GRAPHICAL ABSTRACTS

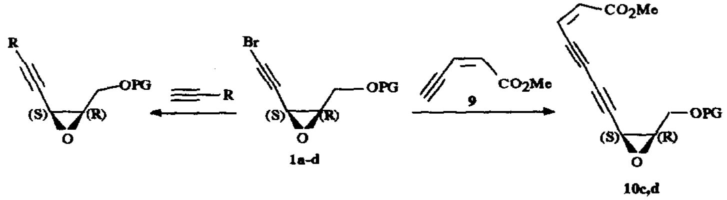
Tetrahedron, **1993**, *49*, 5225

A General Access to Optically Pure Epoxypolyynes: Asymmetric Synthesis of Antifeedants Natural Products.

D. Grandjean, P. Pale*, J. Chuche

Laboratoire de chimie organique physique, associé au CNRS
Université de Reims-Champagne-Ardenne; 51100 Reims, France.

A general asymmetric access to *cis*-epoxy polyyne family of natural products is described using 5-bromo-2,3-epoxy-4-pentyn-1-ol **1a** as a key inter-mediate. From this intermediate, the synthesis of two epoxypolyyne natural products **10c,d** was carried out in 6 steps with a 42% overall yield.



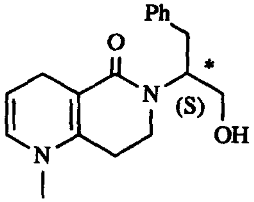
Tetrahedron, **1993**, *49*, 5237

AN APPROACH TO FEATURES RESPONSIBLE FOR THE OBTENTION OF HIGH E.E. WITH A HIGHLY ENANTIOSELECTIVE NADH MODEL

Yves Combret, Jack Duflos, Georges Dupas, Jean Bourguignon and Guy Quéguiner.

URA 1429 CNRS / Institut National des Sciences Appliquées. BP 08. 76131 Mont Saint Aignan (France).

The reduction of Ph-CO-COOMe with NADH models having free, restricted or suppressed rotating ability was studied. A cyclized model allowed the obtention of a 94 % e.e. and showed a high reactivity. It is suggested that the main factor res--ponsible of this behaviour is an entropy feature.



Cyclized model

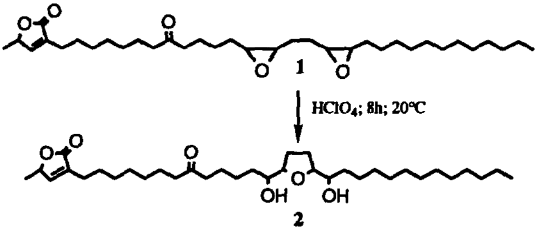
Tetrahedron, **1993**, *49*, 5247

COREPOXYLONE, A POSSIBLE PRECURSOR OF MONO-TETRAHYDROFURAN γ-LACTONE ACETOGENINS: BIOMIMETIC SYNTHESIS OF COROSSOLONE

Danuta GROMEK[1], Bruno FIGADERE[1], Reynald HOCQUEMILLER[1] André CAVÉ[1] and Diego CORTES[2]

[1]Laboratoire de Pharmacognosie, UA-CNRS, Faculté de Pharmacie, Université Paris-Sud, 92290 Châtenay-Malabry; and [2]Laboratoire de Pharmacognosie, Faculté de Médecine-Pharmacie, Université de Rouen, 76800 Saint Etienne du Rouvray, France.

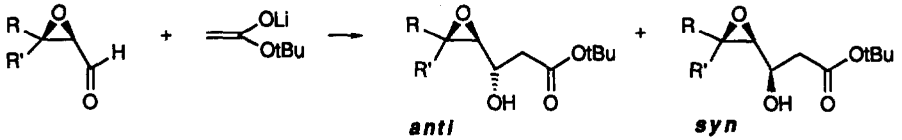
Biomimetic synthesis of corossolone (2) from new diepoxy acetogenin corepoxylone (1) was carried out in acidic medium. Biosynthetic and stereochemical implications are discussed.



DIASTEREOFACE DIFFERENTIATION IN ADDITION OF LITHIUM ENOLATES TO CHIRAL α,β-EPOXYALDEHYDES

Tetrahedron, **1993**, *49*, 5253

J.-M. Escudier, M. Baltas, L. Gorrichon *
Laboratoire de synthèse et physicochimie organique , Université Paul Sabatier, 31062 Toulouse (France)



The aldolisation reaction of chiral α,β-epoxyaldehydes with tert-butyllithium acetate leads to products with *anti* preference (*anti:syn* 4:1) which may be greatly enhanced to 13:1 in the case of *cis* aldehydes (R = H, R' ≠ H) under appropriate conditions.

Tetrahedron, **1993**, *49*, 5267

HOMOLYTIC BOND CLEAVAGE ENERGIES OF THE ACIDIC N-H BONDS IN DIMETHYL SULFOXIDE SOLUTION AND PROPERTIES OF THE CORRESPONDING RADICALS AND RADICAL CATIONS

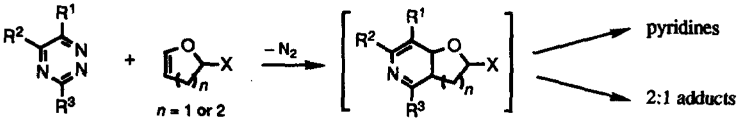
Jin-Pei Cheng* and Yongyu Zhao
Department of Chemistry, Nankai University, Tianjin, China 300071

Homolytic bond dissociation energies of α-substituted aniline compounds with varying *para* substituents were determined in solution phase. Both the *alpha* and the *para* electron-withdrawing substituents were found to strengthen the N-H bond, or, to destabilize the resulting nitrogen-centered radicals, based on the relative BDE's. The corresponding nitrogen radical cations are much less acidic, as compared to the carbon radical cations.

DIELS-ALDER REACTIONS OF 1,2,4-TRIAZINES WITH CYCLIC VINYL ETHERS

Tetrahedron, **1993**, *49*, 5277

António M. d'A. Rocha Gonsalves and Teresa M. V. D. Pinho e Melo, Departamento de Química, Universidade de Coimbra, P-3049 Coimbra, Portugal, and Thomas L. Gilchrist, Chemistry Department, University of Liverpool, Liverpool L69 3BX, U.K.



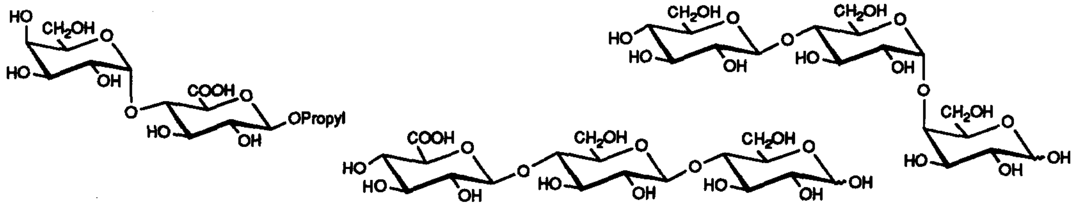
Reaction of 1,2,4-triazines with cyclic vinyl ethers leads either to pyridines or to 2:1 adducts derived by double Diels-Alder addition by the enol ethers.

Tetrahedron, **1993**, *49*, 5291

SYNTHESIS OF STRUCTURAL ELEMENTS OF THE CAPSULAR POLYSACCHARIDE OF *Streptococcus pneumoniae* TYPE 8

Franciscus A. W. Koeman, Johannis P. Kamerling*, and Johannes F. G. Vliegenthart, Bijvoet Center, Department of Bio-Organic Chemistry, Utrecht University, P. O. Box 80.075, NL-3508 TB Utrecht, The Netherlands.

The synthesis is reported of a di- and two trisaccharides, each representing a structural element of the repeating unit of the capsular polysaccharide of *Streptococcus pneumoniae* type 8, [→4)-β-D-Glc*p*A-(1→4)-β-D-Glc*p*-(1→4)-α-D-Glc*p*-(1→4)-α-D-Gal*p*-(1→]$_n$.

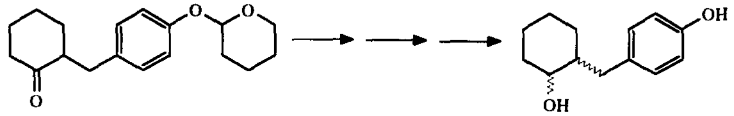


Tetrahedron, **1993**, *49*, 5305

CHIRAL PRECURSORS OF OPTICALLY ACTIVE JUVENOIDS

Marie Zarevúcka, Martin Rejzek*, Zdeněk Wimmer*, David Šaman and Ludvík Streinz,
Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences, Flemingovo nám. 2, Prague 6, 166 10, Czech Republic

For preparation of all four enantiomers of 2-(4-hydroxybenzyl)-1-cyclohexanol (**1a**-**4a**) by biotransformation reactions, *Saccharomyces cerevisiae* and pig pancreatic lipase were used.



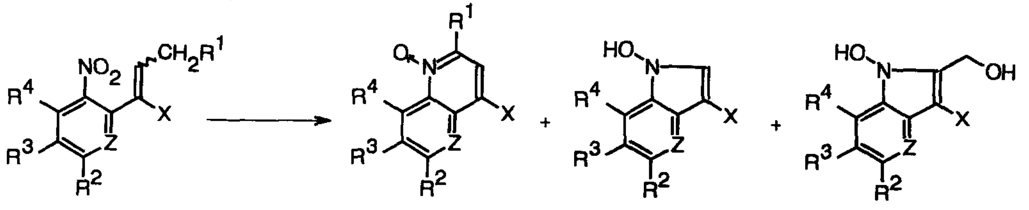
1a: 1S,2S; **2a**: 1R,2R; **3a**: 1S,2R; **4a**: 1R,2S

Tetrahedron, **1993**, *49*, 5315

TRANSFORMATIONS OF o-NITROARYLALLYL CARBANIONS. SYNTHESIS OF QUINOLINE N-OXIDES AND N-HYDROXYINDOLES.

Zbigniew Wróbel and Mieczysław Mąkosza
Institute of Organic Chemistry, Polish Academy of Sciences ul.Kasprzaka 44/52, 01-224 Warsaw, Poland.

Nitriles and esters of 2-(*o*-nitroaryl)crotonic acids are converted in basic medium into substituted quinoline N-oxides, N-hydroxyindoles and N-hydroxy-2-hydroxymethyl indoles.

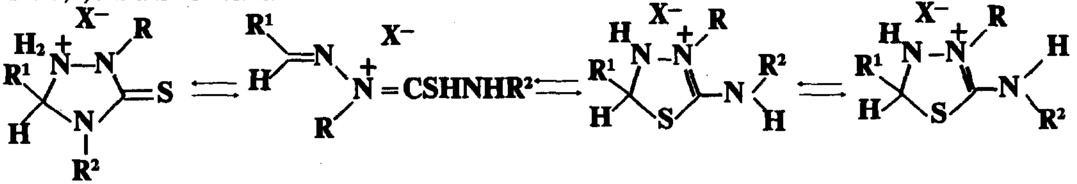


Tetrahedron, **1993**, *49*, 5327

THE CHAIN-RING-RING TAUTOMERISM OF THIOSEMICARBAZONES OF ALKANALS IN ACIDIC MEDIUM

Kirill N. Zelenin*, Valery V. Alekseyev, Olga B. Kuznetsova,
Vladimir N. Torocheshnikov, Ludmila A. Khorseeva
Military Medical Academy, Sanct-Petersburg, 194175, RUSSIA

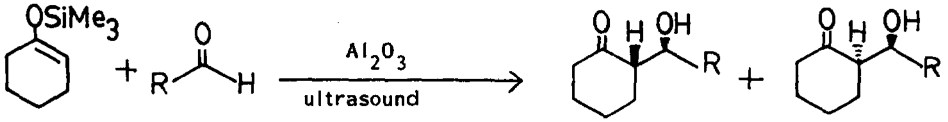
Thiosemicarbazones of alkanals and their 4-substituted derivatives generate in trifluoroacetic acid the three-component equilibrium between the linear and the cyclic of 1,3,4-thiadiazolidine and 1,2,4-triazolin forms.



Tetrahedron, **1993**, *49*, 5333

SURFACE-MEDIATED SOLID PHASE REACTION.[1] ALDOL REACTION OF SILYL ENOL ETHERS WITH ALDEHYDES ON A SOLID SURFACE OF NEUTRAL ALUMINA : SELECTIVITY FOR ANTI ALDOLS

Brindaban C. Ranu* and Rupak Chakraborty
Department of Organic Chemistry, Indian Association for the
Cultivation of Science, Jadavpur, Calcutta - 700 032, India.

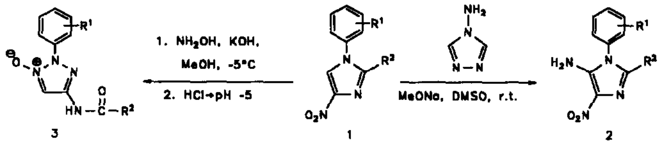


Tetrahedron, **1993**, *49*, 5339

NITROIMIDAZOLES XVII. NUCLEOPHILIC AMINATION OR RING TRANSFORMATION IN REACTIONS OF 1-ARYL-4-NITROIMIDAZOLES WITH 4-AMINO-1,2,4-TRIAZOLE OR HYDROXYLAMINE.

Jerzy Suwiński* and Krzysztof Świerczek, Institute of Organic Chemistry and Technology,
Silesian Technical University,44-100 Gliwice, Poland
Tadeusz Głowiak, Institute of Chemistry,University of Wrocław, 50-383 Wrocław, Poland

Compounds 1 undergo a nucleophilic substitution in reaction with 4-amino-1,2,4-triazole yielding 2, whereas with hydroxylamine undergo a transformation to isomeric 3.

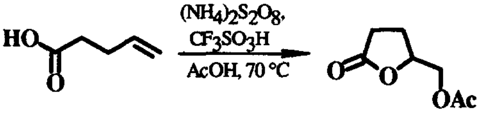


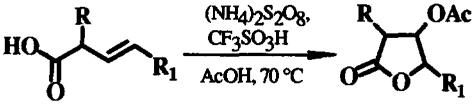
Tetrahedron, **1993**, *49*, 5351

ACETOXY LACTONIZATION OF ALKENYL ACETIC ACIDS PROMOTED BY AMMONIUM PERSULFATE AND TRIFLUOROMETHANESULFONIC ACID IN ACETIC ACID.

Marcello Tiecco,* Lorenzo Testaferri and Marco Tingoli.
Istituto di Chimica Organica, Facoltà di Farmacia, Università di Perugia, 06100-Perugia, Italy.

The reactions of substituted 4-pentenoic and 3-butenoic acids with ammonium persulfate in acetic acid, in the presence of CF_3SO_3H, gave the products of acetoxy lactonization in good yields.



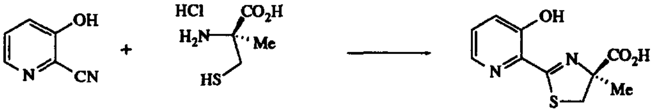


Tetrahedron, **1993**, *49*, 5359

SYNTHESIS OF THE THIAZOLINE-BASED SIDEROPHORE (*S*)-DESFERRITHIOCIN

Gerard C. Mulqueen, Gerald Pattenden,* and Donald A. Whiting
Department of Chemistry, The University, Nottingham, NG7 2RD

A total synthesis of the new thiazoline-based siderophore desferrithiocin **1**, isolated from *Streptomyces antibioticus*, is described.



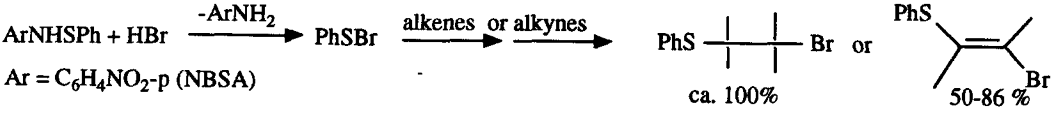
(1)

Tetrahedron, **1993**, *49*, 5365

SYNTHETIC UTILITY OF 4'-NITROBENZENESULFENANILIDE IN THE FUNCTIONALIZATION OF CARBON-CARBON DOUBLE AND TRIPLE BONDS: ITS USE IN THE BROMOSULFENYLATION OF ALKENES AND ALKYNES.

Luisa Benati, Pier Carlo Montevecchi*, Dipartimento di Chimica Organica "A. Mangini", Viale Risorgimento 4, 40136 Bologna, Italy. Piero Spagnolo, Dipartimento di Chimica, Università della Basilicata, Via N. Sauro 85, 85100 Potenza, Italy.

The reaction of NBSA with hydrobromic acid in the presence of alkenes and alkynes can be employed for the stereo and regio-specific synthesis of btomoalkyl and bromovinyl sulfides.



Tetrahedron, **1993**, *49*, 5377

RACEMATE RESOLUTION VIA CRYSTALLIZATION OF DIASTEREOMERIC SALTS: THERMODYNAMIC CONSIDERATIONS AND MOLECULAR MECHANICS CALCULATIONS

Frank J. J. Leusen*, Jan H. Noordik and Heinrich R. Karfunkel†

CAOS/CAMM Center, University of Nijmegen, Toernooiveld,
NL-6525 ED Nijmegen, The Netherlands

* Present address: Molecular Simulations, St. John's Innovation Centre, Cowley Road, Cambridge CB4 4WS, United Kingdom

† Information Technology Dep., Ciba-Geigy AG, R-1008.823, CH-4002 Basel, Switzerland

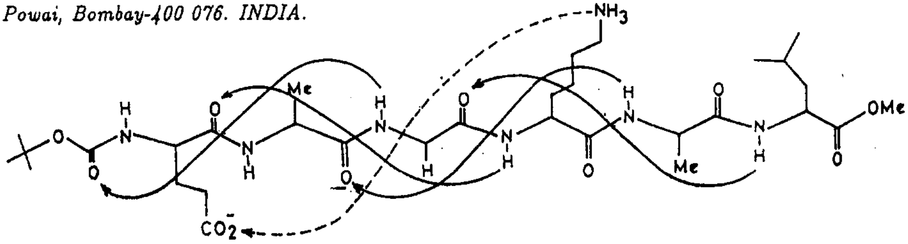
$$\begin{tikzcd}
n_{solution} \arrow[rr, leftrightarrow, "\Delta G_{solution}"] & & p_{solution} \\
n_{melt} \arrow[rr, leftrightarrow, "\Delta G_{melt}"] & & p_{melt} \\
n_{solid} \arrow[u, "\Delta G_{f(n)}"'] \arrow[uu, bend left=60, "\Delta G_{solv(n)}"] \arrow[rr, leftrightarrow, "\Delta G_{solid}"] & & p_{solid} \arrow[u, "\Delta G_{f(p)}"] \arrow[uu, bend right=60, "\Delta G_{solv(p)}"']
\end{tikzcd}$$

Tetrahedron, **1993**, *49*, 5397

Stable Type II' Reverse Turn - 3_{10} Helix Conformation of Boc-D-Glu-Ala-Gly-Lys-Ala-Leu-OMe in Apolar Solvents.

Vivek Bobde, Suresh Beri and Susheel Durani*

Biotechnology Centre, Indian Institute of Technology
Powai, Bombay-400 076. INDIA.

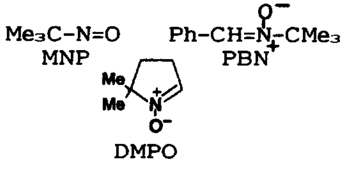


Tetrahedron, **1993**, *49*, 5407

ON THE REACTION OF CHLOROFORM WITH BASE IN THE PRESENCE OF SPIN-TRAPS

Lionel R. Milgrom,[a*] Peter. P. Payne,[a] and William D. Flitter.[b]
[a]Department of Chemistry and [b]Department of Biochemistry, Brunel University, Uxbridge, Middlesex, UB8 3PH, UK.

In the presence of spin-traps (ST = MNP, PBN, or DMPO) and oxygen, chloroform reacts with base generating carbon-centred radical artifacts.



$$CHCl_3 + OH^- \Rightarrow CCl_3^- + H_2O$$

$$CCl_3^- + ST \Rightarrow [ST-CCl_3]^-$$

$$\begin{tikzcd}
& {[ST-CCl_3]^-} \arrow[dl] \arrow[dr, "O_2/OH^-/MeOH"] & \\
{[ST-CO_2Me]^{\cdot}} & + & {[ST-CO_2]^{-\cdot}}
\end{tikzcd}$$