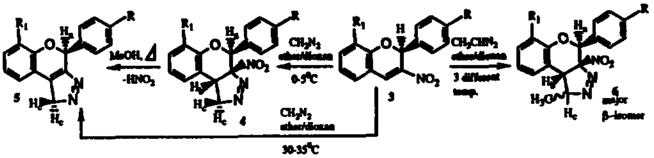
GRAPHICAL ABSTRACTS

Tetrahedron, **1994**, *50*, 4623

STEREOCHEMICAL INVESTIGATION IN THE 1,3-DIPOLAR CYCLOADDITIONS OF 3-NITRO-2-PHENYL-2H-1-BENZOPYRANS TO DIAZOALKANES: SYNTHESIS AND ANTIMICROBIAL ACTIVITY OF NOVEL BENZOPYRANOPYRAZOLE DERIVATIVES

Ram Prasad K. Kodukulla*!, Hariharan.S+, and Girish K. Trivedi+
!Department of Neurology, Charles B. Stout Neuroscience Mass Spectrometry Laboratory, 956 Court Avenue, University of Tennessee Health Science Center, Memphis, TN 38163
+Department of Chemistry, Indian Institute of Technology, Bombay, India 400076

Reactions of diazoalkanes with 3-nitro-2-phenyl-2H-1-benzopyrans lead to the corresponding benzopyranopyrazoles instead of the C-alkylated, ring expansion and ring contraction products as observed with 3-nitrochromones and 3-nitrocoumarins.

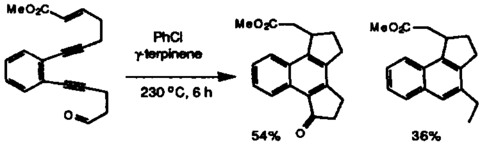


Tetrahedron, **1994**, *50*, 4635

HIGH TEMPERATURE RADICAL CYCLIZATION ANOMALIES IN THE TANDEM ENEDIYNE-*BIS*-RADICAL CYCLIZATION.

Janet Wisniewski Grissom*, Trevor L. Calkins, Dahai Huang, Heidi A. McMillen, Department of Chemistry, University of Utah, Salt Lake City, UT 84112

Here is reported several examples of the tandem enediyne-*bis*-radical cyclization where non-radical accepting tethers will undergo cyclizations to aromatic rings to result in cyclization products.



Tetrahedron, **1994**, *50*, 4651

ELECTRON TRANSFER IN THE REACTIONS OF ARYLLITHIUM COMPOUNDS WITH CARBON MONOXIDE

N. Sbarbati Nudelman* and Fabio Doctorovich

Depto. Química Orgánica, Facultad de Ciencias Exactas y Naturales, U.B.A., Pab. II, P. 3, Ciudad Universitaria, 1428 Buenos Aires, Argentina.

The reactions of aryllithium compounds with CO have been studied under several reaction conditions. Spectroscopic studies, the effect of radical inhibitors, kinetic measurements and isolation of intermediates suggest a mechanism that involves electron transfer as the first and rate determining step of the reaction.

$$\mathrm{ArLi + CO \longrightarrow (Ar\dot{L}i)^{+}(\dot{C}O)^{-}}$$

Tetrahedron, **1994**, *50*, 4667

HYMENAMIDES G, H, J, AND K, FOUR NEW CYCLIC OCTAPEPTIDES FROM THE OKINAWAN MARINE SPONGE *HYMENIACIDON* SP.

Masashi Tsuda, Takuma Sasaki[a], and Jun'ichi Kobayashi*

Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060, Japan, and [a]Cancer Research Institute, Kanazawa University, Kanazawa 920, Japan

Four new cyclic octapeptides, hymenamides G, H, J, and K (1 ~ 4), have been isolated from the Okinawan marine sponge *Hymeniacidon* sp.

cyclo-(Pro-Pro-Tyr-Val-Pro-Leu-Ile-Leu)
1

cyclo-(Pro-Leu-Thr-Pro-Leu-Pro-Trp-Val)
2

cyclo-(Pro-Tyr-Asp-Phe-Trp-Lys-Val-Tyr)
3

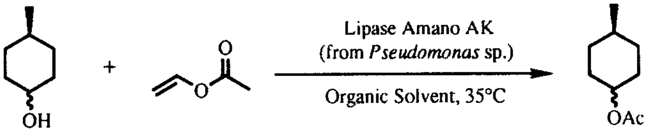
cyclo-(Pro-Tyr-Asp-Phe-Trp-Lys-Ala-Val)
4

Tetrahedron, **1994**, *50*, 4681

EFFECT OF SOLVENT ON LIPASE-CATALYZED TRANSESTERIFICATION IN ORGANIC MEDIA

Kaoru NAKAMURA,* Masamichi KINOSHITA, and Atsuyoshi OHNO
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

The effect of solvent on activity and stereoseletivity in the lipase-catalyzed transesterification has been investigated.



Tetrahedron, **1994**, *50*, 4691

STEREOSELECTIVE SYNTHESIS OF 2(*S*)-(1,1-DIMETHYLETHYL-SULFONYLMETHYL)-3-(1-NAPHTHYL)-PROPIONIC ACID, BUILDING BLOCK FOR PROTEASE INHIBITORS, *VIA* ASYMMETRIC HYDROGENATION.

Gerhard Beck,* Heiner Jendralla,* Bernhard Kammermeier , Hoechst AG, Postfach 800320, D-65926 Frankfurt / M. 80, Germany

The title compound is synthesized from commercial 3-bromo-pyruvic acid *via* asymmetric hydrogenation as the key step.

purity > 99% ; 99.6% ee

no chromatographic purifications

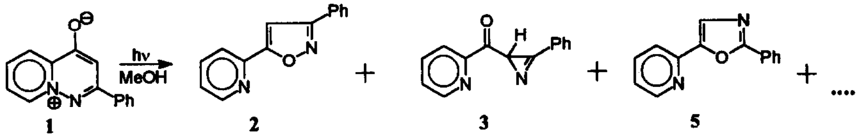
16% overall yield

Tetrahedron, **1994**, *50*, 4699

PHOTOINDUCED RING TRANSFORMATION OF PYRIDO[1,2-b]-PYRIDAZINIUM-4-OLATE

S. Bátori[a,b], D. Döpp[a] and A. Messmer[b]
a, University Duisburg, D-47048 Duisburg, Germany; b, Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1525 Budapest, P.O.BOX 17, Hungary

The photolytic behaviour of pyrido[1,2-b]pyridazinium-4-olate (1) was studied. The photoreaction displayed a remarkable wavelength-dependence. Irradiation with light of λ > 280 nm resulted in 2 and 3 as main products, while the use of light of λ < 280 nm gave mainly 5.



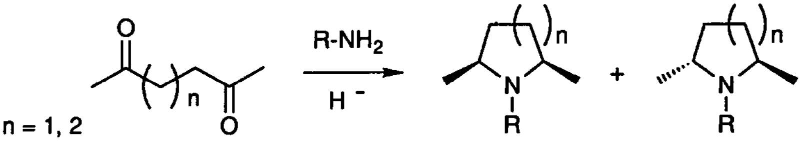
1 2 3 5

Tetrahedron, **1994**, *50*, 4709

DIASTEREOSELECTIVE SYNTHESIS OF 2,5-DIMETHYLPYRROLIDINES AND 2,6-DIMETHYLPIPERIDINES BY REDUCTIVE AMINATION OF 2,5-HEXANEDIONE AND 2,6-HEPTANEDIONE WITH HYDRIDE REAGENTS.

Carla Boga, Francesco Manescalchi, and Diego Savoia*, Dipartimento di Chimica "G. Ciamician", Università di Bologna, via Selmi 2, 40126 Bologna, Italy

The *cis*/*trans* ratio of the cyclic amine depends mainly on the size of the ring and of the nitrogen substituent.

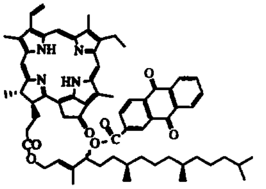


Tetrahedron, **1994**, *50*, 4723

SYNTHESIS OF PYROPHEOPHYTIN-ANTHRAQUINONE LINKED MOLECULES AS MODELS FOR THE STUDY OF PHOTOINDUCED ELECTRON TRANSFER.

Andrei Y. Tauber, Risto K. Kostiainen, Paavo H. Hynninen*, Department of Chemistry, University of Helsinki, P. O. Box 6, FIN-00014 Helsinki, Finland; Environmental Laboratory of Helsinki, Helsinginkatu 24, FIN-00530 Helsinki, Finland

The first synthesis of pyropheophytin-anthraquinone compounds, with the quinone, attached to the P4 allylic position of the phytyl chain is described.

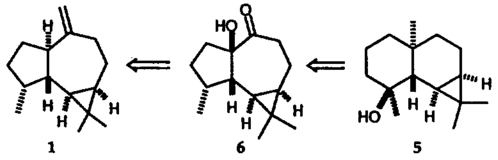


Tetrahedron, **1994**, *50*, 4733

REARRANGEMENT REACTIONS OF AROMADENDRANE DERIVATIVES. THE SYNTHESIS OF (+)-MAALIOL, STARTING FROM NATURAL (+)-AROMADENDRENE-IV.

H.J.M. Gijsen, J.B.P.A. Wijnberg, C. van Ravenswaay, Ae. de Groot, Laboratory of Organic Chemistry, Agricultural University, Dreijenplein 8, 6703 HB Wageningen, The Netherlands.

Via rearrangement of the hydroazulene α-ketol 6, prepared from (+)-aromadendrene (1), several hydronaphthalene compounds with a maaliane skeleton have been synthesized,including (+)-maaliol (5).

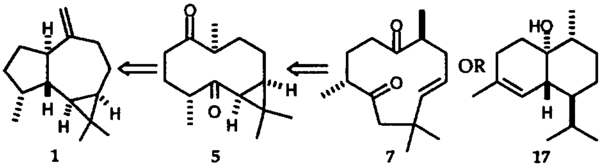


Tetrahedron, **1994**, *50*, 4745

THERMAL REARRANGEMENT OF BICYCLOGERMACRANE-1,8 - DIONE. SYNTHESIS OF HUMULENEDIONE AND (-)-CUBENOL, STARTING FROM NATURAL (+)-AROMADENDRENE-V.

H.J.M. Gijsen, J.B.P.A. Wijnberg, Ae. de Groot, Laboratory of Organic Chemistry, Agricultural University, Dreijenplein 8, 6703 HB Wageningen, The Netherlands.

Bicyclogermacrane-1,8-dione 5, readily prepared from crude (+)-aromadendrene (1), has been selectively thermally rearranged into products with a humulane or cadinane skeleton. Further transformations of these products lead to humulenedione (7) and (-)-cubenol (17), respectively.

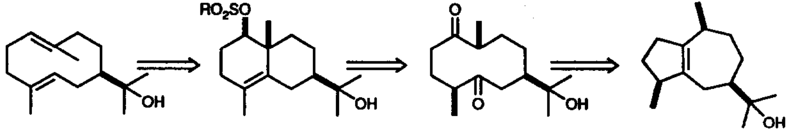


Tetrahedron, **1994**, *50*, 4755

THE SYNTHESIS OF (+)-HEDYCARYOL, STARTING FROM NATURAL (–)-GUAIOL.

A.J. Minnaard, J.B.P.A. Wijnberg and Ae. de Groot, Laboratory of Organic Chemistry, Agricultural University, Dreijenplein 8, 6703 HB Wageningen, The Netherlands.

Starting from the readily available (–)-guaiol the germacrane sesquiterpene (+)-hedycaryol can be synthesized in a 7 steps reaction sequence in an overall yield of 16%. Additionally, (+)-γ-eudesmol has been synthesized, also starting from (–)-guaiol.

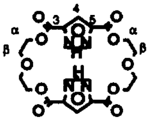


Tetrahedron, **1994**, *50*, 4765

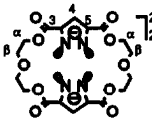
FORMATION OF MONO- AND DI- NUCLEAR COMPLEXES OF Zn^{2+} FROM A 26 MEMBERED TETRAESTER CROWN OF 3,5-DISUBSTITUTED PYRAZOLE ABLE TO ACT AS NEUTRAL AND DIANIONIC LIGAND

C.Acerete[a] , **J. M. Bueno**[b], **L. Campayo**[b], **P. Navarro**[b*],**M. I. Rodriguez-Franco**[b] and **A. Samat**[c]
[a]*Universidad Autónoma de Madrid, Spain.* [b]*Instituto de Química Médica, C.S.I.C. Madrid, Spain.* [c]*Université d'Aix-Marseille II, France.*

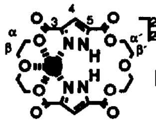
Selective synthesis, deprotonation pK_a values and isolation of the disodium dipyrazolate salt of a proton-ionizable crown 1 are reporterd. A ^{13}CNMR spectroscopic study in DMSO-d_6 solution of mono- and di- nuclear complexes formed from 1 and 2 respectively has been carried out.



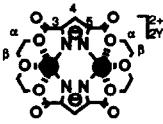
1, L_1



2, $[L_2]^{2-}$ $2Na^+$



$[L_1M]^{2+}2Y^-$



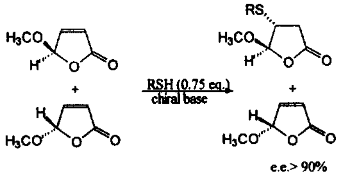
$[L_2M_2]^{2+}2Y^-$

Tetrahedron, **1994**, *50*, 4775

CATALYTIC KINETIC RESOLUTION OF 5-ALKOXY-2(5H)-FURANONES.

Wijnand S. Faber, Johan Kok, Ben de Lange and Ben L. Feringa*
Department of Organic and Molecular Inorganic Chemistry, Groningen Centre for Catalysis and Synthesis, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

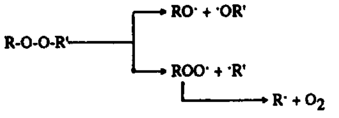
Quinine and quinidine are efficient catalysts for kinetic resolution of 5-methoxy-2(5H)-furanone by enantioselective thiol addition

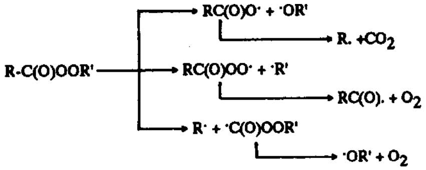


Tetrahedron, **1994**, *50*, 4795

Homolytic Bond-dissociation in Peroxides, Peroxyacids, Peroxyesters and Related Radicals: *ab-initio* MO Calculations.

Rois Benassi and Ferdinando Taddei
Dipartimento di Chimica, Università, Via Campi 183, 41100 Modena, Italy



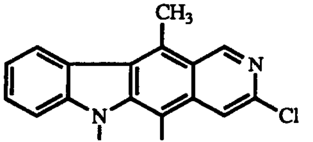


R= H, CH_3 R'=H, CH_3

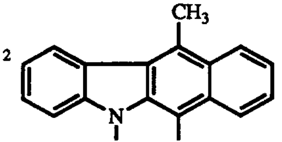
Tetrahedron, **1994**, *50*, 4811

RING D MODIFICATION OF ELLIPTICINE. PART 2. CHLORINATION OF ELLIPTICINE VIA ITS N-OXIDE AND SYNTHESIS AND SELECTIVE ACETYLATION OF 5,6,11-TRIMETHYL-5H-BENZO[b]CARBAZOLE.

Adrian T. Boogaard, Upendra K. Pandit and Gerrit-Jan Koomen; Laboratory of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands.



1



2

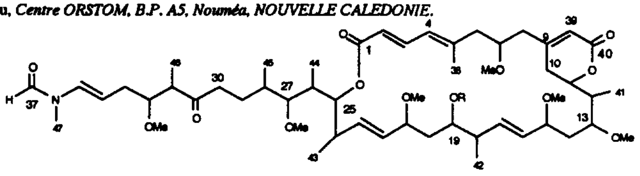
1 Can be synthesized from the corresponding N-oxide. 2 Can be selective acetylated at C-2 with $ZnCl_2$ and Ac_2O.

Tetrahedron, **1994**, *50*, 4829

REIDISPONGIOLIDE A AND B, TWO NEW POTENT CYTOTOXIC MACROLIDES FROM THE NEW CALEDONIAN SPONGE *REIDISPONGIA COERULEA*.

M.V. D'Auria, L.Gomez Paloma, L. Minale* and A. Zampella,
Dipartimento di Chimica delle Sostanze Naturali, via D. Montesano 49, 80131, Napoli, ITALY
J.F. Verbist and C. Roussakis, *Substances Marines à Activité Biologique, Faculté de Pharmacie 1, Rue Gaston Veil 44035 NANTES Cedex, France*
Cécile Debitus and Josiane Patissou, *Centre ORSTOM, B.P. A5, Nouméa, NOUVELLE CALEDONIE.*

Two new 26-membered macrolides, reidispongiolide A and B (**1** R=Me; **2** R=H) have been isolated from the sponge *Reidispongia coerulea*. These macrolides exhibited potent cytotoxicity against various human carcinoma cells.

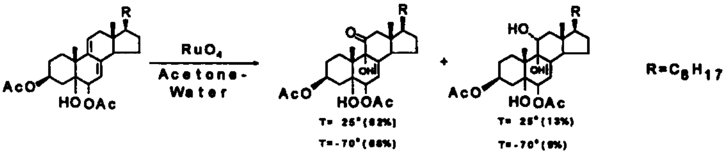


Tetrahedron, **1994**, *50*, 4835

STUDIES TOWARDS THE SYNTHESIS OF POLYOXYGENATED STEROIDS. REACTION OF 7,9(11)-DIENE STEROIDS WITH RuO_4.

Giacomo Notaro, Vincenzo Piccialli, Donato Sica and Dina Smaldone.
Dipartimento di Chimica Organica e Biologica, Università degli Studi di Napoli Federico II, Via Mezzocannone 16, 80134 Napoli, Italy.

RuO_4 has been emploied to oxidize $\Delta^{7,9(11)}$-steroids using equimolecular amounts of the oxidant. Our procedure predominantly furnishes Δ^7-9α-hydroxy-11-ketosterols. An example is shown below.

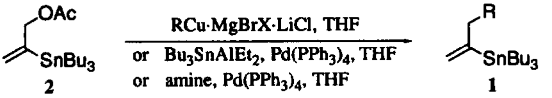


Tetrahedron, **1994**, *50*, 4853

SYNTHESIS OF 2-TRIBUTYLSTANNYL-1-ALKENES FROM 2-TRIBUTYLSTANNYL-2-PROPEN-1-YL ACETATE

Fabio Bellina, Adriano Carpita*, Massimo De Santis and Renzo Rossi*.
Dipartimento di Chimica e Chimica industriale - University of Pisa. - Via Risorgimento 35, I-56126 Pisa, Italy.

2-Tributyl-2-propen-1-yl acetate (**2**) represents a useful precursor to a variety of 2-tributylstannyl-1-alkenes of general formula **1**.



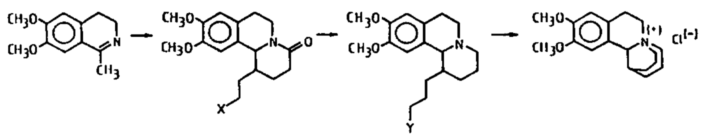
[R = n-C_3H_7, C_6H_5, $C_6H_5CH_2$, CH_2=CH-CH_2, ThpO$(CH_2)_6$, $SnBu_3$, $N(CH_2)_5$, $NH(C_6H_5)$]

Tetrahedron, **1994**, *50*, 4873

SYNTHESIS AND STEREOCHEMICAL STUDY OF *CIS*- AND *TRANS*-1-(3'-SUBSTITUTED-PROPYL)BENZO[*a*]QUINOLIZIDINE

Jenő Kóbor,*,[a] Pál Sohár*,[b] and Ferenc Fülöp[c]

[a]Chemical Department, Pedagogical Training College, H-6720 Szeged; [b]Department of General and Inorganic Chemistry, Eötvös University, POB 32, H-1518 Budapest; [c]Institute of Pharmaceutical Chemistry, Albert Szent-Györgyi Medical University, H-6720 Szeged, POB 121, Hungary



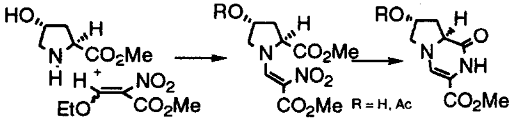
From 1-methyl-6,7-dimethoxy-3,4-dihydroisoquinoline with acrylates, *cis*- and *trans*-1-(3'-substituted-propyl)benzo[*a*]quinolizidinones and quinolizidines were prepared and their predominant conformations were determined

Tetrahedron, **1994**, *50*, 4887

SYNTHESIS OF BICYCLIC PYRAZINONES via ADDITION of HETEROCYCLIC AMINES to a NITRO-ALKENE

Margaret A. Brimble* and Andrew D. Johnston
Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand.

Michael addition of heterocyclic amines to a nitro-alkene followed by reduction/cyclization of the nitro group of the adduct provides a convenient synthesis of bicyclic pyrazinones found in several natural products.

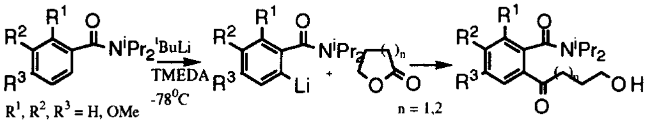


Tetrahedron, **1994**, *50*, 4897

DIRECTED *ORTHO* METALATIONS OF TERTIARY BENZAMIDES USING LACTONES AS ELECTROPHILES

Timothy J. Brenstrum, Margaret A. Brimble* and Ralph J. Stevenson
Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand

Directed ortho metalation of oxygenated tertiary benzamides using tert-butyllithium in THF / TMEDA at -78^{0}C followed by the addition of a range of lactones afforded ortho-substituted keto-alcohols in good yield.

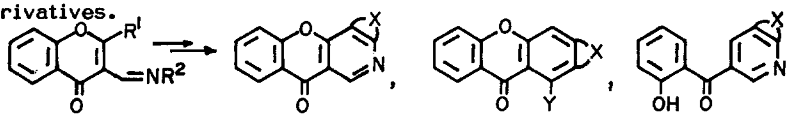


Tetrahedron, **1994**, *50*, 4905

BENZOPYRANS-XXXIII. [4+2]CYCLOADDITION OF *N*,*N*-DIMETHYLHYDRAZONES AND ANILS OF 2-UNSUBSTITUTED AND 2-METHYL-4-OXO-4*H*-1-BENZOPYRAN-3-CARBOXALDEHYDE WITH *N*-PHENYLMALEIMIDE

Chandra Kanta Ghosh*, Kaberi Bhattacharya, and Chandreyi Ghosh
Department of Biochemistry, Calcutta University, Calcutta - 700 019

The title reaction gives adducts convertible to 2-azaxanthone, xanthone, and pyridine derivatives.



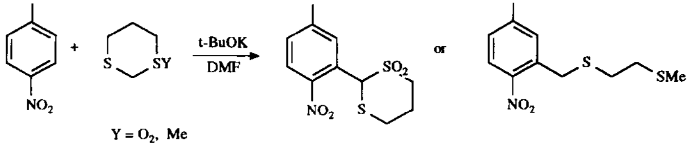
R^1= H,Me; R^2= NMe$_2$,Ar;
X= CONPhCO; Y= H,NHAr

Tetrahedron, **1994**, *50*, 4913

OXIDATIVE VERSUS VICARIOUS NUCLEOPHILIC SUBSTITUTION OF HYDROGEN IN THE REACTION OF DITHIANE DERIVATIVES WITH NITROARENES

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

Carbanions of 1,3-dithiane-1,1-dioxide and 1,3-dithiane-1-methyl iodide react with nitroarenes *via* oxidative and ring opening vicarious nucleophilic substitution pathways

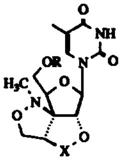


Tetrahedron, **1994**, *50*, 4921

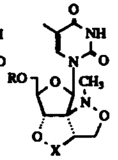
THE SYNTHESIS AND CONFORMATION OF 2'- AND 3'-HYPERMODIFIED TRICYCLIC NUCLEOSIDES AND THEIR USE IN THE SYNTHESIS OF NOVEL 2'- OR 3'-ISOMERIC 4(7)-SUBSTITUTED ISOXAZOLIDINE-NUCLEOSIDES

*J. Rong, P. Roselt, J. Plavec and J. Chattopadhyaya**
Department of Bioorganic Chemistry, Box 581, Biomedical Centre,
University of Uppsala, S-751 23 Uppsala, Sweden

Intramolecular 1,3-dipolar cycloadditon reactions of C-alkenyl nitrones afforded 2'- and 3'-tricyclic nucleosides **10**, **11**, **20** and **29**, the silicon-tethered **20** and **29** were then oxidized to give spiro-4(7)-substituted isoxazolidine-nucleosides **21** and **30**, respectively.

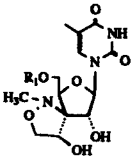


10 & 29

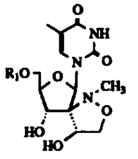


11 & 20

$X = CH_2$ or $SiMe_2$



30



21