9-ALLENYL-9-BBN: A NEW REAGENT FOR THE EFFICIENT ALLENYLBORATION OF CARBONYL COMPOUNDS

PRODUCING THE HOMOPROPARGYLIC ALCOHOLS IN HIGH PURITY AND YIELD

Herbert C. Brown,* Uday R. Khire, Uday S. Racherla

H. C. Brown and R. B. Wetherill Laboratories of Chemistry, Purdue University, West Lafayette, IN 47907

A new reagent, 9-allenyl-9-BBN, has been developed for regiospecific allenylboration of aldehydes and ketones.

Tetrahedron Lett. 1993, 34, 19

ON THE REGIOSELECTIVITY OF PD CATALYZED INTRAMOLECULAR CARBAMETALATIONS

Barry M. Trost and Jacques Dumas, Department of Chemistry, Stanford University, Stanford, California 94305-5080

Pd catalyzed alkylative cyclizations of 1-6-enynes may proceed by either a 5-exo or 6-endo mode.

Synthesis of o-Indan[1.1.1]cyclophane and Potential Indanyl Subunits of the Fullerenes

Philip Magnus* David Witty and Andrew Stamford Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712.

Treatment of indane-5-carbinol with aqueous acid gives the o-indan[1.1.1]cyclophane 7 as the major product.

Tetrahedron Lett. 1993, 34, 23

6 5% H₂SO₄
(w/w)

dioxene-H₂O
(9:1)
88h reflux

7 (25%)

Tetrahedron Lett. 1993, 34, 27

[2+2] CYCLOADDITION OF CYCLIC ENECARBAMATES AND ENAMIDES WITH KETENES. A SHORT AND EFFICIENT SYNTHESIS OF THE GEISSMAN-WAISS LACTONE.

Antônio Rodolfo de Faria, Carlos Roberto R. Matos and Carlos Roque D. Correia, * Núcleo de Pesquisas de Produtos Naturais, Centro de Ciências da Saúde, Bl. H, Universidade Federal do Rio de Janeiro, RJ, 21941, Brasil.

2-Aza-bicyclo[3.2.0]heptan-2-ones were prepared by a [2+2] cycloaddition reaction of cyclic enecarbamates and/or enamides and ketenes. The synthetic potential is illustrated by a four step synthesis of the Geissman-Waiss lactone 1 in 62% overall yield.

NOVEL PHOTOCHEMISTRY OF A STERICALLY CROWDED MONOBENZOBARRELENE DERIVATIVE

Ray Jones, John R. Scheffer,* James Trotter and Melvin Yap Department of Chemistry, University of British Columbia Vancouver. Canada V6T 1Z1

Relief of unfavorable methyl-methyl interactions in monobenzobarrelene derivative **2b** is suggested to be the factor responsible for its unusual photochemistry compared to non-methylated analogues.

SUBSTITUENT EFFECTS ON THE DI- π -METHANE PHOTO-REARRANGEMENT OF 9.10-ETHENOANTHRACENE DERIVATIVES

Tetrahedron Lett. **1993**, 34, 35

Graham Rattray, Jie Yang, Anna D. Gudmundsdottir and John R. Scheffer* Department of Chemistry, University of British Columbia Vancouver, Canada V6T 1Z1

X

The regioselectivities of the $di-\pi$ -methane photorearrangements of vinyl-substituted 9,10-ethenoanthracene derivatives such as 1 are reported and discussed in terms of the radical stabilizing and polar effects of the substituents X and Y on the biradical intermediates involved.

Tetrahedron Lett. 1993, 34, 39

Phosphorus-Containing Inhibitors of HMG-CoA Reductase. 3.

Synthesis of Hydroxyphosphinyl-Analogues of the Mevinic Acids.

Donald S. Karanewsky* and Michael C. Badia, Bristol-Myers Squibb Pharmaceutical Research Institute. PO Box 4000.

Princeton, New Jersey 08543-4000 USA

Unusual Chemo- and Stereoselectivity in the Addition of Chiral

Tetrahedron Lett. 1993, 34, 43

Aminoalcohols to Achiral Nitroalkenes
Michelle L. Morris, Michael A. Sturgess*

Dept. of Chemistry and Biochemistry, Univ. of Arkansas, Fayetteville AR 72701.

Prolinol has been shown to stereospecifically add to achiral nitroalkenes. The resulting adducts may be utilized as precursors to synthetically useful chiral diamines.

An Efficient Enantiomeric Three Step Synthesis of β-Amino Acids (Esters)

Mohamed K. Mokhallalati, Ming-Jung Wu, and Lendon N. Pridgen*
Synthetic Chemistry Department, SmithKline Beecham Pharmaceuticals,
Post Office Box 1539, King of Prussia, Pennsylvania 19406-0939

Ethyl tributylstannylacetate (1) reacts stereoselectively with chiral 1,3-oxazolidines 2 to give 3 which are converted to β-amino esters 4.

Tetrahedron Lett. 1993, 34, 47

Tetrahedron Lett. 1993, 34, 51

OBSERVATIONS ON Sn-Li EXCHANGE IN α -AMINO-ORGANOSTANNANES AND THE CONFIGURATIONAL STABILITY OF NON-STABILIZED α -AMINOORGANOLITHIUMS

Andrew F. Burchat, J. Michael Chong,* and Sheldon B. Park

Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

 α -Aminoorganostannanes may be used as precursors of α -aminoorganolithiums which may be trapped with electrophiles with retention of configuration at -95 °C.

AN ENANTIOSELECTIVE APPROACH TO RING A OF TAXOL USING THE WIELAND-MIESCHER KETONE

Miroslaw Golinski, Sundar Vasudevan, Rey Floresca, Carolyn P. Brock, and David S. Watt,* Department of Chemistry and Division of Pharmaceutics and Medicinal Chemistry, University of Kentucky, Lexington, KY 40506

The selective protection of the S-(+)-enantiomer of the Wieland Miescher ketone (2) and the oxidative cleavage of the B ring provided a model 10 for the A ring of the taxol.

Tetrahedron Lett. 1993, 34, 55

Tetrahedron Lett. 1993, 34, 59

MILD REDUCTION OF α , β -UNSATURATED KETONES AND ALDEHYDES

WITH AN OXYGEN-ACTIVATED PALLADIUM CATALYST

Milena Sommovigo and Howard Alper

Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

The palladium dimer $[R_2PHPdPR_2]_2$ (R=t-Bu) reacts with oxygen to give a very active catalyst for the hydrogenation of α,β -unsaturated aldehydes and ketones.

$$\begin{array}{ccc}
R & & \frac{H_2/THF}{[(t-Bu_2PH)Pd(PBu_2t)]_2, O_2} & & R & & R'
\end{array}$$

AN EFFECTIVE SYNTHESIS OF SCALEMIC 3,5,5-TRISUBSTITUTED PYRROLIN-4-ONES

Armos B. Smith, III,* Ryan C. Holcomb, Mark C. Guzman, Terence P. Keenan, Paul A. Sprengeler, and Ralph Hirschmann*

Department of Chemistry, the Laboratory for Research on the Structure of Matter, and the Monell Chemical Senses Center, University of Pennsylvania, Philadelphia, Pennsylvania 19104, U. S. A.

A new two-step method employs the intramolecular cyclization of metalated imino esters for the construction of scalemic 3,5,5-trisubstituted pyrrolin-4-ones. The imino esters in turn derive from or-disubstituted amino acids, the latter readily available via a new protocol exploiting the enantioretentive alkylation of oxazolidinones.

THE REACTION OF MERCAPTANS WITH DIMETHYLDIOXIRANE. A FACILE SYNTHESIS OF ALKANESULFINIC ACIDS.

Tetrahedron Lett. 1993, 34, 67

Tetrahedron Lett. 1993, 34, 71

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

Dimethyldioxirane (DMD) oxidizes aliphatic thiols to sulfinic acids in very good yield. Benzylic and aromatic thiols give a variety of other oxidation products using DMD.

 $2 R-SH + DMD/O_2 ----> R-S-S-R$

AN ADDITION-ELIMINATION STRATEGY FOR THE

SYNTHESIS OF OXAZOLES

K. M. Short and C. B. Zingler, Ir.*

American Cyanamid Company
Medical Research Division,
Lederle Laboratories, Part River, NY 10965

N-acylpropargylamines have been regionalectively converted to (B)B-iodo(vinyl)sulfones which, in turn, were converted to 2,5-disubstituted oxenoles by been treatment

PhSO₂Na

I₂, EtOAc, RCONH

THF_R

SO₂Ph

SO₂Ph

SO₂Ph

300W/80°C

Tetrahedron Lett. 1993, 34, 75

THE SYNTHESIS OF ISOXAZOLES FROM β,γ-ACETYLENIC OXIMES

K. M. Short and C. B. Ziegler, Jr.* American Cyanamid Company Medical Research Division

 β , γ -Acetylenic enimes (prepared from α -bromooximes) undergo facile conversion to 3,5-disubstituted isoxazoles on mild base treatment.

NOVEL CYCLODEXTRIN-OLIGOSILOXANE COPOLYMERS AND THEIR USE AS STATIONARY PHASES FOR SEPARATING ENANTIOMERS IN OPEN TUBULAR COLUMN SUPERCRITICAL FLUID CHROMATOGRAPHY

Jerald S. Bradshaw, Guoliang Yi, Bryant B. Rossiter, Shawn Reese, Patrik Petersson, Karin R. Markides, and Milton L. Lee. Department of Chemistry, Brigham Young University, Prove UT 84602 U. S. A.

Department of Analytical Chemistry, Uppsala University, S-751 21 Uppsala, Sweden

Tetrahedron Lett. 1993, 34, 83

MB/III) PROMOTED N-O BOND REDUCTION OF N-HYDROXY-2-AZETIDINONES Arun Ghosh and Marvin J. Miller, Dept. of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556.

Treatment of various N-hydroxy-2-azetidinones with Mn(III) acetate unexpectedly afforded the corresponding reduced N-unsubstituted-2-azetidinones in the presence of hydrogen donor solvents.

Tetrahedron Lett. 1993, 34, 87

Metallic Base-Induced and Lewis Acid-Catalyzed Nitrone Cycloadditions to Allvl

Alcohol Dipolarophiles. Highly Effective Regio- and Stereocontrol

Shuji Kanemasa,* Takashi Tsuruoka, and Eiji Wada

Institute of Advanced Material Study, and Department of Molecular Scienece and Technology, Interdisciplinary Graduate School, Kyushu University, Kasugakoen, Kasuga 816, Japan

Tetrahedron Lett. 1993, 34, 91

HIGHLY REGIO-, (E)-STEREO-, AND DIASTEREOSELECTIVE S_2" ADDITION OF ORGANOCUPRATES TO CHIRAL ALLYLIC CYCLIC CARBONATES

Suk-Ku Kang,* Dong-Ha Lee, Hyeong-Su Sim, and Jong-Suk Lim

Department of Chemistry, Sung Kyun Kwan University

Natural Science Campus, Suwon 440-746, Korea

R1 = H. Me. Et P = Bn, t-BuPh2Si

SYNTHESES OF UNSYMMETRICALLY N,N'-BIS(SUBSTITUTED)-4,13-DIAZA-18-CROWN-6-ETHER DERIVATIVES

AS A NEW ELECTRON DONOR-SPACER-ACCEPTOR TRIAD

Minoru Morimoto, Keijiro Pukui, Norioki Kawasaki, Tomokazu Iyoda, and Takeo Shimidzu Division of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 606-01, Japan

A simple and general synthetic strategy of unsymmetrically N,N'-bis(substituted)-4,13-diaza-18-crown-6-ether derivatives was reported.

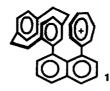
Tetrahedron Lett. 1993, 34, 99

Stabilization of the 1-Naphthyltropylium Ion by [2.2]Paracyclophane Fixed at the Face-to-Face Position to the Tropylium Ring.

Koichi Komatsu,* Ryotaro Tsuji, Yoichiro Inoue, and Ken'ichi Takeuchi

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

The cation 1 was synthesized and was found to be more stabilized than 2 by through-space π -electron donation from the stacked benzene rings.





Nucleosides and Nucleotides. 115. Synthesis of 3-alkyl-3-deazainosines via palladium-catalyzed intramolecular cyclization: A new conformational lock with the alkyl group at the 3-position of the 3-deazainosine in anti-conformation

Mitsutoshi Aoyagi, Noriaki Minakawa, and Akira Matsuda* Faculty of Pharmaceutical Sciences, Hokkaido University, Kita-12, Nishi-6, Kita-ku, Sapporo 060, Japan

Synthesis of the title compounds can be done by intramolecular cyclization of 4a,b with palladium catalysts. The glycosyl conformation of 7a,b was analyzed by NOE experiments.

Tetrahedron Lett. 1993, 34, 103

$$AcO OAc AcO OAc AcO OAc AcO OAc AcO OAc AcO OR 2 Aco OR$$

CATALYTIC ASYMMETRIC INDUCTION OF PLANAR CHIRALITY BY PALLADIUM CATALYZED ASYMMETRIC CROSS-COUPLING OF A MESO (ARENE)CHROMIUM COMPLEX

Tetrahedron Lett. 1993, 34, 107

Motokazu Uemura,* Hikaru Nishimura, Faculty of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558, Japan Tamio Hayashi,* Catalysis Research Center and Graduate School of Pharmaceutical Sciences, Hokkaido University, Sapporo, 060, Japan

Vinylic Metal (RM)

[PdCl(π -C₃H₅)]₂
Chiral Ligand (L*)
44% ee



a; R= CH=CH₂ b; R= CMe=CH₂ c; R= CH=CHBuⁿ

A Highly Stereoselective Synthetic Method for cis-2-Hydroxymethyl-6-alkyltetrahydropyrans

Tadakatsu Mandai*, Masayuki Ueda, Kaori Kashiwagi, Mikio Kawada, Jiro Tsuji Department of Applied Chemistry, Okayama University of Science, Ridai-cho, Okayama 700, Japan

A highly stereoselective synthetic method for cis-2-hydroxymethyl-6-alkyltetrahydropyrans by an intramolecular 1,4- addition of alcohol to α,β-unsaturated sulfoxide as a key reaction is described.

$$\bigcap_{R \to OH} \bigcap_{STol} \longrightarrow \bigcap_{R \to O} \bigcap_{STol} \longrightarrow \bigcap_{R \to O} \bigcap_{OH} \bigcap_{COOH} \bigcap_{STol} \bigcap_{S$$

Tetrahedron Lett. 1993, 34, 115

A Convenient Synthesis of 1,2-Dithietes and α-Dithiocarbonyl Compounds by Sulfuration of Acetylenic Compounds

Juzo Nakayama,* Keun Soo Choi, Isao Akiyama, and Masamatsu Hoshino

Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338, Japan

R¹=SPh, SePh, NEt₂; R²=NEt₂

 $R^1=t$ -Bu, 1-adamantyl, Ph $R^2=t$ -Bu, 1-adamantyl

Tetrahedron Lett. 1993, 34, 119

STABLE ENANTIOMERIC CONFORMATIONS OF 5-ACYL-2-OXO-2H-1,3,4,5-TETRAHYDROBENZODIAZEPINES

N. Kalyanam^{*, +}, P.S. Srinivasan⁺, S.G. Manjunatha[#] and P.R. Rajamohanan[#], ⁺R & D Centre, Pharma Division, SPIC Ltd., Maraimalai Nagar, Tamilnadu 603 209, INDIA and [#]National Q R³

Chemical L aboratory, Pune 411 009, INDIA The enantiomerization barriers of acylated benzodiazepinones are strongly dependent

upon the nature of ring substituents and R.

Tetrahedron Lett. 1993, 34, 123

C2-SYMMETRIC BIS-SULFOXIDES AS CHIRAL LIGANDS IN METAL CATALYSED ASYMMETRIC DIELS-ALDER REACTIONS.

Noureddine Khiar*, Inmaculada Fernández and Felipe Alcudia.

Dpto. de Química Orgánica y Farmacéutica, Facultad de Farmacia, Universidad de Sevilla, 41071 Seville (Spain)

POLYCYCLE CONSTRUCTION \emph{VIA} CASCADE RADICAL FRAGMENTATION-TRANSANNULATION-CYCLISATION PROCESSES

Charles E. Mowbray and Gerald Pattenden*

Department of Chemistry, The University, Nottingham, NG7 2RD

Treatment of the bicyclic dienol (8) with iodosylbenzene diacetate-iodine is shown to lead to the 7.5,5-tricycle (11, 81%) by way of a cascade radical fragmentation-transannulation-cyclisation sequence.

Tetrahedron Lett. 1993, 34, 131

A Route to Spiroketals using Radical Translocation

Christopher D. S. Brown and Nigel S. Simpkins*, Department of Chemistry
University of Nottingham, University Park, Nottingham NG7 2RD, UK
and Keith Clinch, ICI Agrochemicals, Jealott's Hill Research Station, Bracknell, Berkshire RG12 6EY, UK

Abstract: Reaction of β -iodoenones of general structure 4 with Bu₃SnH leads to formation of spiroketal products 5 via 1,5-translocation of the initially formed radical.

9-(SULFOXIMINOALKYL)GUANINE NUCLEOSIDES AS POTENTIAL ANTIHERPETIC AGENTS

Tetrahedron Lett. 1993, 34, 133

Roland E. Dolle* and David McNair

Department of Medicinal Chemistry, SmithKline Beecham Pharmaceuticals, The Frythe, Welwyn, Hertfordshire, U.K. Al6 9AR

A novel series of guanine nucleoside analogues which contain a C-terminal sulfoximine as a phosphate isoster have been synthesized for the first time.

$$\begin{array}{c} Ph & \bigcirc \\ N & N & N \\ H_2N & N & H \\ N & H & Me \\ n = 1-4 & Me \\ \end{array}$$

PERACID OXIDATION OF 1-OXA-8-AZABICYCLO [3,3,0] OCTANES: AN ENTRY TO THE cis-2,5-DISUBSTITUTED PYRROLIDINES.

Tetrahedron Lett. 1993, 34, 137

Sk. Asrof Ali* and Mohammed I. M. Wazeer Chemistry Dept., King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia.

Mechanism of peracid induced ring opening of nitrone cycloadduct (13) and its stereoselective conversion into trans-(14) and cis-amine (17).

SIMPLE AND EFFICIENT CONVERSION OF N,N-DIMETHYL-HYDRAZONES AND ALDEHYDES TO NITRILES

Rosario Fernández¹, Consolación Gasch¹, José-María Lassaletta¹, José-Manuel Llera² and Juan Vázquez^{1. 1}Departamento de Química Orgánica, ²Departamento de Química Orgánica y Farmacéutica. Universidad de Sevilla, Sevilla, Spain.

Aldehyde N,N-dimethylhydrazones are converted into nitriles in high yields on reaction with MMPP under very mild conditions. The reaction is chemoselective and proceeds without racemization. The 'one pot' reaction from aldehydes is described.

Tetrahedron Lett. 1993, 34, 145

FAILURE OF AMINOPHOSPHONATE SYNTHESIS DUE TO FACILE HYDROXYPHOSPHONATE - PHOSPHATE REARRANGEMENT.

Roman Gancarz, Irena Gancarz; Department of Chemistry, Technical University of Wroclaw, Wybrzeze Wyspianskiego 27, 50-370 WROCLAW, POLAND

Fast formation of hydroxyphosphonates, and their further rearrangement to phosphates, unables the formation of aminophosphonates.

TRIFLUOROMETHYLPHOSPHINYL BIS-TRIAZOLIDES IN THE SYNTHESIS OF TRIFLUOROMETHYLPHOSPHONATE ANALOGUES OF NUCLEOTIDES

Tetrahedron Lett. 1993, 34, 149

Tetrahedron Lett. 1993, 34, 153

PALLADIUM CATALYSED CASCADE CYCLOADDITION

REACTIONS. GENERAL CONCEPTS AND ILLUSTRATIVE EXAMPLES.

- R. Grigg, *, * P. Kennewell, * A. Teasdale * and V. Sridharan*.
- a. School of Chemistry, Leeds University, Leeds LS2 9JT.
- b. Roussel Scientific Institue, Kingfisher Drive, Swindon SN3 5BZ.

A general palladium catalysed cycloaddition strategy is proposed and illustrated by several different protocols for 5- and 6- membered ring formation.

PALLADIUM CATALYSED [2+2+2] - CYCLOADDITION REACTIONS VIA CARBOPALLADATION OF 1.6-ENYNES.

S. Brown^a, S. Clarkson^b, R. Grigg^b and V. Sridharan^b, ICI PCMO, Leeds Road, Huddersfield HD2 1FF.

b) School of Chemistry, Leeds University, Leeds LS2 9JT.

1,6 - Enynes react with aryl and heteroaryl halides via a [2+2+2]- cycloaddition process in moderate to good yield.

Z = CH or N

Tetrahedron Lett. 1993, 34, 161

DIELS-ALDER REACTIONS ON 5-ACETYL-2-METHYL-4-NITRO-6-PHENYL PYRIDAZIN-3(24)-ONE: A NEW FACET OF THE PYRIDAZINE SYSTEM

Vittorio Dal Piaz, *a Maria P. Giovannoni, a Giovanna Ciciani, a Donatella Giomi, b Rodolfo Nesib

a) Dipartimento di Scienze Farmaceutiche dell'Università, Via Gino Capponi 9, I-50121 Firenze, Italy; b) Dipartimento di Chimica Organica 'Ugo Schiff' dell'Università - Centro di Studio del C.N.R. sulla Chimica e la Struttura dei Composti Eterociclici e loro applicazioni, Via Gino Capponi 9, I-50121 Firenze, Italy

Treatment of the nitropyridazinone 2 with 2,3-dimethylbuta-1,3-diene gave the phthalazine derivative 3 through a [2+4] cycloaddition process.

FILLED-ORBITAL REPULSION; A NEW FACTOR IN π -FACIAL SELECTIVITY OF DIELS-ALDER REACTIONS.

James M. Coxon,* Siew Tai Fong, D. Quentin McDonald, and Peter J. Steel*
Department of Chemistry, University of Canterbury, Christchurch, New Zealand.

Dimethyl acetylenedicarboxylate and N-phenyl-1,2,4-triazolinedione unlike alkene dienophiles add to ether 1 from the more sterically congested face of the diene syn to the cyclobutane ring. The interaction of the ether oxygen lone pair with the dienophile

acetylenic π -orbital or azo n-orbitals orthogonal to the forming σ -bonds is important in determining the observed facial selection.

el*

Tetrahedron Lett. 1993, 34, 163

Tetrahedron Lett. 1993, 34, 167

A NOVEL APPLICATION OF THE DESS-MARTIN REAGENT TO THE SYNTHESIS OF AN FK 506 ANALOGUE AND OTHER TRICARBONYL COMPOUNDS.

R. J. Gillespie, J. M. C. Golec,* M. J. Batchelor and C. J. R. Hedgecock.

Roussel Laboratories Ltd., Kingfisher Drive, Covingham, Swindon, SN3 5BZ, England.

An Unusual Anti-Markovnikov Hydration of Alkenes with Titanium(III) tetrahydroborates

K.S. Ravikumar^{a,b}, S. Baskaran^a, and S.Chandrasekaran^{a,‡}

- a. Department of Organic Chemistry, Indian Institute of Science, Bangalore-560 012, INDIA
- b. IDL-Nitro Nobel Basic Research Institute, Sankey Road, Malleswaram Bangalore-560 003. INDIA

ELECTROCHEMICAL CYCLIZATION OF 0-TRICHLOROACETYL-ANILIDES: PREPARATION OF 4H-3,1-BENZOXAZIN-4-ONES AND

3,3-33CCR2-OROQUINOLIN-4-ONES.
Pedro Molina, Carlota Conesa and María D. Velasco

Departamento de Química Orgánica, Universidad de Murcia, Campus de Espinardo, E-30071, Murcia, Spain,

Two-electrons electrochemical reduction of compounds type 1 leads to 434-5.1 benzoxazines 2 or 4-principones 3 respectively.

ALLYLIC ALCOHOLS AS SUBSTRATES FOR THE Pd(0)-CATALYZED ALLYLIC SUBSTITUTION

Tetrahedron Lett. 1993, 34, 179

Tetrahedron Lett. 1993, 34, 175

I. Starý, ** I. G. Stara, and P. Kočovský **,b

^ainstitute of Org. Chem. & Biochem, ČSAV, 16610 Prague 6, Czechoslovakia ^bDepartment of Chemistry, University of Leicester, Leicester LE1 7RH, UK

While allytic esters have frequently been used as substrates for the Pd(0)-catalyzed allytic substitution, the parent alcohols are much less reactive. We have now developed a new method which allows the substitution to occur between the alcohols

are much less reactive. We have now developed a new method which allows the substitution to occur between the alcohols and C-nucleophiles: on reaction with Ph_3B , the allylic alkoxide 1 is believed to be first converted in situ into the more reactive species 2 which then undergoes a Pd(0)-catalyzed reaction with $LiCH(CO_2Et)_2$ via the $(\pi$ -allyl)-Pd-complex 3.

$$\begin{array}{c|c}
 & & & & & & & & & & & & \\
\hline
 & & & & & & & & & & \\
\hline
 & & & & & & & & & \\
\hline
 & & & & & & & & \\
\hline
 & & & & & & & \\
\hline
 & & & & & & & \\
\hline
 & & & & & \\
\hline
 & & & &$$