
Bulletin of the French Chemical Society

A brief history:
- The French Chemical society formed informally in 1857 by a group of Parisian chemists
- Charles Wurtz (Wurtz coupling) joined in 1858, transformed it into a learned society (modelled after the Royal Society of London)
- First issue of "Bulletin de la société chimique de France" published in 1858
- Last issue published in 1997, was amalgamated into the European Journal of Chemistry

1990

\[
\begin{align*}
\text{I}_2\text{CH}_2 & \xrightarrow{\text{M-HMDS, THF, } -90^\circ \text{C}, M = \text{Na, Li}} \text{I}_2\text{CHM} \\
& \xrightarrow{\text{R-X, } -90^\circ \text{C to } -20^\circ \text{C}} \text{alkyl-I} \\
& \xrightarrow{\text{reaction with } \alpha-\text{lithio sulfones = vinyl iodides}} \text{n-Bu-I} \\
& \xrightarrow{\text{favors } E-\text{isomer}} 73\% \\
& \xrightarrow{85:15 \text{ E/Z}} 73\% \\
& \xrightarrow{90\%} 86\%
\end{align*}
\]

Reductive homocoupling of acetals derived from aromatic aldehydes with aluminum/lead bimetal redox systems. Tori. p. 283. [french]

\[
\begin{align*}
\text{OMe} & \xrightarrow{\text{Al, acid, PbCl}_2, \text{THF, rt}} \text{OMe} \\
& \xrightarrow{\text{Acid (eq.)}} \text{A} \\
& \xrightarrow{82\% (A/B)} \text{B}
\end{align*}
\]

Fluorofunctionalization of 1-alkylidenes. Comparative stereoselectivity electrochemical fluorocatalytization and bromofluorination. Laurent p.468. [french]

anodic alkenes difunctionalization

\[
\begin{align*}
\text{CH}_2\text{CN} & \xrightarrow{\text{TREAT-HF, Pt (+/-, 1.6 V undivided cell)}} \text{NAc} \\
& \xrightarrow{\text{TREAT-HF, solution pre-electrolyzed for 1 hr.}} \text{NAc} \\
& \xrightarrow{\text{R = Me, Et, i-Pr}} 49, 72, 81 \\
& \xrightarrow{\text{R = Me, Et, i-Pr}} 9, 10, 19 \\
& \xrightarrow{\text{R = Me, Et, i-Pr}} 28, 12, 0 \\
& \xrightarrow{\text{R = Me, Et, i-Pr}} 14, 6, 0
\end{align*}
\]

Synthesis of indoloquinolizidines through isomerization and cyclization of secoprecursors. Massiot, 648. [french]

Years 1990–1997:
- 979 articles published (60-70% in English)
- Electronic copies not available online (including Sci-Hub)
**1992**


\[
\begin{align*}
R - N_3 & \xrightarrow{P(OMe)_3, \text{H}_2\text{O}} R - N - P(OMe)_2 \\
\text{THF or Et}_2\text{O} & \quad \text{81–94\% yield} \\
\text{"protected amine"} & \quad \text{PMe} \\
\text{PhMe} & \quad \text{rt, 48 hrs} \\
\text{70–90\%} & \quad \text{R = Me (80\%)} \\
& \quad \text{Et (75\%)} \\
& \quad \text{Bn (63\%)} \\
& \quad \text{N-alkylation not observed}
\end{align*}
\]

**Stereospecific chloroalkylation a hydroxyalkylation of formal oxaly anion via \(\alpha\)-chloro and \(\alpha\)-methoxy glycicyc esters. Amos, p. 550. [french]

**1991**

Reaction of \(\alpha\)-aminoalcohols with \(\alpha\)-ketoaldehydes and gem-dihalogenoketones: Obtention of \(\alpha\)-ketooxazolidines, morpholinones and heterodecalines. Rouzic, p. 952.

**prior work**

Me\(\text{HN} \xrightarrow{\text{aq. glyoxal}} \)OH

(see saturated 1,4 heteroatom heterocycles, Chu, 2017)

**this work**

1) Me\(\text{HN} \xrightarrow{\text{Et}_2\text{O, CaSO}_4} \)OH

2) Cl\(\text{CO}_2\text{H, }\Delta\)

R = tolyl, \(p\)-\(\text{NO}_2\)Ph, furan, thiophene

**Synthesis and reactivity of diazomethylenephosphoranes. Bertrand, p. 367.**

**General synthesis:**

\[
\begin{align*}
\text{R}_2\text{PCl} & \xrightarrow{\text{TMSCH}_2\text{N}_2} \text{R}_2\text{P} - \xrightarrow{\text{rX} \text{X}} \text{N}_2 \\
\text{Cl} & \xrightarrow{\text{C}_6\text{H}_6} \text{N}_2 \\
\text{X} & \xrightarrow{\text{N}_2 \text{N}_2} \text{Cl} \\
\text{R} & = \text{N(alkyl)}_2, \text{t-Bu}
\end{align*}
\]

**Applications:**

- [3+2] cycloaddition

- heterocycle synthesis

- reacts with \(\text{CS}_2\), alkenes, alkynes

Intramolecular cyclization of boronic acids with azides via in-situ activation

\[
\begin{align*}
\text{R} + \text{N}_{3} & \xrightarrow{\text{NaN}_{3}} \text{R} - \text{Cl} - \text{B} - \text{Cl} - \text{N}_{3} \\
& \xrightarrow{\text{B(OH)}_{2}} \text{R} - \text{N} - \text{HCl} \\
\text{R} & = \text{H}, \text{alkyl} \\
\text{n} & = 0-3
\end{align*}
\]

- alkyl migrates preferentially over Cl
- poor reactivity using BPin esters

Intramolecular cyclization of alkenes with azides via in-situ hydroboration

\[
\begin{align*}
\text{Me} & \xrightarrow{\text{MeOH}} \text{Me} \\
\text{N}_{3} & \xrightarrow{\text{TMS}} \text{N} - \text{N} \\
\text{PhMe}, 40 ^\circ \text{C} & \rightarrow \text{PhMe} \\
\text{THF}, \text{rt}, 16 \text{ hrs.} & \rightarrow \text{NaH}
\end{align*}
\]

- C-glycosidation from halides α-selective
- C2 –OPG gives glycal

A ready method for generating oxycarbonyl radicals for conjugate-addition-alkylation or radical cyclization reactions. Fraser-Reid, p. 428.

1993 Sml₂-promoted chemistry at the anomic center of carbohydrates, reductive formation and reaction of glycosyl samarium (III) reagents. Sinay, p. 256.

Cyclohexanone, Sml₂ (3 eq.)

\[
\begin{align*}
\text{BnO} & \xrightarrow{\text{THF/HMPA}} \text{BnO} \\
\text{R} & = \text{H}, 87\% \\
\text{4:1} & \alpha/\beta
\end{align*}
\]

- stable, easily preparable

Stereocontrol in sulfonyl radical-induced cyclizations of 1,6-dienes. Jamie, 229.

\[
\begin{align*}
\text{PhCO}_{2} & \xrightarrow{\text{TsBr, hv}} \text{PhCO}_{2} \\
\text{CH}_{3}CN, 14 \text{ hrs.} & \rightarrow \text{73:27}
\end{align*}
\]

- cis-selective addition
- unique to 3,3-di-substituted systems

Lewis acid catalyzed rearrangements of 2-oxabicyclo[4,2,0]oct-7-ene-5-ones. Fétizon, p. 287. [French]

Initial studies

\[
\begin{align*}
\text{AcO} & \xrightarrow{\text{BF}_{3} \cdot \text{OE}_{2} \cdot \text{NaHCO}_{3}} \text{AcO} \\
\text{CH}_{2}Cl_{2}, 60 ^\circ \text{C} & \rightarrow \text{rt}
\end{align*}
\]

- remove acetate
- different LA


1) mCPBA, 98%
2) NaOMe
3) TMS-AcOEt, LDA, 55%

Corey [4+2] (enantioselective)

Leclaire [6π] (racemic)

N,N-dimethylaniline
290 °C, 1 hr.
40%

byproduct
30% isolated

1) BF₃•OEt₂
2) PhNMe₂Br₃, DBU
22% (2 steps)

60% (2 steps) NAME?


Mukaiyama-aldol/Michael of sensitive furan substrates (1993, p. 832)

Alcohol halogeneration via Bi(III) halide catalysis (1995, p.522)

R–CHO
acrylates
-cat. BiCl₃, ZnI₂
CH₂Cl₂, rt

furyl
70–94%

Allyl alcohol

n-hex-Cl

66% + isomers

R = X = Br, I quant.


R¹ = OMe, alkyl, aryl
R² = alkyl, aryl


1) (COCI)₂, Et₃N
2) s-BuLi, TMEDA, DMF
3) KCN, 18-crown-6, TMS-CN
54% (3 steps)

Northern fragment

1) NH₃, formic acid
2) Ag₂CO₃, Mel
3) NPG, HC(O)Me₂, PPTS, 46% (3 steps)


1 step from 1,3-butadiene

2 steps
82%

1) LiAlH₄
2) MsCl, LiBr
3) crotyl-p-sulfone, n-BuLi
4) t-BuOK, THF, rt
49% (4 steps)

1,3,4-TCB
reflux
16%

endofavored
unable to epimerize C-9
Low-valent titanium reductive elimination: a direct and highly stereoselective synthesis of vitamin A aldehyde and all-trans retinoic acid orthoester. Solladié, p 568.


Synthesis of polycyclic phosphorous cage compounds containing diphosphirane and phosphirane units. Regitz, p. 652.


[5,6,5] ring systems

[5,7,5] ring systems

Hydroxylation of carbanions with lithium tert-butyl peroxide acting as an oxenoid. M. Julia, p. 15. (see: Julia, Synlett 1993, 233)

Arene oxidation

α-oxidation

Alkyne oxidation


Catalyzed oxidation of alcohols by cis-dioxomolybdenum(VI) complexes via oxygen atom transfer from sulfoxides. Osborn, p. 755.


Formation of symmetrical alkenes by homocoupling of metallated sulfoxides under nickel catalysis. M. Julia p. 805.

Initial studies

Optimization

Alkyl sulfoxones

Heterocoupling

Conversion of non-activated alkenes into cyclopropanes with lithiated sulfoxones under nickel catalysis. M. Julia, p. 817.

Catalytic acryloxypalladation of vinylcycloalkanes and exo-methylene cycloalkanes.

Asymmetric addition of organometallic reagents to chiral α-alkoxy hydrazones.
Denmark, p. 395. (see Denmark, 1987, 109, 2224)

Diastereoselective carbonyl addition reactions promoted by ytterbium(III) trflate.

Isomerization of terminal alkynes catalyzed by ytterbium(II)-aromatic imine complexes.
Fujiiwa, p. 349.

Intramolecular annulation reactions of alkyne-functionalized aminocarbene complexes.
A one-pot route to 9H-carbazoles and 11H-benzocarbazoles. Dötz, p. 503. (see Fischer carbene complexes in organic synthesis, Chen, 2007)

Enantioselective synthesis of 1,2-diamines via nucleophilic 1,2-addition of dibenzylamino-acetaldehyde-SAMP-hydrazones. Enders, p 289 (see: Enders, Synthesis, 1996, 1443)
Zinc-ene-allene cyclizations: A way to substituted tetrahydrofurans or pyrrolidines.

THF rings

Pyrrolidines

Syntheses not covered


aldehydes

kетones

Anhydrides

isolations

(10Z,13Z,16Z)-nonadeca-10,13,16,18-tetraen-1-ol
19-hydroxy LTB₄
Depeyaz, 1990, p. 798

22,23-dihydroavermectin B1b glycone
key disconnections: Yamaguchi, NHK, Stille

ent-12-epi-PGF2α methyl ester
from Corey lactone, 8 steps
Rossi, 1996, p. 1149

reticulatatin-1 (n = 10)
reticulatatin-2 (n = 8)
Figadère, 1995, p. 324