Canadian Journal of Chemistry

History
- Founded in 1951
- Monthly journal managed by the National Research Council (NRC)
- 30982 Articles published to date
- 2014 impact factor = 1.061

Top Cited Articles
1. Optimization of Gaussian-type basis sets for local spin density functional calculations. Part I. Boron through neon, optimization technique and validation. 1992, 70, 560 (1318 citations)
2. Relativistic compact effective potentials and efficient, shared-exponent basis sets for the third-, fourth-, and fifth-row atoms. 1992, 70, 612 (1120 citations)
3. Thermal expansion and structure in water and aqueous solutions. 1969, 47, 4613 (235 citations)

Significant events in Canada 1980 - 1985

1980
- Terry Fox begins his Marathon of Hope
- "O Canada" becomes the official national anthem
- New York Islanders win the Stanley Cup

1981
- Gasoline and diesel are sold by the litre rather than the gallon
- The Canadarm sees its first use aboard the space shuttle
- New York Islanders win the Stanley Cup

1982
- The charter of rights and freedoms is signed
- Dominion Day becomes Canada Day (July 1st)
- New York Islanders win the Stanley Cup

1983
- The metric system is officially adopted
- New York Islanders win the Stanley Cup

1984
- The sports network (TSN) and Much Music first air
- Marc Garneau becomes the first Canadian in space
- Edmonton Oilers win the Stanley Cup

1985
- The first cell phone call is made in Canada
- The wrecking of the RMS Titanic found off the coast of Newfoundland

Method for the selective dimethoxytritylation and silylation of ribonucleosides

Selective protection of nucleosides at the 5' and 3' positions for use as substrates in automated RNA synthesis

Ogilvie, Can. J. Chem. 1982, 60, 1106 (cited by 121)

![Chemical structure diagram]

©-Nitrophenylethylene glycol as photoremovable protective group for aldehydes and ketones

Photolabile acid/base stable carbonyl protecting group


<table>
<thead>
<tr>
<th>Substrate</th>
<th>Protection</th>
<th>Deprotection</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexane</td>
<td>98</td>
<td>85</td>
</tr>
<tr>
<td>p-nitrobenzaldehyde</td>
<td>97</td>
<td>86</td>
</tr>
<tr>
<td>benzophenone</td>
<td>94</td>
<td>90</td>
</tr>
<tr>
<td>Δ 5-Pregnen-3β-ol-20-one acetate</td>
<td>80</td>
<td>83</td>
</tr>
</tbody>
</table>

- Stable towards 10% H2SO4 in THF >5 hrs
- Stable towards NaOH, t-BuOK, Na in aprotic solvents
- Unstable towards L/AIHand LDA at room temp.

Cyclo aromatization of enol silyl ethers to access the fungal metabolite sclerin


![Chemical reaction diagram]
Dimeric imidazoyl steroid catalyses cleavage of aromatic esters using hydrophobic stabilization

Hydrophobic pocket

Catalyst prepared in 6 steps from coricosterone

Empirical rate acceleration for hydrolysis of phenanthryl derivative 200-fold higher than imidazole

Increasing hydrolysis rate

Ullmann condensation using copper under base free conditions

Selected substrate scope

R-Z-H
Cu or CuO
neat
150-240°C
12 hrs
- Solvent-free conditions
- Base-free
- Stoichiometric copper

Condensation of thiophenols with aryl halides using metallic copper

Selected substrate scope

R-Z-H
Cu or CuO
neat
240-300°C
6 hrs
- As above
- Proceeds via Cu-SAr intermediate

- Subsequent work has made these transformations catalytic at lower temperatures

Selective halogenation of guanine nucleosides under aqueous free conditions

Reagents
DMA, Et₃NCl, POCl₃
CH₃CN,
100°C, 10 min
87%

Me₃N (cat.)
KF
DMF
14 hrs. 93%

CI can also be substituited with N₃, NH₂

Regioselective 3-acetylalation of pyrrole using removable directing groups

Regioselective 3-acetylalation of pyrrole using removable directing groups
Loader, Can. J. Chem. 1985, 63, 896 (cited by 95)

1) AlCl₃, ArCl
CH₂Cl₂,
3 min
51

2) KOH, MeOH,
60°C, O/N

X = yield (%)
2-Me
57

4-Cl
42

4-OMe
22

2-Me
57

3-Me
57

4-OMe
22

4-Cl
42

X = yield (%)
51
Controlled electrochemical reduction of per-halogenated thiophene to synthesize 2,3,4-trihalo, 3,4-dihalo, and 3-halothiophene derivatives

<table>
<thead>
<tr>
<th>SM</th>
<th>Potential (V)</th>
<th>Cell type</th>
<th>Additive</th>
<th>P yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a,b</td>
<td>-0.88</td>
<td>undivided</td>
<td>1-hexene</td>
<td>69</td>
</tr>
<tr>
<td>3a,b</td>
<td>-1.20</td>
<td>*</td>
<td>DMA</td>
<td>75</td>
</tr>
<tr>
<td>3a,b</td>
<td>-1.70</td>
<td>*</td>
<td>DMA</td>
<td>60</td>
</tr>
<tr>
<td>1b</td>
<td>-0.93</td>
<td>divided</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4b</td>
<td>-1.20</td>
<td>*</td>
<td>-</td>
<td>55</td>
</tr>
</tbody>
</table>

*additive required to trap X₂ generated in undivided cells

Facile access to (S)-1,2,4-butanetriol as a chiral building block in synthesis

(S)-1,2,4-butanetriol
BH₂-DMS, B(OCH₃)₃ THF, O/N, quant.

(S)-malic acid

1) BMS-THF 83%
2) p-TsOH, acetone, O/N 92% + 6-ner penton (9.2%) Synthese d'une α-methylene-γ-lactone: application des reactifs organiques du selenium
"Organoselenium mediated synthesis of α-methylene-γ-lactones"
Ferraz, Can. J. Chem. 1985, 63, 3216 (cited by 4)

K₂CO₃

60 hrs, 85%

1) BzCl, pyr 73%, 3 steps
2) TBAT, THF
3) CrO₃, pyr, CH₂Cl₂ 3hrs, 79%

ZnBH₄

Et₂O, 3 hrs, 50%

1) K₂CO₃, MeOH
2) NaOH, MeOH, then H⁺ resin 81%

(+)-thromboxane B₂

15 linear steps
7.2% yield, 16 mg isolated
C-2 OH exists as a 35:65 mixture of α/β anomers

1) MeO₂CCCH₃P(O)(OMe)₂ t-BuOK, PhMe, 8 hrs
2) Pd(OH)₂/C H₂, 24 hrs, 64%, 2 steps

from glucose
Can. J. Chem. 1968, 46, 2868

Hanussian, Can. J. Chem. 1968, 46, 2868

Baran Group Meeting 10/6/15
Synthesis of glucosamine derivatives
Treatment of glycols with ceric ammonium nitrate provides beta-C-2 azide which can be reduced to the amine and used in the synthesis of several natural N-acetyl trisaccharides
Lemieux, J. Chem. 1979, 57, 1244; US Pat. 4308376 A

This work: Lemieux, J. Chem. 1982, 60, 63

Diastereospecific Tsuji-Trost reaction of alkyl hex-2-enopyranosides
Reaction of a glucose derivative bearing a vinyl acetate moiety with amine or methylene based nucleophiles using catalytic palladium(0) gives exclusively the C-4 substitution products with retention of configuration

Total synthesis of marine antibiotic (-)-malyngolide from 2,3-O-isopropylidene-D-apiose
Starting material prepared in one step from D-Manosone (Tet. Lett. 1978, 19, 1623)
Ho, J. Chem. 1985, 63, 2221

Synthesis of poly-amino sugar derivatives
Treatment of methyl-2-acetamido-glucopyranoside with sulfuryl chloride gives access to selective chlorination products which can be used in the synthesis of numerous amino-sugars
Bundle, J. Chem. 1980, 58, 2679
Synthesis of β-halo enones from β-diketones

General
\[ \text{O} \quad \text{Et}_3\text{N}, \quad \text{PPh}_3\text{X}_2 \]
\[ \text{C}_6\text{H}_5\text{C}_6, \text{RT} \quad \text{or} \quad \text{CH}_3\text{CN}, \Delta \quad 4-24 \text{ hours} \quad \text{X} = \text{Cl, Br, I} \]

Selected substrate scope

<table>
<thead>
<tr>
<th>R</th>
<th>%</th>
<th>R</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me, 92%</td>
<td>82%</td>
<td>iPr, 85%</td>
<td>99:1</td>
</tr>
</tbody>
</table>

Five-membered ring annulation via thermal rearrangement of β-cyclopropyl α,β-unsaturated ketones

General
\[ \text{CuSPH Li} \quad \text{THF, -78°C, 2.5 hrs} \]
\[ n = 1, 84% \quad \text{or} \quad n = 2, 97% \]

1) 425°C
2) basic Al_2O_3
\[ n = 1, 88% \quad \text{n} = 2, 60% \]

Use of phenyl(thio)alkyl cuprates for the selective 1,4-alkylation of of β-halo enones

General
\[ \text{[PhsCuR]Li} \quad \text{THF, 2.5 hrs} \]
\[ \text{X} = \text{Cl, Br, I} \]

- Initial attempts with di-alkyl cuprates gave a mixture of mono- and bis-alkylation products at the γ position
- Thio-alkyl cuprates gave selective mono-alkylation

Selected substrate scope

<table>
<thead>
<tr>
<th>X = Br</th>
<th>X = Br, 0°C 94%</th>
<th>X = Br, -78°C 70%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X = Br, -20°C 82%</td>
<td>X = Br, 22°C 95%</td>
</tr>
<tr>
<td></td>
<td>X = Br, -20°C 84%</td>
<td></td>
</tr>
</tbody>
</table>

Applied to the synthesis of (Z)-jasmine

OTHP 5 steps 22%

Five-membered ring annulation via thermal rearrangement of β-cyclopropyl α,β-unsaturated ketones

\[ \text{CuSPH Li} \quad \text{THF, -78°C, 2.5 hrs} \]
\[ \text{then w/u, 120°C neat} \quad n = 1, 64% \quad \text{n} = 2, 77% \]

Baran Group Meeting 10/6/15
Synthesis of (±)-capnellene using a donor-acceptor annulation strategy


Synthesis of (±)-capnellene using an intramolecular Diels-Alder approach


Proposed mechanism of rearrangement
Synthesis of (±)-epiisopodophyllotoxin


\[\text{Ar} = \text{MeO} \]

1) n-BuLi, THF
2) n-Bu$_3$P, CuI
3) (MeO)$_3$BnBr
4) HCl, MeOH
84% one-pot

via "photo-enolization"

1) LiBHEt$_3$, THF, -78°C
2) (H$_3$C)$_2$C(OMe)$_2$, $p$-TsOH, CH$_2$Cl$_2$, 63%
2 steps

1) KOH, wet dioxane
2) HCl, 83%
one-pot

(±)-epiisopodophyllotoxin
(atoposide aglycon)
7 steps, 15% overall

DCC
THF, 75%