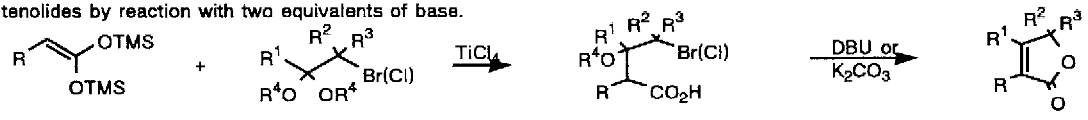
GRAPHICAL ABSTRACTS

Tetrahedron Lett. 30,6109 (1989)

THE MUKAIYAMA REACTION OF KETENE BIS(TRIMETHYLSILYL) ACETALS WITH α-HALO ACETALS - A CONVENIENT BUTENOLIDE SYNTHESIS

F. W. J. Demnitz
Departamento de Química Fundamental, Universidade Federal de Pernambuco, 50.739 - Recife - PE, Brazil

Ketene bis(trimethylsilyl) acetals were reacted with α-halo acetals giving β-alkoxy-γ-halo acids which were converted to butenolides by reaction with two equivalents of base.



Tetrahedron Lett. 30,6113 (1989)

AN EXPEDIENT SYNTHESIS OF α-FLUORO-β-KETOESTERS

Alagappan Thenappan and Donald J. Burton
Dept. of Chemistry, The University of Iowa,
Iowa City, IA 52242, USA

Acylation of fluorocarboethoxymethylene tri-n-butylphosphorane followed by hydrolysis under mild basic conditions provides the title compounds in good yields.

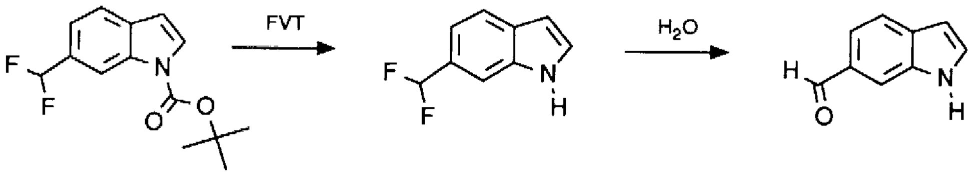
$$R_3P{=}CFC(O)OEt \xrightarrow[2)\ NaHCO_3\ (aq)]{1)\ RC(O)Cl} RC(O)CFHCOOEt$$

R = n-Bu, EtO (38-77%)

Tetrahedron Lett. 30,6117 (1989)

SYNTHESIS AND REACTIVITY OF 6-(FLUOROMETHYL)-INDOLE AND 6-(DIFLUOROMETHYL)INDOLE

Elisa M. Woolridge and Steven E. Rokita*, Department of Chemistry, SUNY at Stony Brook, Stony Brook, NY 11794-3400

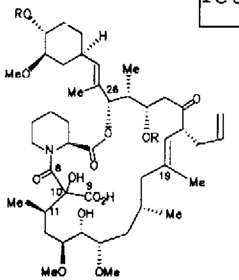


Tetrahedron Lett. 30,6121 (1989)

A MECHANISTIC STUDY OF THE FK-506 TRICARBONYL SYSTEM REARRANGEMENT: SYNTHESIS OF C.9 LABELED FK-506

D. Askin*, R.A. Reamer, Daisy Joe, R.P. Volante and I. Shinkai

Department of Process Research, Merck Sharp & Dohme Research Laboratories
P.O. Box 2000, Rahway, New Jersey 07065



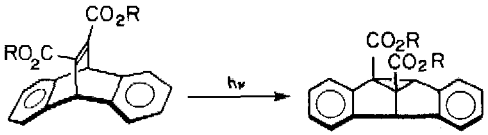
Hydroxide mediated benzilic acid rearrangement of a C.9-^{13}C labeled FK-506 derivative gave 97% rearrangement thru a C.8→C.10 acyl shift mechanism.

Tetrahedron Lett. 30, 6125 (1989)

CHIRAL HANDLE-INDUCED DIASTEREOSELECTIVITY IN AN ORGANIC PHOTOREARRANGEMENT: SOLUTION VERSUS SOLID STATE RESULTS

Jianxin Chen, Miguel Garcia-Garibay and John R. Scheffer*
Department of Chemistry, University of British Columbia, Vancouver, Canada, V6T 1Y6

The extent of asymmetric induction in the di-π-methane photorearrangement of some substituted dibenzobarrelenes is assessed as a function of the structure and location of the chiral handle as well as the solid state versus solution nature of the reaction medium.

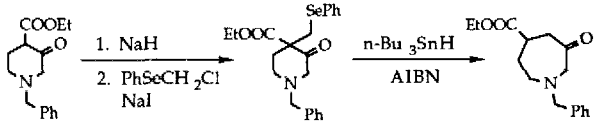


Tetrahedron Lett. 30, 6129 (1989)

FREE RADICAL RING-EXPANSION LEADING TO NOVEL SIX- AND SEVEN-MEMBERED HETEROCYCLES

Paul Dowd* and Soo-Chang Choi
Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260

Heterocyclic β-keto esters are readily expanded to the next higher ring size by free radical rearrangement of the phenylselenomethyl derivative.

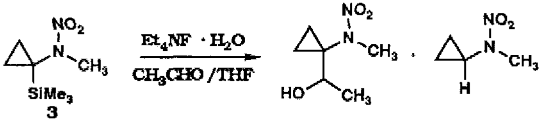


Tetrahedron Lett. 30, 6133 (1989)

DESILYLATION OF α-TRIMETHYLSILYL NITRAMINES: THE FIRST NITRAMINE α-ANION

C. Peter Lillya* and Thomas P. Sassi
Department of Chemistry, University of Massachusetts, Amherst, MA 01003

Treatment of α-trimethylsilyl nitramine **3** with fluoride ion generates the nitramine α-anion which is trapped *in situ* by various electrophiles (H_2O, D_2O, or CH_3CHO).

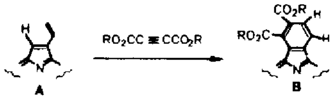


Tetrahedron Lett. 30, 6135 (1989)

TRANSFORMATION OF A MONOVINYLPORPHYRIN TO BENZOPORPHYRINS VIA DIELS-ALDER ADDUCTS

Paul Yon-Hin, Tilak P. Wijesekera, and David Dolphin*
Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada V6T 1Y6

A β-unsubstituted-β'-vinylporphyrin [A] reacts with excess acetylenedicarboxylate ester to give monobenzoporphyrins [B] in high yield.

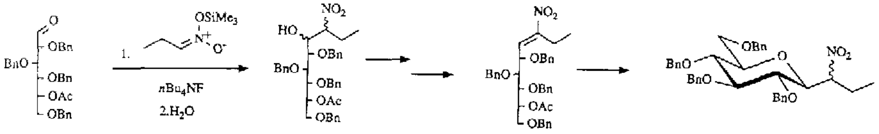


Tetrahedron Lett. 30, 6139 (1989)

SILYL NITRONATES IN CARBOHYDRATE CHEMISTRY. CHAIN-EXTENSION REACTIONS

O.R. Martin*, F.E. Khamis, H.A. El-Shenawy, and S.P. Rao,
Department of Chemistry, S.U.N.Y.-University Center, Binghamton, NY 13901, U.S.A.

Chain-extension of *aldehydo*-sugars to higher nitro sugars is achieved under extremely mild and specific conditions using Seebach's silyl nitronate nitroaldol methodology, e.g.:

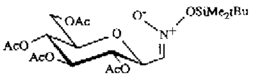


Tetrahedron Lett. 30, 6143 (1989)

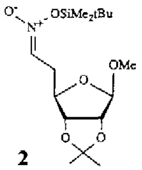
SYNTHESIS AND REACTIVITY OF NITRO SUGAR-DERIVED SILYL NITRONATES

O.R. Martin*, F.E. Khamis, and S.P. Rao, Department of Chemistry, S.U.N.Y.-University Center, Binghamton, NY 13901, U.S.A.

The generation of nitro sugar-derived silyl nitronates (e.g., 1 and 2), their reactivity in F$^-$-catalyzed nitroaldol reactions and the oxidative cleavage of 1 to an *aldehydo*-sugar are described.



1

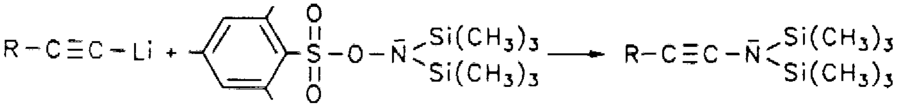


2

Tetrahedron Lett. 30, 6147 (1989)

N,N-BIS(TRIMETHYLSILYL)YNAMINES

Reinhard H. Weigmann and Ernst-Ulrich Würthwein*
Org.-Chem. Institut, Universität Münster, D-4400 Münster, FRG

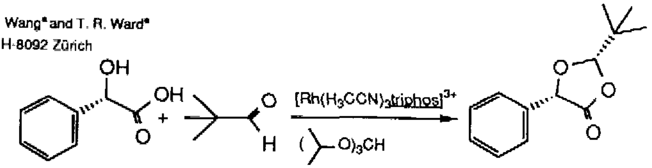


2 1a-d

Tetrahedron Lett. 30, 6151 (1989)

A VERSATILE RHODIUM CATALYST FOR ACETALIZATION REACTIONS UNDER MILD CONDITIONS.

J. Ott[a], G.M. Ramos Tombo[b], B. Schmid[a], L.M. Venanzi*[a], G Wang[a] and T. R. Ward[a]
[a]Laboratorium für Anorganische Chemie, ETH-Zentrum, CH-8092 Zürich
[b]Agricultural Division, Ciba-Geigy AG, CH-4002 Basel.



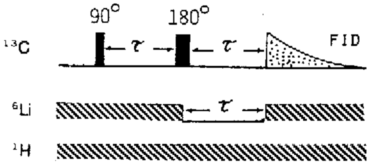
92% yield, diastereomerically pure (proven by ^{1}H NMR)

Tetrahedron Lett. 30, 6155 (1989)

^{13}C Spin-Echo NMR Spectroscopy with Gated ^{6}Li Decoupling: Spectral Editing for Simple Alkyl- and Aryllithium Compounds - Scope and Limitations

*Oswald Eppers and Harald Günther**
University of Siegen, FB 8, OC II, 5900 Siegen, Germany

J-modulation of ^{13}C NMR signals by $^1J(^{13}C,^6Li)$ has been achieved with the simple spin-echo sequence (1) with ^{13}C observation, ^{6}Li gated decoupling, ^{1}H broadband decoupling and a delay of $\tau = 1/2^1J(^{13}C,^6Li)$. The method was used successfully to characterize the multiplicity of NMR signals of lithiated carbons in phenyl- and n-butyllithium.



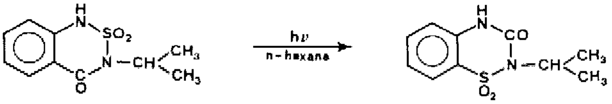
(1)

Tetrahedron Lett. 30, 6159 (1989)

PHOTOISOMERIZATION OF BENTAZONE

Klaus Hustert and Mohammed Mansour

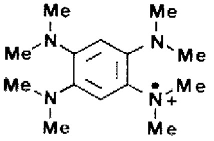
GSF - Institut für Ökologische Chemie
Schulstraße 10
D-8050 Freising-Attaching

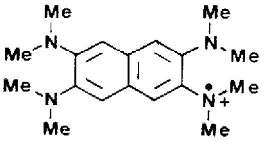


Tetrahedron Lett. 30, 6161 (1989)

Radical Cations of 1,2,4,5-Tetrakis(dimethylamino)benzene and 2,3,6,7-Tetrakis(dimethylamino)naphthalene: an ESR and ENDOR Study

Karin Elbl-Weiser, Franz A. Neugebauer, and Heinz A. Staab
Abteilung Organische Chemie, Max-Planck-Institut
für medizinische Forschung, Jahnstr. 29,
D-6900 Heidelberg, FRG



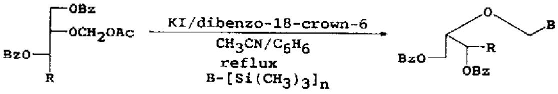


Tetrahedron Lett. 30, 6165 (1989)

EFFICIENT SYNTHESIS OF 1,2-*seco* AND 1,2-*seco* 2-*nor* PYRIMIDINE AND PURINE NUCLEOSIDES.

M. AZYMAH, C. CHAVIS, M. LUCAS and J.-L. IMBACH*
Laboratoire de Chimie Bio-Organique associé au
CNRS, Université de Montpellier II,
34060 Montpellier-Cédex 1, France.

The regiospecific synthesis of N-9 purine and N-1 pyrimidine acyclic nucleosides is described under solid PTC conditions with 76-87% yields from acetoxymethyl ether (acyclic sugar analogues).



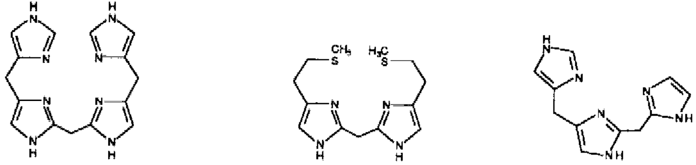
3 R = H
4 R = CH_2OBz

B = Ad,Cy,Gu,T

Tetrahedron Lett. 30, 6169 (1989)

SYNTHESIS OF POLYIMIDAZOLES AS BIOMIMETIC LIGANDS FOR METALLOPROTEIN ACTIVE SITE MODELING.

E. MULLIEZ - Laboratoire de Chimie et Biochimie Pharmacologiques et Toxicologiques, URA 400, Université René Descartes, 45 rue des Saints Pères, 75270 Paris Cédex 06, France.



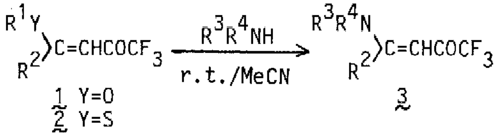
Imidazole-containing ligands for metalloprotein active site modeling.

Tetrahedron Lett. 30, 6173 (1989)

O-N, S-N AND N-N EXCHANGE REACTIONS AT OLEFINIC CARBON ATOMS: FACILE SYNTHETIC METHOD FOR β-TRIFLUOROACETYLVINYLAMINES

Masaru Hojo*, Ryoichi Masuda, Etsuji Okada,
Syuhei Sakaguchi, Hitoshi Narumiya and Katsushi Morimoto
Department of Industrial Chemistry, Faculty of Engineering,
Kobe University, Kobe 657, Japan

β-Trifluoroacetylvinyl ethers 1 and sulfides 2 react with various amines to give β-trifluoroacetylvinylamines 3. This O-N and S-N exchange reaction can be extended to N-N exchange reaction.



$$\begin{matrix}R^1Y & & R^3R^4N & \\ \quad\rangle C=CHCOCF_3 & \xrightarrow[\text{r.t./MeCN}]{R^3R^4NH} & \quad\rangle C=CHCOCF_3 \\ R^2 & & R^2 & \end{matrix}$$

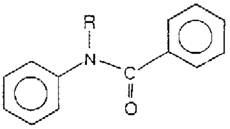
1 Y=O
2 Y=S
3

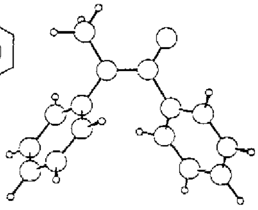
Tetrahedron Lett. 30, 6177 (1989)

STEREOCHEMISTRY OF N-METHYLBENZANILIDE AND BENZANILIDE

Akiko Itai, Yoshiharu Toriumi, Nobuo Tomioka, Hiroyuki Kagechika, Isao Azumaya and Koichi Shudo, Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Tokyo 113, Japan

The structure of N-methylbenzanilide was elucidated by X-ray analysis and examination of ^{1}H- and ^{13}C-nmr spectra. The stereochemistry of the amide bond was proved to be cis in the crystal and in solution, whereas that of benzanilide is trans.

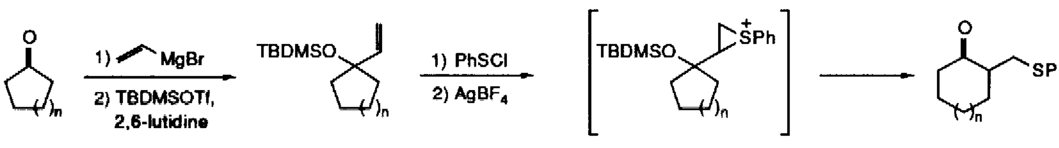




Tetrahedron Lett. 30, 6181 (1989)

AN EPISULFONIUM ION MEDIATED RING EXPANSION OF 1-ALKENYLCYCLOALKANOLS.

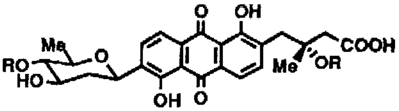
Sunggak Kim* and Jung Ho Park
Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 130-012, Korea

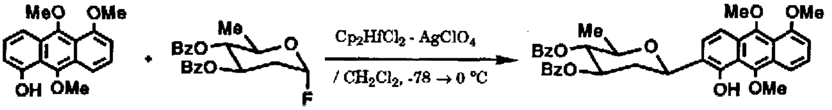


Tetrahedron Lett. 30, 6185 (1989)

Synthetic Study toward Vineomycins. Synthesis of C-Aryl Glycoside Sector via Cp_2HfCl_2-$AgClO_4$-Promoted Tactics

Takashi Matsumoto, Miyoko Katsuki, Hideki Jona, and Keisuke Suzuki*
Department of Chemistry, Keio University, Yokohama 223, Japan

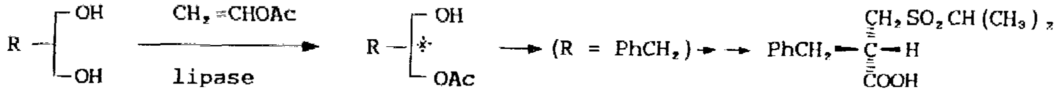




Tetrahedron Lett. 30, 6189 (1989)

LIPASE-CATALYZED ASYMMETRIC SYNTHESIS OF CHIRAL 1,3-PROPANEDIOLS AND ITS APPLICATION TO THE PREPARATION OF OPTICALLY PURE BUILDING BLOCK FOR RENIN INHIBITORS.

Keiichiro Tsuji, Yoshiyasu Terao, and Kazuo Achiwa* School of Pharmaceutical Sciences, University of Shizuoka, 395 Yada, 422 Shizuoka, Japan

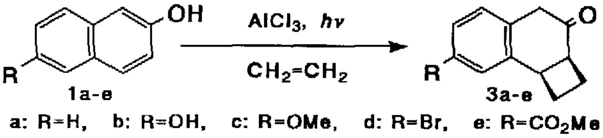


Tetrahedron Lett. 30, 6193 (1989)

NOVEL PHOTOCYCLOADDITION OF 2-NAPHTHOLS TO ETHYLENE IN THE PRESENCE OF LEWIS ACID

Masaki Ue, Masahiko Kinugawa, Kiyomi Kakiuchi*, Yoshito Tobe, and Yoshinobu Odaira
Department of Applied Fine Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

The photoreaction of 2-naphthols **1a-e** with ethylene in the presence of aluminum halide gave the [2+2] cycloadducts **3a-e** in good yields.



Tetrahedron Lett. 30, 6195 (1989)

THE PREPARATION AND REACTIVITY OF BIS(BROMOMAGNESIO)BIS-(TRIMETHYLSILYL)METHANE

M. Hogenbirk, N.J.R. van Eikema Hommes, G. Schat, O.S. Akkerman, F. Bickelhaupt, G.W. Klumpp
Scheikundig Laboratorium, Vrije Universiteit, De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands

The di-Grignard compound 1 was prepared by:

1) $(Me_3Si)_2CBr_2 \xrightarrow[R.T.]{Mg\,/\,Et_2O} (Me_3Si)_2C(MgBr)_2 \quad (\mathbf{1})$

2) $(Me_3Si)_2CCl_2 \xrightarrow[THF,\,-90°C]{LiDBB\,/\,MgBr_2} \mathbf{1} + (Me_3Si)_2C(Li)MgBr$

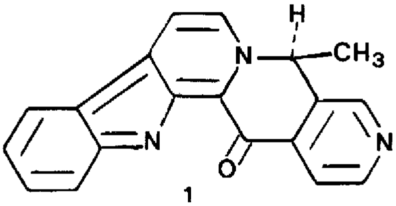
The reactivity of 1 towards Me_3GeCl and Me_3SnCl is remarkably low; the reduced nucleophilicity must be caused by polysubstitition with electropositive elements (Mg,Si) and by steric hindrance.

Tetrahedron Lett. $\underline{30}$,6199(1989)

MAXONINE, A NOVEL ALKALOID FROM SIMIRA MAXONII

Carlos P. Hasbun, Minor Calderon, Oscar Castro, Eszter Gács-Baitz, Giuliano Delle Monache, and Franco Delle Monache
Depto de Quimica,Universidad Nacional,Heredia,Costa Rica

A novel alkaloid, maxonine (1), with an indole-pyrido-naphthyridine nucleus, has been isolated from Simira maxonii. Its structure was established on the basis of 2D NMR spectral data. Compound 1 showed an unexpected bathochromic shift in the UV spectrum with HCl.



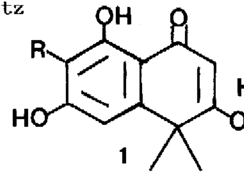
1

Tetrahedron Lett. $\underline{30}$,6203(1989)

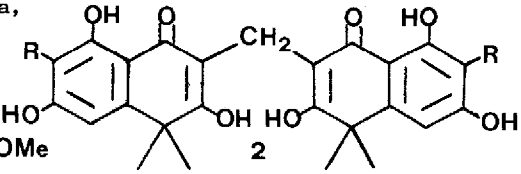
TWO NOVEL 1,4-DIHYDRONAPHTHALENE TYPE COMPOUNDS FROM CASSIA SEMICORDATA

G. Delle Monache, B. Botta, M.A. De Moraes e Souza, J.F. De Mello, and E. Gács-Baitz
Centro Chimica dei Recettori, Largo F. Vito 1, 00168 Roma

The structures of compounds 1 and 2, isolated from Cassia semicordata, were determined by 2D NMR and mass spectral data.



1



2

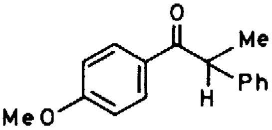
R=COMe throughout

Tetrahedron Lett. $\underline{30}$,6207(1989)

'PREFERENTIAL SPONTANEOUS RESOLUTION' OF p-ANISYL α-METHYLBENZYL KETONE.

Sosale Chandrasekhar*, Mukkamala Ravindranath, Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, India.

The titled compound may be obtained in optically-active form merely by crystallisation in the presence of DBU as catalyst.



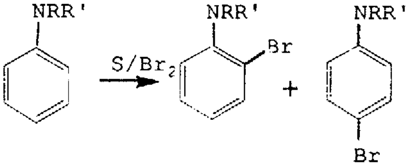
Tetrahedron Lett. $\underline{30}$,6209(1989)

SURFACTANT CONTROL OF THE ORTHO/PARA RATIO IN THE BROMINATION OF ANILINES

Giorgio Cerichelli*, Luciana Luchetti, Giovanna Mancini
Centro CNR di Studio sui Meccanismi di Reazione c/o Dip. di Chimica
Universita' "La Sapienza" P.le Aldo Moro 2, 00185 Roma, Italy

a) S = Solvent, ortho/para < 0.11

b) S = CTAB/H_2O, ortho/para > 0.66



1, R = R'= H

2, R = H, R'= Me

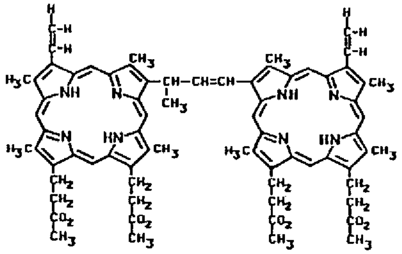
3, R = R'= Me

Tetrahedron Lett. 30,6211(1989)

THE IDENTIFICATION OF A CARBON LINKED OLIGOMER IN HEMATOPORPHYRIN DERIVATIVE AND PHOTOFRIN II

Christopher J. Byrne and A. David Ward*
Department of Organic Chemistry, The University of Adelaide,
G.P.O. Box 498, Adelaide, South Australia, 5001.

The presence of carbon linked oligomeric porphyrins in hematoporphyrin derivative and Photofrin II has been established. A dimer derived from this material has been isolated and characterized by nmr spectroscopy.

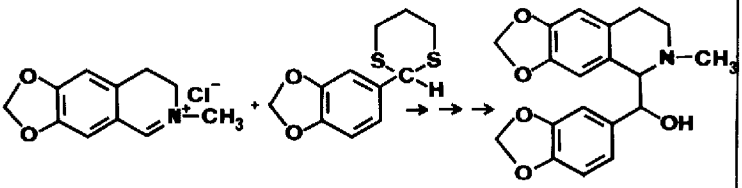


Tetrahedron Lett. 30,6215(1989)

(+)-DECUMBENSINE AND (+)-EPI-α-DECUMBENSINE ARE NOT α-HYDROXYBENZYLTETRAHYDROISOQUINOLINES

Maria D.Rozwadowska*, Dorota Matecka and Danuta Brózda
Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

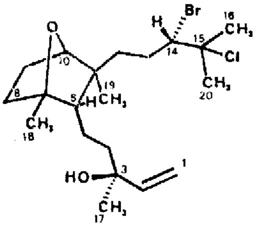
The synthesized diastereomeric α-hydroxybenzyltetrahydroisoquinolines are not identical with the alkaloids: (+)-decumbensine and (+)-epi-α-decumbensine.



Tetrahedron Lett. 30,6219(1989)

DACTYLOMELOL, A NEW CLASS OF DITERPENE FROM THE SEA HARE APLYSIA DACTYLOMELA.

Dulce M. Estrada, José L. Ravelo, Catalina Ruiz-Pérez and Julio D. Martín. Centro de Productos Naturales Orgánicos Antonio González, Universidad de La Laguna-C.S.I.C., Carretera de La Esperanza 2, 38206 La Laguna, Tenerife, Spain. Xavier Solans. Departamento de Cristalografía, Mineralogía y Depósitos Minerales, Universidad de Barcelona, 08028 Barcelona, Spain.



Tetrahedron Lett. 30,6221(1989)

REACTION OF PYRROLO[2,1-c][1,4]BENZODIAZEPINE-2,5,11-TRIONES WITH PHOSPHORUS OXYCHLORIDE

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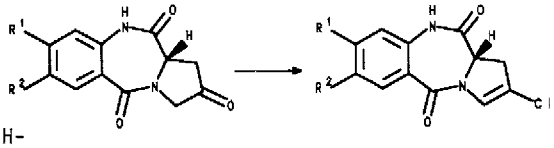
Formation of 5,10,11,11a-tetrahydro-2-chloro-1H-pyrrolo[2,1-c][1,4]benzodiazepine-5,11-diones (1).



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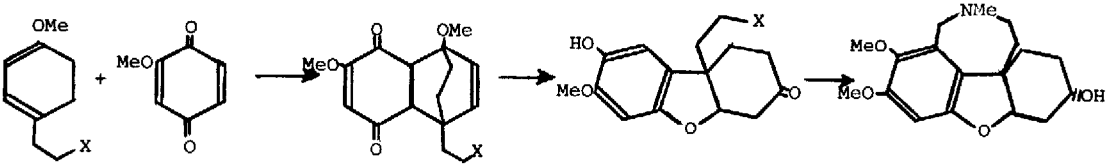
Tetrahedron Lett. 30, 6223 (1989)

A GENERAL SYNTHETIC APPROACH TO AMARYLLIDACEAE ALKALOIDS

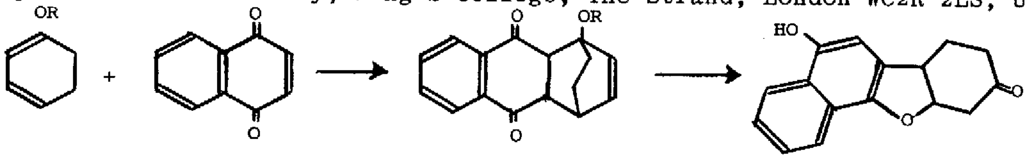
C.W. Bird, A.L. Brown, C.C. Chan and A. Lewis
Department of Chemistry, King's College, The Strand, London WC2R 2LS, U.K.



Tetrahedron Lett. 30, 6227 (1989)

ASYMMETRIC DIELS-ALDER REACTIONS WITH CHIRAL ALKOXYCYCLOHEXADIENES

C.W. Bird and A. Lewis
Department of Chemistry, King's College, The Strand, London WC2R 2LS, U.K.



R is a chiral group

Tetrahedron Lett. 30, 6229 (1989)

FMOC-POLYAMIDE SOLID PHASE SYNTHESIS OF AN O-PHOSPHOTYROSINE-CONTAINING TRIDECAPEPTIDE

E. A. Kitas, J. W. Perich, J. D. Wade,+ R. B. Johns* and G. W. Tregear+
*Dept. of Organic Chemistry, University of Melbourne, Parkville 3052, Victoria, Aust.
+Howard Florey Institute of Experimental Physiology and Medicine,
University of Melbourne, Parkville 3052, Victoria, Australia.

Derivative (4) was used in the solid phase synthesis of the PTyr tridecapeptide with the BOP/HOBt method for peptide bond formation. The protected peptide-resin was treated with 1 M TMSBr-thioanisole/TFA to give the PTyr peptide (5) in 70 % yield.

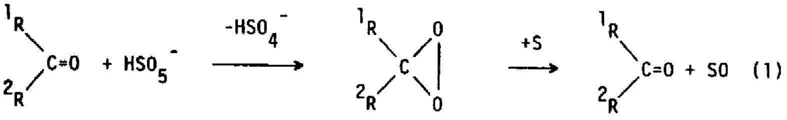
Fmoc-Tyr(PO_3Me_2)-OH (4)   H-Arg-Leu-Ile-Glu-Asp-Asn-Glu-PTyr-Thr-Ala-Arg-Gln-Gly-OH (5)

Tetrahedron Lett. 30, 6233 (1989)

ENANTIOSELECTIVE OXIDATION OF SULPHIDES BY DIOXIRANES IN THE PRESENCE OF BOVINE SERUM ALBUMIN.

Stefano Colonna and Nicoletta Gaggero
Dipartimento Chimica Organica Industriale dell'UNiversità, Via Golgi 19, 20133 Milano-Italy.

E.E. up to 89% are reached in the sulphoxidation reaction by dioxiranes with **bovine serum ambumin** as chiral auxiliary.



Tetrahedron Lett. 30,6237(1989)

Intramolecular Trapping of a Phosphazide by an Imine: Formation of 2,3-Diamino-2H-indazole Derivatives from *o*-Azidobenzaldimines and Tertiary Phosphines

Pedro Molina*, Antonio Arques and Maria Victoria Vinader
Departamento de Quimica Organica, Facultad de Ciencias, Universidad de Murcia, Campus de Espinardo, 30071 Murcia, Spain.

Treatment of 2-azidobenzaldimines with tertiary phosphines leads to iminophosphoranes derived from 2-amino-3-alkyl-(aryl)amino indazoles.