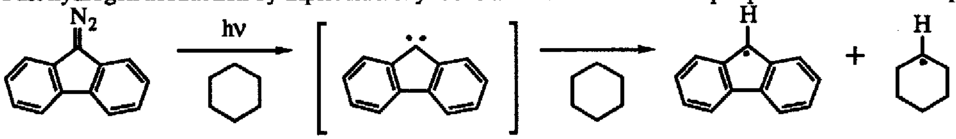
GRAPHICAL ABSTRACTS

Tetrahedron Lett. 30, 4469 (1989)

INDIRECT OBSERVATION OF SPIN POLARIZATION IN TRIPLET FLUORENYLIDENE AT ROOM TEMPERATURE

William S. Jenks and Nicholas J. Turro*
Department of Chemistry, Columbia University, New York, New York 10027

Fast hydrogen abstraction by triplet fluorenylidene allows observation of spin polarization in the triplet carbene.

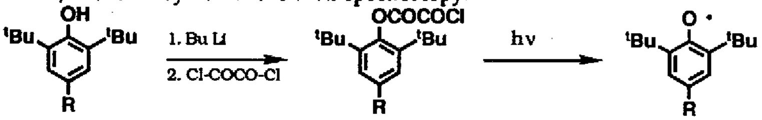


Tetrahedron Lett. 30, 4473 (1989)

CONVENIENT UNIMOLECULAR SOURCES OF ARYLOXYL RADICALS I – ARYLOXYOXALYL CHLORIDES

by David A. Modarelli, Frank C. Rossitto, Paul M. Lahti*
Department of Chemistry, Lederle Graduate Research Tower, University of Massachusetts, Amherst, MA 01003

UV photolysis of readily synthesized aryloxyoxalyl chloride half-esters provides a new unimolecular source of aryloxyl radicals, as shown by ESR and UV-vis spectroscopy.

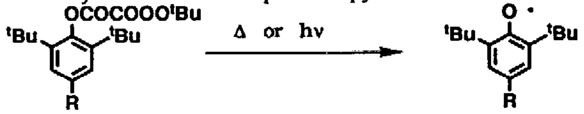


Tetrahedron Lett. 30, 4477 (1989)

CONVENIENT UNIMOLECULAR SOURCES OF ARYLOXYL RADICALS. II -- ARYLOXYOXALYL *tert*-BUTYLPEROXIDES

by David A. Modarelli, Frank C. Rossitto, Paul M. Lahti*
Department of Chemistry, Lederle Graduate Research Tower, University of Massachusetts, Amherst, MA 01003

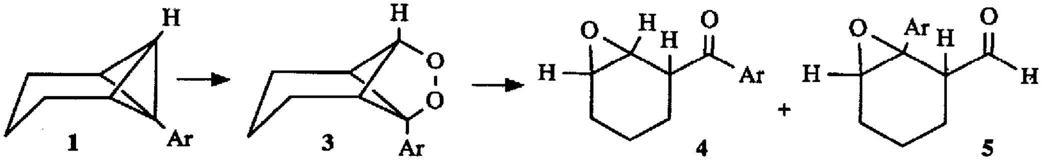
UV photolysis and mild thermolysis of aryloxyoxalyl *tert*-butylperoxides provides a new unimolecular source of aryloxyl radicals, as shown by ESR and UV-vis spectroscopy.



Tetrahedron Lett. 30, 4481 (1989)

ELEKTRONEN-TRANSFER-INDUZIERTE PHOTO-OXYGENIERUNG VON 1- ARYL-SUBSTITUIERTEN TRICYCLO[4.1.0.0^{2,7}]HEPTANEN

Klaus Gollnick und Uwe Paulmann, Institut für Organische Chemie der Universität München, D-8000 München 2, Bundesrepublik Deutschland

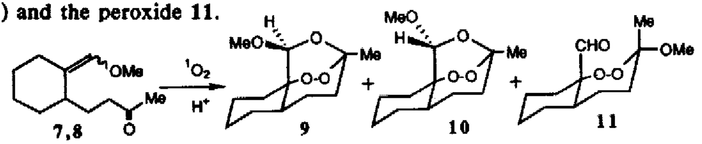


Tetrahedron Lett. 30,4485(1989)

SYNTHESIS OF ARTEANNUIN-LIKE COMPOUNDS

Charles W. Jefford, Javier Velarde, and Gérald Bernardinelli, Department of Organic Chemistry and Laboratory of Crystallography, University of Geneva, 1211 Geneva 4, Switzerland

The E and Z enol ethers 7 and 8 react with singlet oxygen to give dioxetanes which on acid catalysis rearrange to 1,2,4-trioxanes (9 and 10) and the peroxide 11.

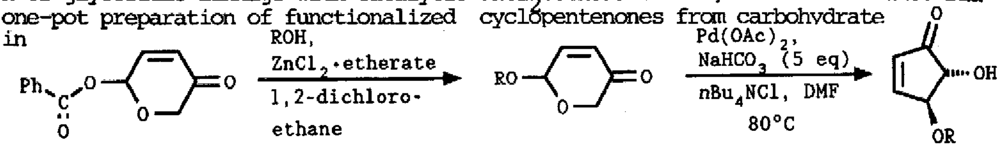


Tetrahedron Lett. 30,4489(1989)

IMPROVED PROCEDURE FOR THE SYNTHESIS OF 6-ALKOXY-2,3-DIHYDRO-6H-PYRAN-3-ONES (2,3-DIDEOXY-DL-PENT-2-ENOPYRANOS-4-ULOSES). NEAT CONVERSION INTO POLYFUNCTIONALIZED CYCLOPENTENONES.

B. Mucha and H.M.R. Hoffmann, Dep. of Organic Chemistry, University of Hannover, Schneiderberg 1B, D-3000 Hannover, F.R. Germany

Construction of glycosidic linkage with catalytic ZnCl$_2$.etherate in 1,2-dichloroethane. Diastereosel. one-pot preparation of functionalized cyclopentenones from carbohydrate precursors in good yield.

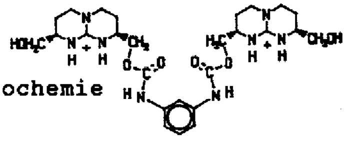


Tetrahedron Lett. 30,4493(1989)

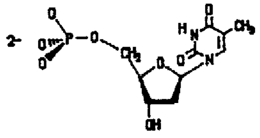
A NON-MACROCYCLIC HOST FOR BINDING ORGANIC PHOSPHATES IN PROTIC SOLVENTS

F.P. Schmidtchen

Inst. f. Org. Chemie und Biochemie
Techn. Univ. München
D-8046 Garching, FRG



2



9

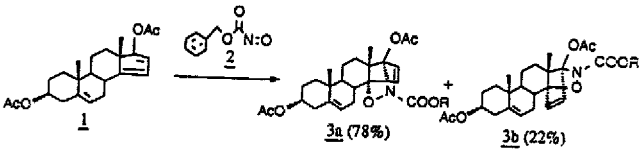
The synthesis of the novel linear ditopic guanidinium host 2 and its host-guest complexation with thymidine-5'-phosphate 9 in water is described.

Tetrahedron Lett. 30,4497(1989)

A CYCLOADDITION ROUTE TO 14-HYDROXYSTEROIDS

Gerald Kirsch, Roland Golde and Günter Neef*

Research Laboratories of Schering AG,
D-1000 Berlin 65,
Federal Republic of Germany

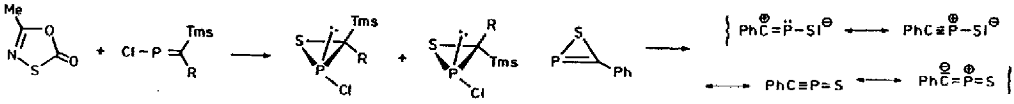


R = benzyl

Tetrahedron Lett. 30,4501(1989)

2-CHLOR-1-THIA-2-PHOSPHIRANE – SYNTHESE UND REAKTIONEN – HINWEISE FÜR DEN 1,3-DIPOL $Ph\overset{\oplus}{C}{=}P{-}S|^{\ominus}$

G. Märkl und W. Hölzl, Institut für Organische Chemie der Universität Regensburg, Universitätsstr. 31, 8400 Regensburg.

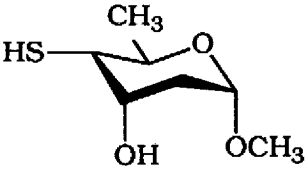


Tetrahedron Lett. 30,4505 (1989)

SYNTHESIS OF METHYL 2,6-DIDEOXY-4-THIO-α-D-*RIBO*-HEXOPYRANOSIDE, A NEW THIO SUGAR FOUND IN CALICHEMICINS

Kai van Laak, Hans-Dieter Scharf*, Institut für Organische Chemie der RWTH Aachen, Prof.-Pirlet-Str. 1, 5100 Aachen, F.R.G.

The 4-thio-digitoxoside, a rare sugar derived from the calichemicins, is prepared

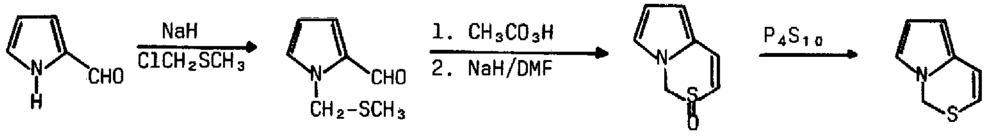


Tetrahedron Lett. 30,4507 (1989)

SYNTHESIS OF 1H-PYRROLO-[1.2-c]-[1.3]-THIAZINE: A NEW SULPHUR-NITROGEN HETEROCYCLE

T. Thielmann*, M. Güntert, M. Köpsel, P. Werkhoff
Haarmann + Reimer GmbH, Rumohrtalstraße 1, 3450 Holzminden

Summary: A total synthesis of 1H-pyrrolo-[1.2-c]-[1.3]-thiazine from pyrrolo-2-carbaldehyde has been accomplished in 4 steps:

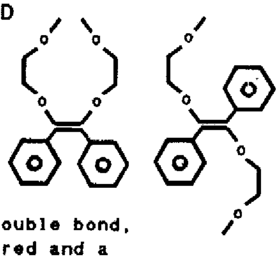


Tetrahedron Lett. 30,4509 (1989)

PHOTORESPONSIVE COMPLEXING STILBENE α, α' DISUBSTITUTED BY ETHYLENEDIOXY SIDE ARMS

J.PH.SOUMILLION*, J.WEILER, X.DE MAN, R.TOUILLAUX, J.P.DECLERCQ, B.TINANT.

CATHOLIC UNIVERSITY OF LOUVAIN, LOUVAIN-LA-NEUVE, BELGIUM.

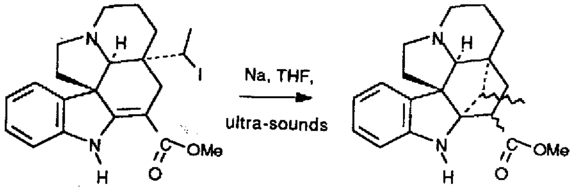


A photoresponsive stilbene, bearing complexing side arms on the double bond, was synthesized and photoisomerized. Extracting ability was measured and a stable complex with sodium thiocyanate was isolated.

Tetrahedron Lett. 30, 4513 (1989)

SYNTHESIS OF HEXACYCLIC INDOLE ALKALOIDS RELATED TO VINDOLININE BY SONOCHEMICAL CYCLIZATION.

Georgette Hugel, Dominique Cartier and Jean Lévy,
Laboratoire de Transformations et Synthèse de Substances Naturelles, associé au CNRS,
Université de Reims, 51, rue Cognacq-Jay, 51096 Reims Cedex, FRANCE.



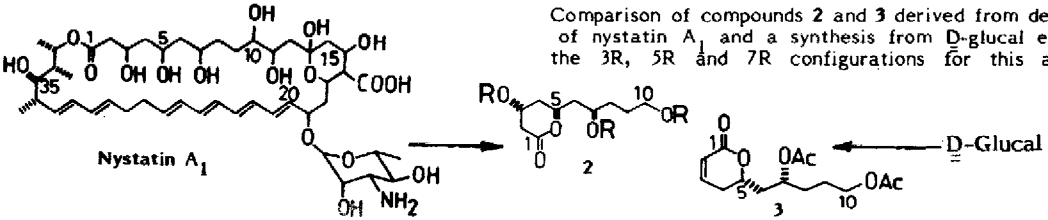
Tetrahedron Lett. 30, 4517 (1989)

STEREOSTRUCTURE OF NYSTATIN A_1: A SYNTHETIC ASSIGNMENT OF THE C1-C10 FRAGMENT

Jacques Prandi and Jean-Marie Beau*

Université d'Orléans, Laboratoire de Biochimie Structurale associé au CNRS,
Rue de Chartres, BP 6759, 45067 Orléans, France

Comparison of compounds **2** and **3** derived from degradation of nystatin A_1 and a synthesis from D-glucal establishes the 3R, 5R and 7R configurations for this antibiotic.



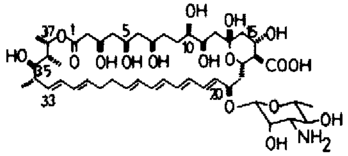
Tetrahedron Lett. 30, 4521 (1989)

COMPLETE STEREOSTRUCTURE OF NYSTATIN A_1: A PROTON NMR STUDY

Jean-Marc Lancelin and Jean-Marie Beau

Université d'Orléans, Laboratoire de Biochimie Structurale associé au CNRS,
Rue de Chartres, BP 6759, 45067 Orléans, France

Based on 2D-proton nmr protocols, the 10R, 11R, 13S, 15S, 16R, 17S, 19R, 1'R configurations have been assigned for nystatin A_1.



- Nystatin A_1 -

Tetrahedron Lett. 30, 4525 (1989)

IMPROVED PREPARATION OF ALIPHATIC PROPYNOIC ESTERS

L. BALAS, B. JOUSSEAUME* and B. LANGWOST
Laboratoire de Chimie Organique et Organométallique (associé au CNRS),
Université Bordeaux I, 351, cours de la Libération, 33405 - TALENCE (France)

$$HC{\equiv}C{-}CO_2H \quad + \quad ROH \xrightarrow{\text{DCC - DMAP}} HC{\equiv}C{-}CO_2R$$

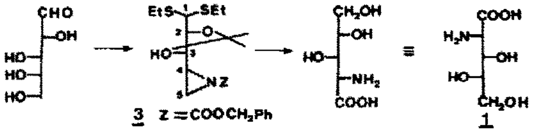
An improved procedure of esterification of propynoic acid, based on the N, N'-dicyclohexylcarbodiimide 4-dimethylaminopyridine condensation, is presented, which gives good results with primary, secondary, allylic and homoallylic alcohols. Reactions conditions are mild. Some limitations are given.

Tetrahedron Lett. 30, 4527 (1989)

AN ENANTIOSPECIFIC SYNTHESIS OF POLYOXAMIC ACID FROM L-ARABINOSE

A. Duréault, F. Carreaux, J.C. Depezay, Université René Descartes, UA 400, 45 rue des Saints Pères, 75006 Paris.

The five-carbon chiral hydroxylated aziridine 3 derived from L-arabinose is the precursor of polyoxamic acid 1.

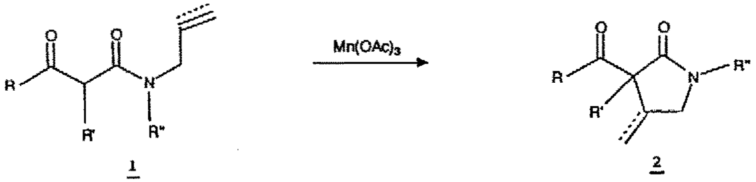


Tetrahedron Lett. 30, 4531 (1989)

NEW SYNTHESIS OF LACTAMS AND SPIROLACTAMS RADICAL CYCLIZATION INDUCED BY MANGANESE(III) ACETATE

J. Cossy, C. Leblanc
Laboratoire de Photochimie associé au CNRS, U.F.R. Sciences de Reims, B.P. 347, 51062 Reims, France

Treatment of N,N-unsaturated dialkyl-β-oxoamides 1 by $Mn(OAc)_3$ leads to the formation of lactams 2.

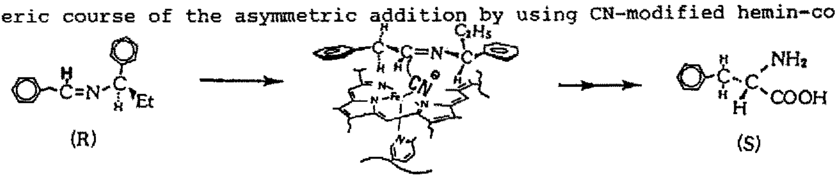


Tetrahedron Lett. 30, 4535 (1989)

Asymmetric Syntheses of Amino Acids by Addition of Cyanide to the Schiff Bases in the Presence of Cyanide-Modified Hemin-Copolymer

Kiyoshi Saito and Kaoru Harada*
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki, 305 Japan

A possible steric course of the asymmetric addition by using CN-modified hemin-copolymer.

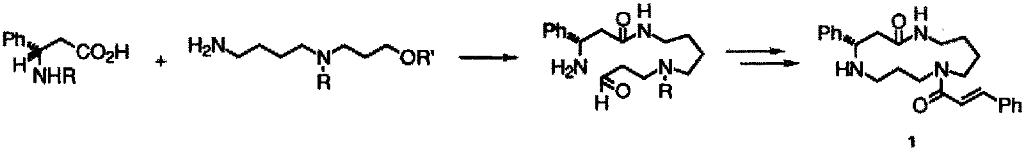


Tetrahedron Lett. 30, 4539 (1989)

ENANTIOSELECTIVE TOTAL SYNTHESIS OF (+)-(S)-DIHYDROPERIPHYLLINE

Takehiko Kaseda, Toyohiko Kikuchi, and Chihiro Kibayahsi*
Tokyo College of Pharmacy, Horinouchi, Hachoji, Tokyo 192-03, Japan

The enantioselective total synthesis of (+)-(S)-dihydroperiphylline (1) was achieved by a new strategy for 13-membered lactam formation.

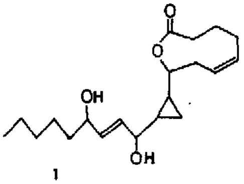


Tetrahedron Lett.30,4543(1989)

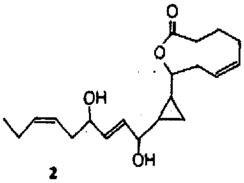
HALICHOLACTONE AND NEOHALICHOLACTONE, TWO NOVEL FATTY ACID METABOLITES FROM THE MARINE SPONGE HALICHONDRIA OKADAI KADOTA

Haruki Niwa, Kazumasa Wakamatsu, and Kiyoyuki Yamada*
Department of Chemistry, Faculty of Science,
Nagoya University, Chikusa, Nagoya 464, Japan

Isolation and structural elucidation of halicholactone (1) and neohalicholactone (2).



1



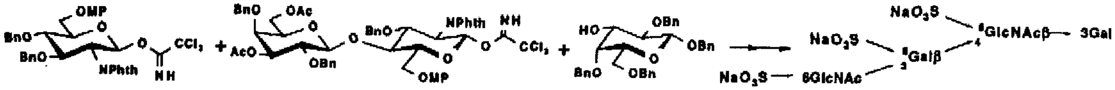
2

Tetrahedron Lett.30,4547(1989)

A SYNTHETIC APPROACH TO KERATAN SULFATE I: SYNTHESIS OF TRISULFATED GLYCOTETRAOSE

Masanori Kobayashi, Fumito Yamazaki, Yukishige Ito, and Tomoya Ogawa*
RIKEN (The Institute of Physical and Chemical Research), Wako-shi, Saitama, 351-01 Japan

A stereocontrolled synthesis of trisulfated glycotetraose was achieved by use of two key glycosyl donors and a key glycosyl acceptor.

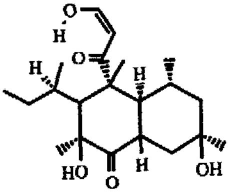


Tetrahedron Lett.30,4551(1989)

TOTAL SYNTHESIS OF (-)-BETAENONE C

Akitami Ichihara, Shokyo Miki, Hirokazu Kawagishi and Sadao Sakamura
Department of Agricultural Chemistry, Faculty of Agriculture
Hokkaido University, Sapporo 060, Japan

Stereoselective synthesis of (-)-betaenone C (1) has been completed through intramolecular Diels-Alder reaction.



1

Tetrahedron Lett.30,4555(1989)

Synthesis of Optically Active Chloro Alkanoic Esters

U. Azzena,[a,*] G. Delogu,[b] G. Melloni,[a] and O. Piccolo.[c,*]
[a]Dipartimento di Chimica, and [b]Istituto C.N.R. A.T.C.A.P.A., via Vienna 2, I-07100 Sassari; [c]Studio di Consulenza Scientifica, via Borno´ 5, I-22060 Sirtori. ITALY.

$$CH_3\text{-}{}^*CH(OSO_2CH_3)\text{-}(CH_2)_n\text{-}COOR \xrightarrow{AlCl_3} CH_3\text{-}{}^*CH(Cl)\text{-}(CH_2)_n\text{-}COOR$$

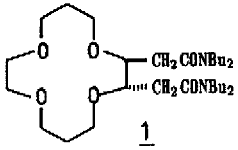
$n = 0, 1$
$R = CH_3, C_2H_5$
o.y. up to 94%

Tetrahedron Lett. 30, 4559 (1989)

SYNTHESIS AND BINDING PROPERTIES OF LITHIUM-SELECTIVE [14]-O_4 MACROCYCLES AND THEIR USE IN A LITHIUM ION-SELECTIVE ELECTRODE

Ritu Kataky, Patrick E. Nicholson and David Parker*
Department of Chemistry, University of Durham, South Road, Durham DH1 3LE.

The [14]-O_4 dibutylamide derivative 1 is a selective lithium ionophore



1

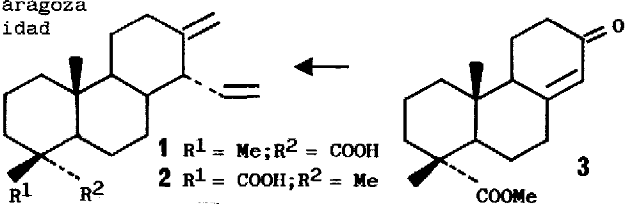
Tetrahedron Lett. 30, 4563 (1989)

STEREOSTRUCTURAL REVISION OF AURICULARIC ACID

SYNTHESIS OF 4-EPI-AURICULARIC ACID

A. Abad, C. Agulló, M. Arnó and R.J. Zaragozá
Departamento de Química Orgánica, Universidad de Valencia, 46100 Valencia, Spain.

1 has been synthesised from 3. It is demonstrated that auricularic acid is an epimer at C-4 of 1, so it must be re-formulated as cleistanth-13,15-dien-19-oic acid (2)



1 $R^1 = Me; R^2 = COOH$

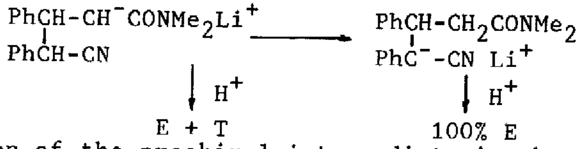
2 $R^1 = COOH; R^2 = Me$

Tetrahedron Lett. 30, 4565 (1989)

CONJUGATE ADDITION OF ARYLACETONITRILES TO CINNAMIC ACID DERIVATIVES. A CASE OF HIGH DIASTEREOSELECTIVE ASYMMETRIC PROTONATION.

L.Viteva, Y.Stefanovsky.
Institute of Organic Chemistry.
Bulgarian Academy of Sciences,
Sofia 1040, Bulgaria.

Complete erythro selectivity as a result of asymmetric protonation of the prochiral intermediate is observed.



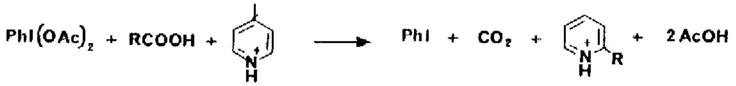
$$\begin{array}{ccc} \underset{\text{PhCH-CN}}{\text{PhCH-CH}^-\text{CONMe}_2\text{Li}^+} & \longrightarrow & \underset{\text{PhC}^-\text{-CN Li}^+}{\text{PhCH-CH}_2\text{CONMe}_2} \\ \downarrow H^+ & & \downarrow H^+ \\ E + T & & 100\%\ E \end{array}$$

Tetrahedron Lett. 30, 4569 (1989)

A NEW GENERAL METHOD OF HOMOLYTIC ALKYLATION OF PROTONATED HETEROAROMATIC BASES BY CARBOXYLIC ACIDS AND IODOSOBENZENE DIACETATE .

F.Minisci , E.Vismara , F.Fontana and M.C.Nogueira Barbosa - Dipartimento di Chimica del Politecnico - piazza L.da Vinci , 32 - 20133 Milano - Italy

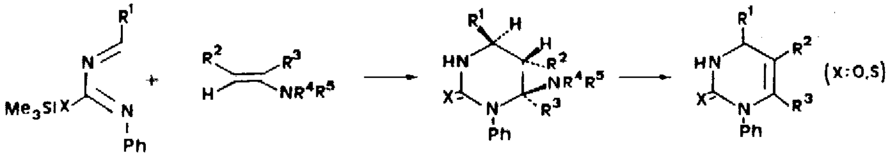
The photochemically induced decomposition of carboxylic acids by iodosobenzene diacetate has been used to obtain the substitution of protonated heteroaromatic bases by alkyl radicals .



Tetrahedron Lett. 30, 4573 (1989)

1,4-CYCLOADDITION OF 1,3-DIAZABUTADIENES WITH ENAMINES: AN EFFICIENT ROUTE TO THE PYRIMIDINE RING

José Barluenga*, Miguel Tomás, Alfredo Ballesteros, and Luis A. López
Dpto. de Química Organometálica, Facultad de Química, Universidad de Oviedo, 33071 Oviedo, Spain

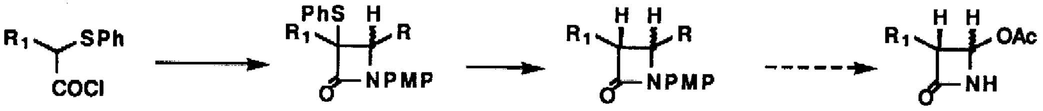


Tetrahedron Lett. 30, 4577 (1989)

ALKYL(PHENYL)KETENES AS SYNTHETIC EQUIVALENTS OF MONOALKYLKETENES: A CONCISE GENERAL ROUTE TO 3-ALKYL β-LACTAMS AS CARBAPENEM BUILDING BLOCKS.

C. Palomo, F.P. Cossío, J.M. Odriozola, M. Oiarbide and J.M. Ontoria.
Departamento de Química Aplicada, Unidad de Química Orgánica. Facultad de Químicas. Universidad del Pais Vasco
Apdo. 1072. 20080 San Sebastián. Spain

The dehydrochlorination of α-phenylthioalkanoyl chlorides with triethylamine in the presence of imines produced a high yield formation of α-phenylthio β-lactams which upon desulfuration furnished a wide variety of 3-alkyl β-lactams in a high stereoselective fashion.

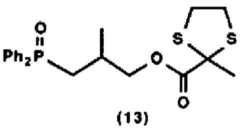


Tetrahedron Lett. 30, 4581 (1989)

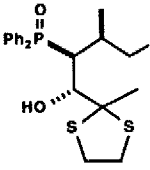
EXTENSION OF THE HORNER-WITTIG REACTION TO THE SYNTHESIS OF E-ALKENES WITH CHIRAL SUBSTITUENTS: STEREOCHEMICAL CONTROL BY ACYL TRANSFER

Peter M. Ayrey and Stuart Warren,
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

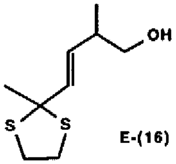
Acyl transfer and reduction on ester (13) gives a single crystalline isomer of erythro-(15) and hence pure E-(16).



(13)



(15)



E-(16)

Tetrahedron Lett. 30, 4585 (1989)

DIVERSE ORIGINS OF CONFORMATIONAL EQUILIBRIUM ISOTOPE EFFECTS FOR HYDROGEN IN 1,3-DIOXANS

Carolyn A. Carr, Stephen L.R. Ellison, and Michael J.T. Robinson*
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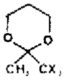
Conformational equilibrium isotope effects and their solvent dependence for 1-5($X={}^2H$) are attributed to (i) steric hindrance, (ii) orbital interactions transmitted through σ-bonds, and (iii) the isotope effect on the polarity of a C-H bond.



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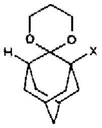

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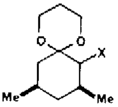

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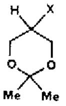

4

5

Tetrahedron Lett. 30,4589(1989)

ORIGINS OF CONFORMATIONAL EQUILIBRIUM ISOTOPE EFFECTS FOR HYDROGEN IN KETONES

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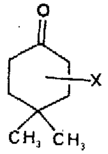
Conformational equilibrium isotope effects (CEIEs) for hydrogen have been measured for 1-4 and, together with other CEIEs for ketones and hydrocarbons, can be explained by hyperconjugation and other orbital interactions transmitted through σ-bonds.



1: X = 2-^{2}H
2: X = 3-^{2}H
3: X = *cis*-2,3-$^2H_2$
4: X = *trans*-2,3-$^2H_2$

Tetrahedron Lett. 30,4593(1989)

THE ORIGIN OF CONFORMATIONAL EQUILIBRIUM ISOTOPE EFFECTS FOR CARBON

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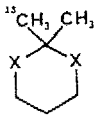
Oxford OX1 3QY, England

Conformational equilibrium isotope effects for carbon have been measured for 1-3 and are interpreted as arising from hyperconjugative and anomeric interactions.



1: X = CH_2
2: X = O
3: X = C=O

Tetrahedron Lett. 30,4597(1989)

REACTION OF TRYPTOPHAN WITH TRIFLUOROACETIC-ANHYDRIDE

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