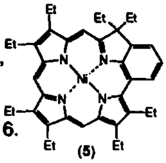
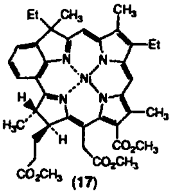
GRAPHICAL ABSTRACTS

Tetrahedron Lett. **1990,** *31*, 1365

EFFICIENT NEW SYNTHESES OF BENZOCHLORINS, BENZOISOBACTERIOCHLORINS, AND BENZOBACTERIOCHLORINS.

M. Graça H. Vicente, Irene N. Rezzano, and Kevin M. Smith*,
Department of Chemistry,
University of California, Davis, CA 95616.


(5)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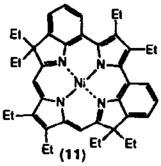
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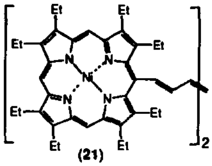
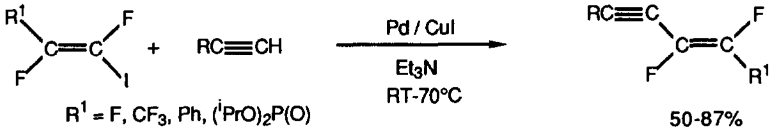

(21)

Treatment of Cu(II) or Ni(II) porphyrins with 3-dimethylaminoacrolein/$POCl_3$ gives meso-(2-formylvinyl)porphyrins which can be cyclized in acid to give access to benzochlorins e.g. (5). Cu(II) or Ni(II) chlorins give benzoisobacteriochlorins e.g. (17) and/or benzobacteriochlorins e.g. (11). The (2-formylvinyl) compounds give dimers e.g. (21) upon reductive coupling.

Tetrahedron Lett. **1990,** *31*, 1369

A FACILE, GENERAL METHOD FOR THE PREPARATION OF FLUORINATED ENYNES

Zhen-Yu Yang and Donald J. Burton*
Department of Chemistry, The University of Iowa,
Iowa City, Iowa 52242, U.S.A.

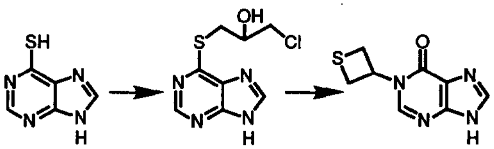


Tetrahedron Lett. **1990,** *31*, 1373

A REMARKABLE THIETANE FORMATION FROM A 6-MERCAPTOPURINE DERIVATIVE

Jeffery B. Press*, Zoltan G. Hajos* and Rebecca A. Sawyers
R. W. Johnson Pharmaceutical Research Institute, Raritan, New Jersey 08869-0602

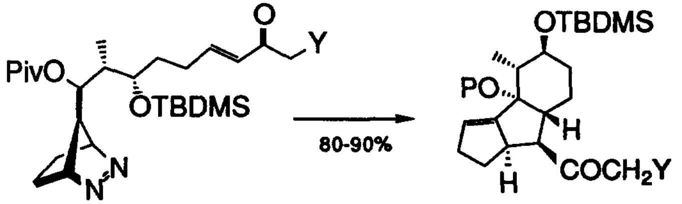
6-Oxo-1-(thietan-3-yl)purine was derived from 6-mercaptopurine and epichlorohydrin by treatment with base.



Tetrahedron Lett. **1990,** *31*, 1377

STEREOSELECTIVITY IN INTRAMOLECULAR DIYL TRAPPING REACTIONS. MODEL STUDIES DIRECTED TOWARD THE PHORBOLS.

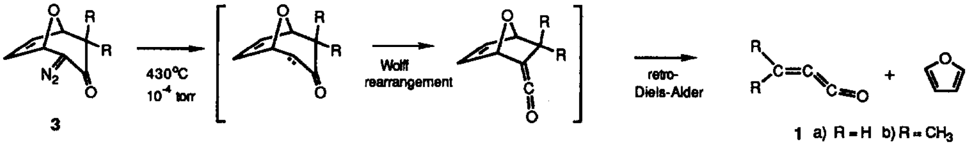
J.I. McLoughlin, R. Brahma, O. Campopiano, R. D. Little*, Department of Chemistry, UCSB, Santa Barbara, CA 93106



Tetrahedron Lett. **1990**, *31*, 1381

FLASH VACUUM PYROLYSIS OF 2-DIAZO-8-OXA-BICYCLO[3.2.1]OCT-6-EN-3-ONES. A NEW METHOD FOR THE PREPARATION OF PROPADIENONES.

John C. Brahms and William P. Dailey*, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323.



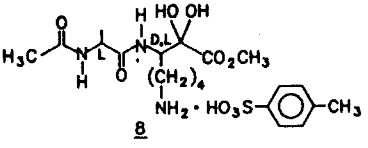
Tetrahedron Lett. **1990**, *31*, 1385

A NOVEL METHOD FOR THE PREPARATION OF PEPTIDYL α-KETO ESTERS

Joseph P. Burkhart, Norton P. Peet* and Philippe Bey

Merrell Dow Research Institute, 2110 E. Galbraith Road, Cincinnati, OH 45215

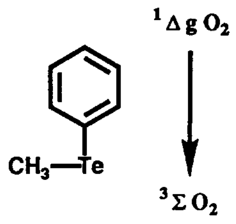
Addition of an acyloxy anion equivalent to a differentially protected lysinal was the key step in the preparation of 8. This new synthesis of α-keto esters is useful for the preparation of proteinase inhibitors with a lysine sidechain.



Tetrahedron Lett. **1990**, *31*, 1389

HEAVY ATOM QUENCHING OF THE SINGLET DELTA DIOXYGEN MOLECULE ($^1\Delta g\ O_2$)

E. J. Corey, Ahsan U. Khan and Deok-Chan Ha
Department of Chemistry, Harvard University, Cambridge, MA 02138

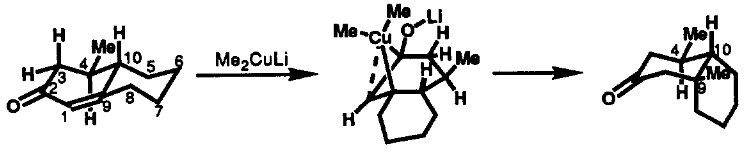


Quenching constants, k_Q (M^{-1} sec^{-1}), for $^1\Delta g\ O_2$ deactivation: β-carotene, 1 x 10^{10}; PhTeMe, 3.8 x 10^9; $(PhCH_2)_2$ Te, 7.3 x 10^9.

Tetrahedron Lett. **1990**, *31*, 1393

A POSSIBLE TRANSITION STATE ASSEMBLY FOR HIGHLY DIASTEREOSELECTIVE CONJUGATE ADDITION REACTIONS OF LITHIUM DIMETHYLCUPRATE WITH α,β-ENONES

E. J. Corey and Francis J. Hannon
Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138



Tetrahedron Lett. **1990**, *31*, 1397

A PRACTICAL ONE-STEP SYNTHESIS OF PRIMARY THIOLS UNDER MILD AND NEUTRAL CONDITIONS USING BIS(TRIORGANOTIN) SULFIDES

Marc Gingras and David N. Harpp*
Department of Chemistry
McGill University
Montreal, Quebec, Canada, H3A 2K6

A useful synthesis of thiols is presented involving the reaction of primary organic halides and bis(triaryl/alkyltin)sulfides in the presence of fluoride ion in CH_3CN/H_2O at 20°C. This fluorodestannylation procedure is carried out under mild and neutral conditions in contrast to many other methods.

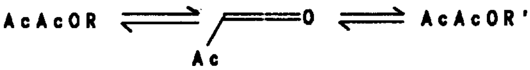
$R\text{-}Br + R'_3Sn\text{-}S\text{-}SnR'_3 + Bu_4N^+ F^-.3H_2O \text{ ------> } R\text{-}SH + R'_3Sn\text{-}F$

Tetrahedron Lett. **1990**, *31*, 1401

THE TRANSACETOACETYLATION REACTION: MECHANISTIC IMPLICATIONS

J. Stewart Witzeman, Eastman Chemicals Division Research Laboratories,
Kingsport, TN 37662

Kinetic and spectroscopic evidence is presented which indicates that the uncatalyzed transesterification of acetoacetates in organic solvents (transacetoacetylation) proceeds via the intermediacy of acetylketene.

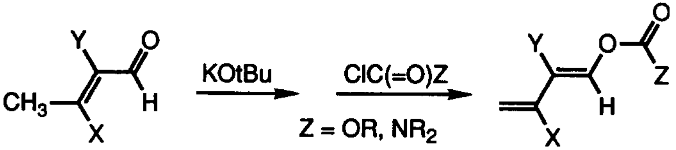


Tetrahedron Lett. **1990**, *31*, 1405

A SIMPLE SYNTHESIS OF 1-(1,3-BUTADIENYL) CARBONATES AND CARBAMATES

Paul F. De Cusati and R. A. Olofson*
Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, USA

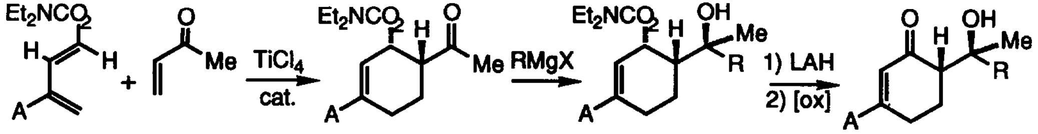
Reaction works if Y is H, Me, Cl and is stereospecific if X = H. Reaction also is stereospecific with mesityl oxide



Tetrahedron Lett. **1990**, *31*, 1409

O-1-(1,3-BUTADIENYL) CARBAMATES AS DIELS-ALDER DIENES: STEREOSPECIFIC SYNTHESIS OF (±)-HERNANDULCIN AND CONGENERS

Paul F. De Cusati and R. A. Olofson*
Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, USA

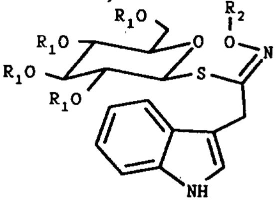


Tetrahedron Lett. **1990,** *31*, 1417

FIRST SYNTHESIS OF AN INDOLE GLUCOSINOLATE

M.C.Viaud & P.Rollin*, *Laboratoire de Chimie Bioorganique et Analytique,*
Université d'Orléans, B.P.6759, 45067 Orléans Cedex 2, France.

The synthesis of glucobrassicin 8, the parent structure of the indole glucosinolate family, and its desulfo-analogue 6 is described.



6 $R_1 = R_2 = H$

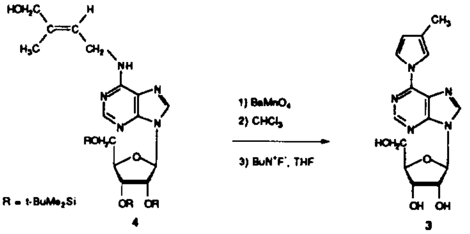
8 $R_1 = H \quad R_2 = SO_3K$

Tetrahedron Lett. **1990,** *31*, 1419

SYNTHESIS OF 6-(3-METHYLPYRROL-1-YL)-9-β-D-RIBOFURANOSYL PURINE, A NOVEL METABOLITE OF ZEATIN RIBOSIDE

M. HAIDOUNE[a], R. MORNET[a*] and M. LALOUE[b].
[a] Groupe de Recherches de Chimie Organique et Bioorganique,
Ensemble Scientifique, 2, Boulevard Lavoisier, 49045 ANGERS, France.
[b] Laboratoire de Physiologie Cellulaire Végétale, CNRS,
Avenue de la Terrasse, 91198 GIF-sur-YVETTE, France

The title compound 3 was synthesized by oxidation of ribose-protected zeatin riboside 4 with $BaMnO_4$, followed by heating in $CHCl_3$, and deprotection. Uv and mass spectra of 3 were similar to the spectra of a new metabolite of zeatin riboside, a common cytokinin. Its aglycone was prepared through a similar route from N-9 protected zeatin.

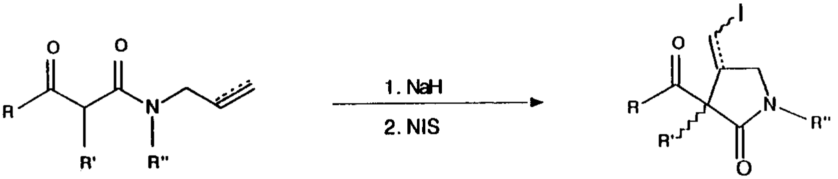


Tetrahedron Lett. **1990,** *31*, 1427

A ONE STEP SYNTHESIS OF FUNCTIONALIZED LACTAMS AND SPIROLACTAMS FROM UNSATURATED β-KETOAMIDES

J. COSSY, A. THELLEND*
Réarrangements thermiques et photochimiques, Associé au CNRS, U.F.R. Sciences, 51062 REIMS Cédex

When N,N-diallyl, and N-alkyl,N-propargyl-β-ketoamides are treated with NaH and then with N-iodosuccinimide, iodomethyl and iodomethylene-β-ketolactams are obtained respectively.

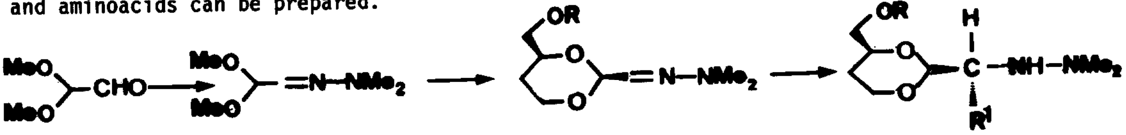


Tetrahedron Lett. **1990,** *31*, 1429

ENANTIOSELECTIVE SYNTHESIS VIA THE NUCLEOPHILIC ALKYLATION OF HYDRAZONES : ACETALS AS CHIRAL AUXILIARIES.

M. THIAM and F. CHASTRETTE. Laboratoire de Chimie Organique Physique. Université Claude Bernard Lyon I. 43 Bd du 11 novembre 1918. 69622 VILLEURBANNE Cedex. FRANCE.

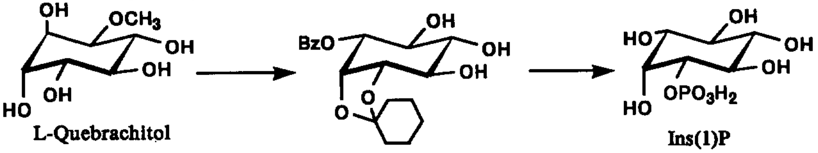
Diastereoselective addition of organolithium reagents on hydrazones vicinal to chiral cyclic acetals provide chiral hydrazinoacetals from which optically active aminoacetals and aminoacids can be prepared.



Tetrahedron Lett. **1990**, *31*, 1433

CHIRAL SYNTHESIS OF D-MYO-INOSITOL 1-PHOSPHATE STARTING FROM L-QUEBRACHITOL

Takahiko Akiyama, Naoto Takechi, Shoichiro Ozaki* Department of Resources Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790, Japan

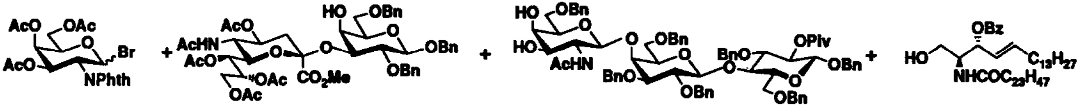


Tetrahedron Lett. **1990**, *31*, 1435

TOTAL SYNTHESIS OF AN EXTENDED *GANGLIO*-GANGLIOSIDE, IV^{4}GalNAcβGM1b

Mamoru Sugimoto[a)], **Kazushige Fujikura**[a)], **Shigeki Nunomura**[b)], **Yukishige Ito**[b)], **and Tomoya Ogawa**[b)]
a) Central Research Institute, MECT Co., 1780, Kitano, Tokorozawa-shi, Saitama 359 Japan, b) RIKEN (The Institute of Physical and Chemical Research), Wako-shi, Saitama, 351-01 Japan

First total synthesis of the extended *ganglio*-ganglioside IV^{4}GalNAcβGM1b is described.



$\Longrightarrow$ β-D-Gal*p*NAc-(1→4)-[α-D-Neu*p*5Ac-(2→3)]-β-D-Gal*p*-(1→3)-β-D-Gal*p*NAc-(1→4)-β-D-Gal*p*-(1→4)-β-D-Glc*p*-(1→1)-Cer

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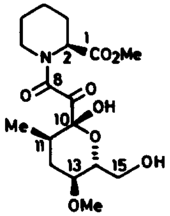
Tetrahedron Lett. **1990**, *31*, 1439

STUDIES DIRECTED TOWARDS THE SYNTHESIS OF IMMUNOSUPPRESSIVE AGENT FK-506 : CONSTRUCTION OF THE TRICARBONYL MOIETY

A V Rama Rao*, T K Chakraborty and K Laxma Reddy
Indian Institute of Chemical Technology, Hyderabad 500 007, India

Alkylation of a suitably functionalised dithiane precursor with L-N-(α-haloacetyl) pipecolic acid methyl ester, followed by oxidation of the active methylene group provided an easy route to 1,2,3-tricarbonyl functionality of FK-506.

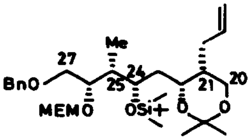


Tetrahedron Lett. **1990**, *31*, 1443

STUDIES DIRECTED TOWARDS THE SYNTHESIS OF IMMUNOSUPPRESSIVE AGENT FK-506 : SYNTHESIS OF C-20 TO C-27 MOIETY

A V Rama Rao*, T K Chakraborty and A V Purandare
Indian Institute of Chemical Technology, Hyderabad 500 007, India.

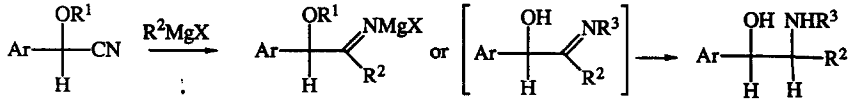
Regioselective ring opening of (2S,3R)-epoxide of 4-benzyloxy-cis-2-buten-1-ol with Me$_2$CuLi and diastereofacial selective aldol reaction with enolsilane are the key steps involved in the stereospecific construction of "2-methyl-1,3-diol" backbone of FK-506.



Tetrahedron Lett. **1990**, *31*, 1447

Stereoselective Synthesis of Ephedrine and Related 2-Amino alcohols of High Optical Purity from Protected Cyanohydrins

W. Roy Jackson, Howard A. Jacobs, Barry R. Matthews, Gamini S. Jayatilake
Department of Chemistry, Monash University, Clayton, Victoria, Australia 3168 and
Keith G. Watson, ICI Australia, Central Research Laboratories, Ascot Vale, Victoria, Australia 3032



Ephedrine can be prepared from optically active benzaldehyde cyanohydrin without loss of optical purity

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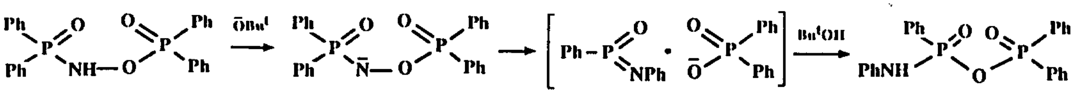
Tetrahedron Lett. **1990**, *31*, 1451

N,O-BIS(DIPHENYLPHOSPHINOYL)HYDROXYLAMINE

BASE-INDUCED REARRANGEMENT TO A PHOSPHONAMIDIC-PHOSPHINIC MIXED ANHYDRIDE

Martin J.P.Harger
Department of Chemistry, The University, Leicester LE1 7RH

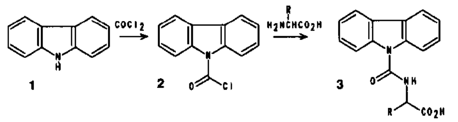


Tetrahedron Lett. **1990**, *31*, 1455

A USEFUL REAGENT FOR DERIVATIZATION OF AMINO ACIDS

Stig Allenmark
Laboratory of Microbiological Chemistry, University of Gothenburg, Guldhedsgatan 10A,
S-41346 Gothenburg, Sweden

Amino acids have been reacted with N-(chloroformyl)-carbazole (2). This yields fluorescent, stable derivatives (3) with excellent behaviour on reversed-phase liquid chromatography. Enantiomers of 3 are well separated on BSA-silica columns.

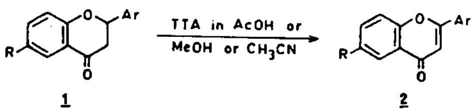


Tetrahedron Lett. **1990**, *31*, 1459

Dehydrogenation of Flavanones to Flavones using Thallium(III) Acetate(TTA)

Om V.Singh and R.P.Kapoor*
Department of Chemistry, Kurukshetra University, Kurukshetra-132 119, Haryana (India)

A facile conversion of flavanones (1) to flavones (2) using thallium(III) acetate in acetic acid/methanol/acetonitrile.



R = H, Ch_3, Cl; Ar = C_6H_5, $4\text{-}CH_3OC_6H_4$, $4\text{-}ClC_6H_4$.

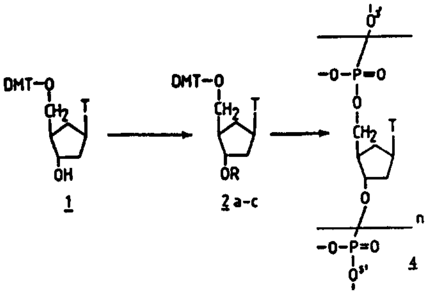
Tetrahedron Lett. **1990**, *31*, 1463

FIRST SYNTHESIS OF CARBOCYCLIC OLIGOTHYMIDYLATES

A. Szemző*, J. Szécsi, J. Sági and L. Ötvös

Central Research Institute for
Chemistry, Hung. Acad. of Sci.,
H-1525 Budapest, P.O. Box 17, Hungary

(+)-Carbocyclic oligothymidylates were chemically synthesized by different methods.



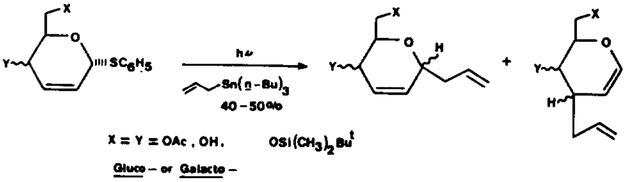
Tetrahedron Lett. **1990**, *31*, 1467

FREE-RADICAL REACTIONS OF SOME PHENYLTHIO-2,3-DIDEOXYHEX-2-ENOPYRANOSIDES

J.L. Marco-Contelles *, C. Fernández , Ana Gómez and N. Martín-León

[a]*Instituto de Química Orgánica General, C.S.I.C., Juan de la Cierva 3, 28006-Madrid (Spain)*

[b]*Departamento de Química Orgánica, Facultad de Ciencias, Universidad Complutense, 28040-Madrid (Spain).*

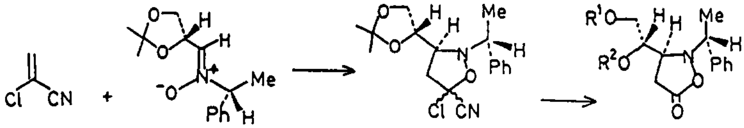


Tetrahedron Lett. **1990**, *31*, 1471

SYNTHESIS OF A POTENTIAL INTERMEDIATE TO β-LACTAM ANTIBIOTICS

Andrew Freer, Karl Overton* and Richard Tomanek
Department of Chemistry, Glasgow University, Glasgow G12 8QQ

The carbapenem intermediate (7) has been synthesised as a single diastereomer and its structure determined by X-ray analysis of (9).



(7) $R^1 = R^2 = H$

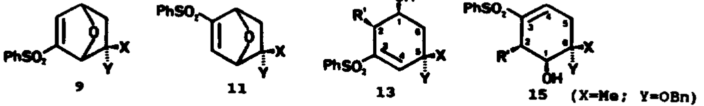
(9) $R^1 + R^2 = OSO_2O$

Tetrahedron Lett. **1990**, *31*, 1475

REGIO- AND STEREOCONTROLLED SYNTHESIS OF HYDROXYCYCLOHEXENYL SULFONES FROM OXANORBORNENES.

O. Arjona[a*], R. Fernández de la Pradilla[b*], A. Mallo[a], J. Plumet[a], A. Viso[a]. [a] Dpto. Química Orgánica, Facultad de Química. Universidad Complutense, 28040 Madrid, Spain. [b] Instituto de Química Orgánica General, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain.

Organolithium reagents and $LiAlH_4$ undergo conjugate additions to oxanorbornenic vinyl sulfones 9-12 to generate funtionalized cyclohexenyl phenyl sulfones 13-16 in high yields.



9 10

11 12

13 14

15 (X=Me; Y=OBn)
16 ($X=Y=OCH_2CH_2O$)

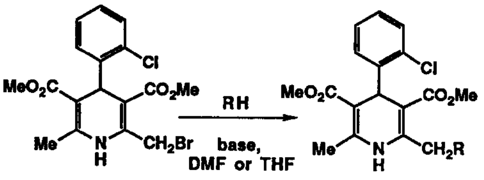
R'= Me, n-Bu, Ph, $-CH=CH_2$, H

Tetrahedron Lett. **1990**, *31*, 1479

FORMATION , SYNTHETIC UTILITY AND STRUCTURE ELUCIDATION OF A 2-BROMOMETHYL 1,4-DIHYDROPYRIDINE

D. Alker* and A.G. Swanson

The structure of the 2-bromomethyl 1,4-dihydropyridine 7 has been proved by ^{1}H-NMR spectroscopy and its reaction with a range of nucleophiles to give compounds 8 studied.

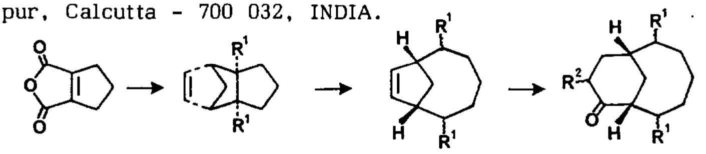


7 8

Tetrahedron Lett. **1990**, *31*, 1483

A SIMPLE APPROACH TO THE CONSTRUCTION OF BICYCLO-[5.2.1] AND [5.3.1] RING SYSTEMS FROM BICYCLO[2.2.1]HEPTANE PRECURSORS

Goutam Saha, Atashi Bhattacharya, Supti Saha Roy and Subrata Ghosh*
Department of Organic Chemistry, Indian Association for the Cultivation of Science
Jadavpur, Calcutta - 700 032, INDIA.



R^1 = COOMe;
R^2 = COOEt

Tetrahedron Lett. **1990**, *31*, 1485

COBALT(II) CHLORIDE CATALYSED CONDENSATION OF ACETOACETATE WITH VINYLETHERS

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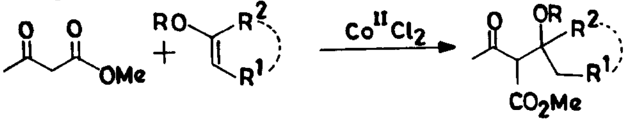
Department of Chemistry, Indian Institute of Technology, Kanpur-208016, India

Summary : Cobalt(II) chloride catalyses the diastereoselective condensation of methylacetoacetate with vinyl ethers to give β-alkoxy carbonyl compounds or α, β-unsaturated compounds in excellent yields.



Tetrahedron Lett. **1990**, *31*, 1487

HETEROCYCLIC O-XYLYLENES: THIAZOLE, OXAZOLE AND IMIDAZOLE ANALOGUES

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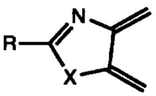

1 X = O, R = H
2 X = S, R = H, Ph
3 X = NMe, R = H

The xylylene derivatives (1) to (3) have been generated flash-pyrolytically and trapped with SO_2 and PhSH and, in the case of (1), with methyl acrylate.

Tetrahedron Lett. **1990**, *31*, 1491

THE GENERATION OF 2,3-DIHYDRO-2,3-bis-(METHYLENE)THIOPHENES FROM 4,6-DIHYDROTHIENO[3,4-b]THIOPHENE 5,5-DIOXIDES

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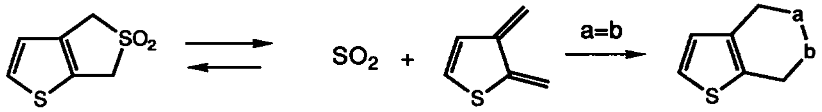

Tetrahedron Lett. **1990**, *31*, 1495

A NOVEL SINGLE POT REACTION FOR SUBSTITUTION AND COUPLING OF VINYLACETATE TO TRANS-STILBENES BY INTERLAMMELLAR MONTMORILLONITE PALLADIUM CATALYST

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