosphine ligand

- total cyclodimers
- total dimethyl-COD

10.1016/S0040-4020(01)97949-9
Trispiro-2.1.2.1.2.11dodecane-4,8,12-trion

Heterogeneous Redox Catalysis on Ti/TiO₂ Cathodes:
Reduction of Nitrobenzene

1. Ti/TiO₂ ceramic as the electrodes This work
2. Ti/TiO₂ electrodes prepared thermally by heating Ti sheets in air
3. Ti/TiO₂ electrodes prepared by anodization

Faraday conversion: 33%
65% yield
No H₂ evolution

Slope of 47-56 mV/pH ===> indicative of protonated oxidized species

Beyond the dimer and trimer


Cathod potential: -0.23 V
Pb as anode
Total Synthesis of (+/-)-Bonellin Dimethyl Ester

Hagemann ester

1. O₃, DMS
2. HC(OMe)₃, p-TsOH
3. MeO₂C
4. CO₂Me

1. PR₃, TFA
2. Ni(OAc)₂

a. prevent atmospheric oxidation
b. easier separation of epimers

1. Pd/C, H₂
2. MeCHO

1. Zn(OAc)₂, KO'Bu
2. CH₂N₂

rac-Bonellin dimethyl ester
Selectivity and Mechanism of Diene Cyclodimerization on Iron(0) Complexes


Highly Enantioselective Intramolecular Hetero Diels-Alder Reactions for the Synthesis of Enantiomerically Pure Tricyclic Lactones

Tietze (1985), ACIEE, 24: 784-785

* Bulky (dad) suppresses catalytic activity or induce disproportionation.

If R=H: VCH/COT=4  ee = 45%

low-valent iron catalysis

What Catalyst Features Enable Reversible [2+2] Cycloaddition?


Simply Substituted Boraethenes

Maier (1985), ACIEE, 24: 1065-1066

X = NMe₂, OMe
Stereoe- and Enantioselective Synthesis of Both cis-Chrysanthemic Acid Methyl Esters in High Optical Purity

1. Malic anhydride
2. H₂O
3. ROC(S)Cl, pyr
4. Δ

Oxo-di-π-methane rearrangement

Nickel(0)-Catalyzed Synthesis of Sorbanilide from 1,3-Pentadiene and Phenyl isocyanate
Hoberg (1985), ACIEE, 24: 961-962

Photochemical Synthesis of an L-Erythrose Building Block and its use in the Preparation of Methyl 2,3,0-Isopropylidene-β-L-apio-L-furanoside
Neherings (1985), ACIEE, 24: 877-878

Extensions of the Tricyclooctanone Concept. A General Principle for the Synthesis of Linearly and Angularly Anelated Triquinanes
Demuth (1985), ACIEE, 24: 973-975.
Selectivity of the Anodic Oxidation of CH- and CH2-Groups; Selective Oxidation of Steroids at C-6

Schäfer (1985), ACIE, 24: 1055-1056

Mechanism

J. Am. Chem. Soc. 1973, 95, 12, 3947–3957

Pd(II)-Catalyzed Stereoselective Bis-Lactonization

Yoshida (1985), ACIE, 24: 1045-1046

Mechanism

Bicyclic Acetals from Oxacarbene

Asymmetric Addition of a Chiral Cyclic Phosphite to a Cyclic Imin-Synthesis of Phosphonic Acid Analogues of D- and L-Penicillamine

Schölkopf (1985), ACIEE, 24: 1057-1068

facile separation of diastereomers by column chromatography

d.r. = 1:1

1,1- and 1,0-Dilithioallyl Phenyl Sulfone: Synthesis, Geminal Cycloalkylation, and Lithium-Titanium Exchange

Pirung (1985), ACIEE, 24: 1043-1044

deprotonation process was followed by $^1$H NMR

exhibit similar product mixtures due to complete fast transmetalation after first alkylation step

Photochemistry of 1-Methoxybicyclo[2.2.2]octenones