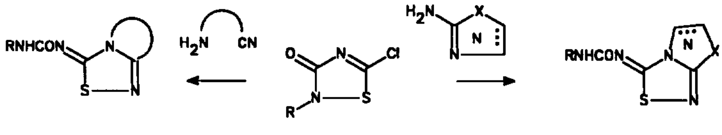
GRAPHICAL ABSTRACTS

SYNTHESIS OF FUSED 1,2,4-THIADIAZOLES FROM 5-CHLORO-1,2,4-THIADIAZOL-3(2H)-ONES

Tetrahedron, **1994**, *50*, 7019

G. L'abbé[a], J. Buelens[a], W. Dehaen[a] and S. Toppet[a], J. Feneau-Dupont[b] and J.P.-Declercq[b]
[a]Department of Chemistry, University of Leuven, Celestijnenlaan 200 F, 3001 Leuven (Heverlee), Belgium. [b]Laboratoire de Chimie Physique et de Cristallographie, Université Catholique de Louvain, Pasteur 1, 1348 Louvain-La-Neuve, Belgique.

Fused 1,2,4-thiadiazoles are readily obtained from 5-chloro-1,2,4-thiadiazol-3-ones by two synthetic routes.

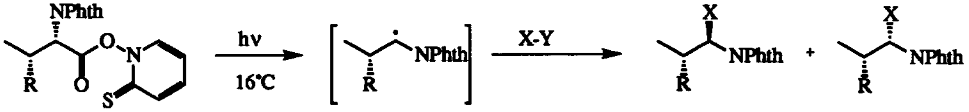


STEREOSELECTIVE REACTIONS OF α-IMIDE SUBSTITUTED RADICALS

Tetrahedron, **1994**, *50*, 7029

Wolfgang Damm, Ursula Hoffmann, Ludwig Macko, Markus Neuburger, Margareta Zehnder and Bernd Giese*
Department of Chemistry, University of Basel, St. Johanns Ring 19, CH-4056 Basel, Switzerland

Chiral α-imide substituted radicals, generated from the corresponding Barton esters, react stereoselectively with different traps.

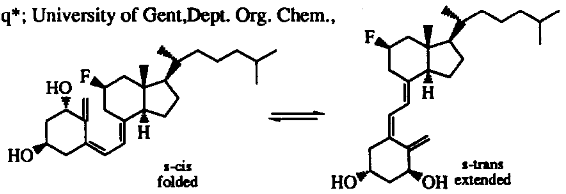


11-FLUORO-1α-HYDROXYVITAMIN D$_3$: THE QUEST FOR EXPERIMENTAL EVIDENCE OF THE FOLDED VITAMIN D CONFORMATION

Tetrahedron, **1994**, *50*, 7049

G.-D. Zhu, D. Van Haver, H. Jurriaans and P.J. De Clercq*; University of Gent,Dept. Org. Chem., Krijgslaan, 281 (S4), B-9000 GENT (Belgium)

MM calculations indicate the folded conformation of 11β-F-1α-OH Vit D$_3$ to be preferred due to intramolecular hydrogen bonding. This could not be confirmed by ^{1}H NMR in solution.

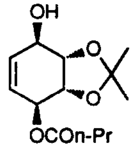


CYCLOHEXANE POLYOLS : ENANTIOSELECTIVE SYNTHESIS OF (+)-FORTAMINE AND OF PSEUDO-SUGARS

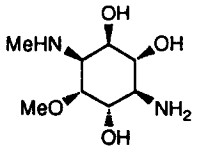
Tetrahedron, **1994**, *50*, 7061

Pingli Liu and M. Vandewalle*
University of Gent, Dept. Org. Chem., Krijgslaan, 281 (S4), B-9000 GENT (Belgium)

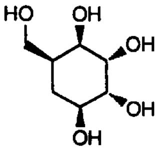
Applications of the homochiral building block (+)-1 are described



(+)-1



(+)-fortamine **10**

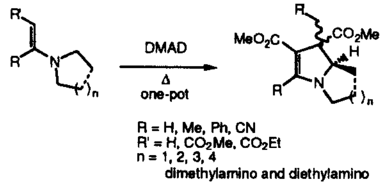


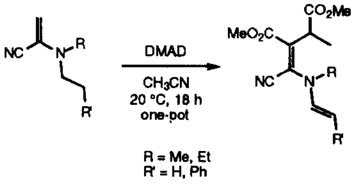
5a-carba-β-L-gulopyranose **35**

α-CYCLIZATION OF TERTIARY AMINES. PART 3 CAPTODATIVE OR PUSH-PULL ENAMINES FORM PYRROLINES, PYRROLIZIDINES AND THEIR RING HOMOLOGUES WITH DIMETHYL ACETYLENEDICARBOXYLATE IN A HIGHLY DIASTEREOSELECTIVE REACTION

Tetrahedron, **1994**, *50*, 7075

Benoît De Boeck, Shuiping Jiang, Zdenek Janousek and Heinz G. Viehe*
Laboratoire de Chimie Organique, Université Catholique de Louvain, Place L. Pasteur, 1, B-1348 Louvain-la-Neuve, Belgium

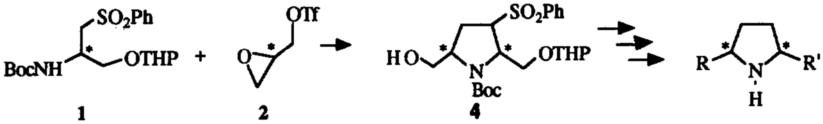




A NOVEL METHOD FOR CHIROSPECIFIC SYNTHESIS OF 2,5-DISUBSTITUTED PYRROLIDINES

Tetrahedron, **1994**, *50*, 7093

N. André Sasaki* and Isabelle Sagnard
Institut de Chimie des Substances Naturelles, CNRS, Avenue de la Terrasse, 91198 Gif-sur-Yvette Cedex France



1 **2** **4**

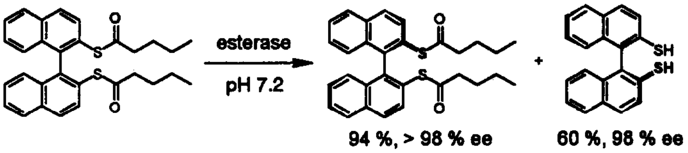
A 2,5-disubstituted pyrrolidine of any desired stereochemistry at C-2 and C-5 can be prepared *via* a pivotal intermediate 4 formed by one-pot cyclization reaction of homochiral nucleophile 1 and electrophile 2.

RESOLUTION OF (1,1'-BINAPHTHALENE)-2,2'-DITHIOL BY ENZYME CATALYSED HYDROLYSIS OF A RACEMIC DIACYL DERIVATIVE

Tetrahedron, **1994**, *50*, 7109

Matthias Kiefer, Rainer Vogel and Günter Helmchen*, Organisch-Chemisches Institut der Universität,
Bernhard Nuber, Anorganisch-Chemisches Institut, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany.

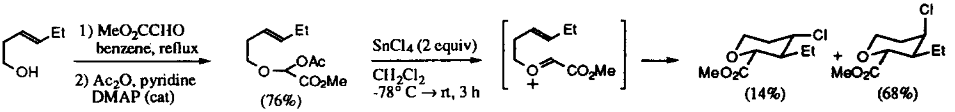
Both enantiomers of (1,1'-binaphthalene)-2,2'-dithiol can be obtained with 98 % ee by enzymatic resolution of the corresponding *S,S'*-dipentanoate. Absolute configuration was determined by crystal structure of a diastereomeric derivative.



π-CYCLIZATIONS OF α-METHOXYCARBONYL OXYCARBENIUM IONS; SYNTHESIS OF OXACYCLIC CARBOXYLIC ESTERS

Tetrahedron, **1994**, *50*, 7115

Lucie D. M. Lolkema, Henk Hiemstra*, Cindy Semcyn and W. Nico Speckamp*
Laboratory of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

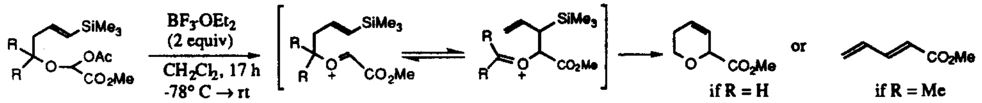


Eleven examples are described of the π-cyclization process of an α-ester oxycarbenium ion intermediate onto an olefin or an acetylene. The stereochemistry of the major product in many cases suggests participation of a pseudo axial ester function in the mechanism of cyclization and the occurrence of a 2-oxonia-Cope rearrangement.

Tetrahedron, **1994**, *50*, 7129

STUDIES ON THE ROLE OF THE 2-OXONIA COPE REARRANGEMENT IN π-CYCLIZATIONS OF α-METHOXYCARBONYL OXYCARBENIUM IONS

Lucie D. M. Lolkema, Cindy Semeyn, Loulou Ashek, Henk Hiemstra* and W. Nico Speckamp*
Laboratory of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

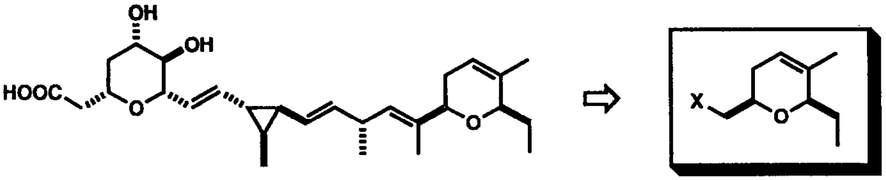


The 2-oxonia-Cope rearrangement plays an important role in the Lewis acid-induced π-cyclization process of α-ester oxycarbenium ion intermediates. The absolute stereochemistry is retained in the cyclization of enantiopure substrates.

Tetrahedron, **1994**, *50*, 7141

THE INTRAMOLECULAR SILYL-MODIFIED SAKURAI (ISMS) REACTION. SYNTHETIC STUDIES TOWARDS AMBRUTICINE

István E Markó* and Daniel J Bayston
Université Catholique de Louvain, Louvain-La-Neuve, Belgium

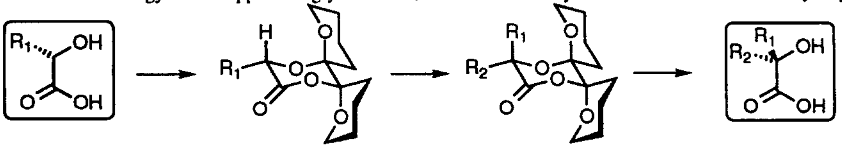


Tetrahedron, **1994**, *50*, 7157

DISPIROKETALS IN SYNTHESIS (PART 10): FURTHER REACTIONS OF DISPOKE PROTECTED LACTATE AND GLYCOLATE ENOLATES.

Geert-Jan Boons, Robert Downham, Kun Soo Kim, Steven V. Ley* and Martin Woods. Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK.

α-Hydroxy acids have been protected as dispiroketals. Subsequent alkylation and deprotection gives disubstituted compounds with high *ee*. This methodology can be applied to glycolic acid, where the chirality is introduced *via* the bis-dihydropyran used.

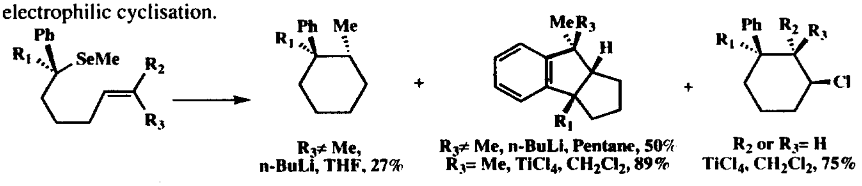


Tetrahedron, **1994**, *50*, 7177

Synthesis of Arylcycloalkanes from ω-Alkenyl Benzylselenides

Alain Krief *,+, Benoit Kenda,+ Phillipe Barbeaux+ and Eric Guittet°
+Departement of Chemistry, Facultés Universitaires Notre-Dame de la Paix, 61 rue de Bruxelles, B-5000, Namur (Belgium). ° Institut des Substances Naturelles, avenue de la terrasse, 91190, Gif-sur-Yvette, France.

Arylcycloalkanes are produced from ω-alkenyl benzylselenides on reaction with alkyllithiums or on Lewis acid mediated electrophilic cyclisation.

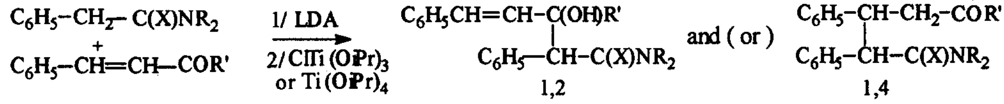


Tetrahedron, **1994**, *50*, 7193

TITANIUM ENOLATES AND 'ATE' COMPLEXES OF N,N-DISUBSTITUTED AMIDES AND THIOAMIDES IN THE MICHAEL REACTION.

Lilia Z. Viteva, Tzveta S. Gospodova and Yuri N. Stefanovsky*
Institute of Organic Chemistry with Centre of Phytochemistry,
Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

Titanium enolates and "ate" complexes of N,N-disubstituted amides and thioamides are investigated in reaction with α,β-unsaturated carbonyl compounds. Probable transition structures for the conjugate addition are discussed.



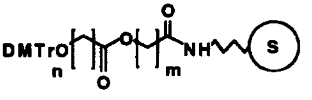
$$\begin{array}{c} C_6H_5-CH_2-C(X)NR_2 \\ + \\ C_6H_5-CH=CH-COR' \end{array} \xrightarrow[\begin{array}{c}2/ClTi(OPr)_3 \\ \text{or } Ti(OPr)_4\end{array}]{1/\ LDA} \begin{array}{c} C_6H_5CH=CH-C(OH)R' \\ | \\ C_6H_5-CH-C(X)NR_2 \\ 1,2 \end{array} \text{ and (or) } \begin{array}{c} C_6H_5-CH-CH_2-COR' \\ | \\ C_6H_5-CH-C(X)NR_2 \\ 1,4 \end{array}$$

Tetrahedron, **1994**, *50*, 7203

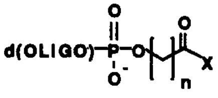
Novel Solid Supports for the Preparation of 3′-Derivatized Oligonucleotides: Introduction of 3′-Alkylphosphate Tether Groups Bearing Amino, Carboxy, Carboxamido, and Mercapto Functionalities.

Jari Hovinen, Andrei Guzaev,* Alex Azhayev, and Harri Lönnberg; Dep. of Chemistry, Univ. of Turku, FIN-20500 Turku, Finland

Synthesis of non-nucleosidic solid supports with a general structure of 1 is described. They have been used in the preparation of oligonucleotides 2 bearing various functionalities at their 3′-terminus.



1



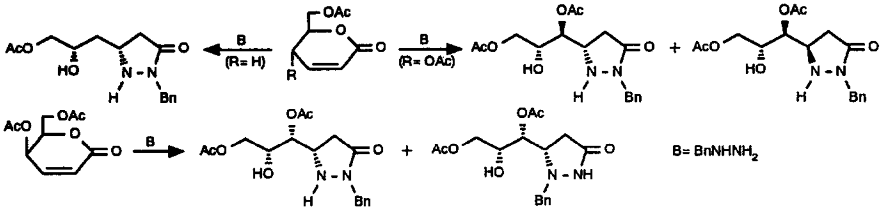
2

1,2: m,n = 1,3; **2**: X = OH, NH_2, $NH(CH_2)_2NH_2$, $NH(CH_2)_3NH_2$, $NH(CH_2)_4NH_2$, $NH(CH_2)_2SR$; R = $S(CH_2)_2NH_2$, H, SPy.

Tetrahedron, **1994**, *50*, 7219

ADDITION OF N-BENZYLHYDRAZINE TO SUGAR δ-ENLACTONES

I. Panfil, J. Krajewski, P. Głuziński, L. Stefaniak, M. Chmielewski
Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland



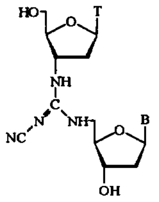
Tetrahedron, **1994**, *50*, 7231

SYNTHESIS, ENZYMATIC STABILITY AND PHYSICOCHEMICAL PROPERTIES OF OLIGONUCLEOTIDES CONTAINING A N-CYANOGUANIDINE LINKAGE

C. Pannecouque, F. Vandendriessche, J. Rozenski, G. Janssen, R. Busson, A. Van Aerschot, P. Claes and P. Herdewijn

Laboratory of Medicinal Chemistry (F.F.W.), Rega Institute for Medical Research, Katholieke Universiteit Leuven, Minderbroedersstraat 10, B-3300 Leuven, Belgium

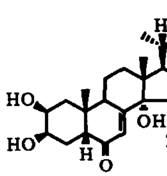
Nucleoside dimers with a N-cyanoguanidine linkage were synthesized and used as building blocks for oligonucleotide synthesis. Oligonucleotides composed of alternating phosphodiester and cyanoguanidine functions are still able to hybridize with a complementary natural oligodeoxynucleotide.

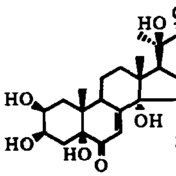


Tetrahedron, **1994**, *50*, 7247

NEW ECDYSTEROIDS FROM *Polypodium vulgare*

Josep Coll, Natàlia Reixach, Francisco Sánchez-Baeza, Josefina Casas and Francisco Camps*
Dpt. of Biological Organic Chemistry, CID (CSIC). J. Girona, 18. 08034 Barcelona, Spain.


24-Hydroxyecdysone

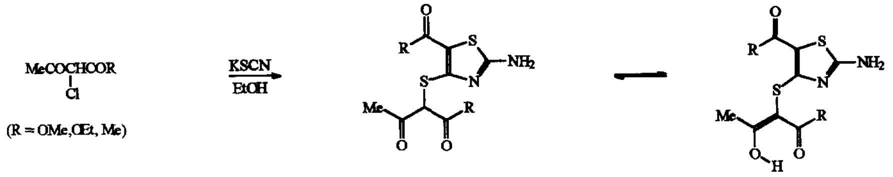

5-Hydroxyabutasterone

Tetrahedron, **1994**, *50*, 7253

PSEUDOHALOGEN CHEMISTRY. XI. SOME ASPECTS OF THE CHEMISTRY OF α-THIOCYANATO-β-DICARBONYL COMPOUNDS

Elaine F. Atkins, Steven Dabbs, Robert G. Guy, Akbar A. Mahomed and Philip Mountford
School of Natural Sciences, The University of Hertfordshire, Hatfield, Hertfordshire, AL10 9AB, England, UK

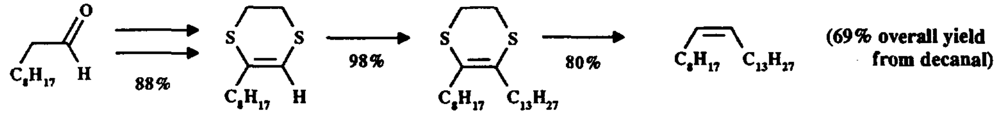
Enolised α-thiocyanato-β-dicarbonyl compounds dimerise in ethanol giving enolised 2-aminothiazoles as the main products.



Tetrahedron, **1994**, *50*, 7265

Diastereoselective Desulfurization of 5,6-Dihydro-1,4-dithiins. Synthesis of Muscalure from *Musca domestica* L.

Romualdo Caputo, Giovanni Palumbo,* Silvana Pedatella
Dipartimento di Chimica Organica e Biologica dell'Università
Via Mezzocannone, 16 I-80134 Napoli (Italy)



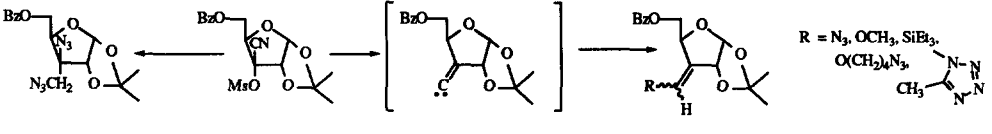
The pheromone muscalure was synthesized to provide an example of the 5,6-dihydro-1,4-dithiin approach to the stereoselective synthesis of *cis* configurated olefins.

Tetrahedron, **1994**, *50*, 7269

ALKYLIDENE CARBENES AS INTERMEDIATES IN THE SYNTHESIS OF HIGHLY FUNCTIONALIZED BRANCHED-CHAIN SUGARS AND NUCLEOSIDES.

María-Jesús Pérez-Pérez and María-José Camarasa
Instituto de Química Médica (C.S.I.C.), Juan de la Cierva 3, 28006-Madrid, Spain

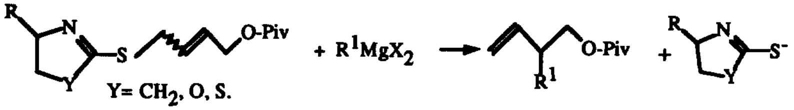
Reaction of cyanomesylates of furanos-3-uloses with NaN3 has lead to a variety of branched-chain sugars and nucleosides through a mechanism involving an alkylidene carbene.



Tetrahedron, **1994**, *50*, 7283

Chelation-Controlled Chemo-, Regio- and Enantio-Selective Synthesis of Homoallylic Alcohols

Vincenzo Caló[a],* Vito Fiandanese[a], Angelo Nacci[a] and Antonio Scilimati[b], [a]CNR Centro di Studio sulle Metodologie Innovative di Sintesi Organiche, Dipartimento di Chimica, [b]Dipartimento Farmacochimico,Università di Bari, via Orabona 4-70125 Bari (Italy)



Very high chemo-, regio- and enantio-control is obtained in the reactions of optically active substrates **11-13** with organocopper reagents. This is due to the chelation by the heterocyclic azomethine group towards the organometal.

Tetrahedron, **1994**, *50*, 7293

COMBINATION OF ^{17}O AND ^{13}C NMR SPECTRA OF ISOMERIC ALLYL AND (*Z*)-PROPENYL ETHERS WITH THEIR RELATIVE THERMODYNAMIC STABILITIES

Esko Taskinen, Department of Chemistry, University of Turku, FIN-20500 Turku, Finland

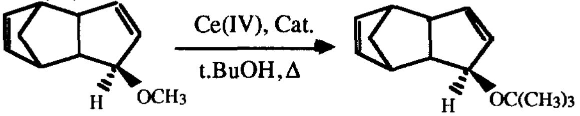
The values of $\Delta G^{\ominus}$ for the reaction $ROCH_2CH{=}CH_2 \rightarrow$ (*Z*)-ROCH=CHMe are discussed with relation to the ^{17}O and ^{13}C NMR shifts of these compounds, with emphasis on p-π conjugation.

Tetrahedron, **1994**, *50*, 7299

CATALYTIC AND EFFICIENT CLEAVAGE OF ALLYLIC AND TERTIARY BENZYLIC ETHERS AND ESTERS WITH Ce(IV).

N. Iranpoor, E. Mottaghinejad
Department of Chemistry , Shiraz University, Shiraz, 71454 Shiraz

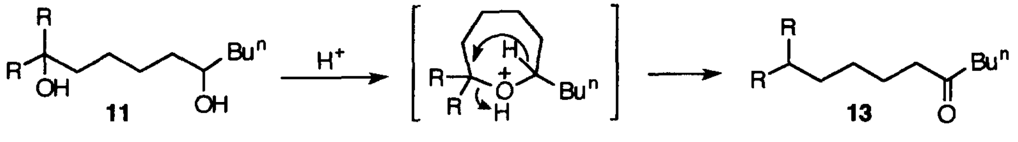
A catalytic method is described for the efficient alcoholysis and acetolysis of allylic and tertiary benzylic ethers and esters with Ce(IV) as ceric ammonium nitrate.



Tetrahedron, **1994**, *50*, 7307

INTRAMOLECULAR 1,6-HYDRIDE TRANSFER IN ACYCLIC 1,6-DIOLS: A MECHANISTIC STUDY

J. F. Gil, D. J. Ramón and M. Yus*
Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain



Tetrahedron, **1994**, *50*, 7315

Mononuclear Heterocyclic Rearrangements. Effect of the Structure of the Side Chain on the Reactivity. Part 3. Rearrangement of Some *N*-(5-phenyl-1,2,4-oxadiazol-3-yl)-*N'*-arylformamidines into 1-Aryl-3-benzoylamino-1,2,4-triazoles in Acetonitrile in the Presence of Triethylamine

Vincenzo Frenna, Gabriella Macaluso and Nicolò Vivona
Dipartimento di Chimica Organica, Via Archirafi 20, Palermo, I-90123, Italy
Domenico Spinelli, Giovanni Consiglio and Elisabetta Mezzina
Dipartimento di Chimica Organica 'A. Mangini', Via S. Donato 15, Bologna, I-40127, Italy

The kinetic study of the title reaction at variable triethylamine (TEA) concentration has provided evidence for the occurrence of two different reaction pathways (the one [TEA]-independent, the other [TEA]-dependent) according to the equation:

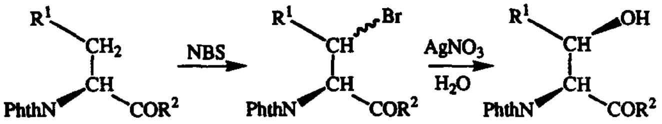
$$k_A = (k_u + K_1 k_2\ [\mathrm{TEA}])/(1 + K_1\ [\mathrm{TEA}]).$$

Tetrahedron, **1994**, *50*, 7327

STEREOCONTROLLED SYNTHESIS OF β-HYDROXYPHENYLALANINE AND β-HYDROXYTYROSINE DERIVATIVES

Christopher J. Easton,* Craig A. Hutton, Peter D. Roselt and Edward R. T. Tiekink
Department of Chemistry, University of Adelaide, Adelaide, South Australia 5005, Australia

Elaboration of (*S*)-amino acid derivatives affords (2*S*,3*R*)-β-hydroxy-α-amino acids, enantiospecifically and diastereoselectively. *tert*-Butyl esters display greater diastereoselectivity than the corresponding methyl esters, while *N*-*tert*-butylamides react diastereospecifically.



R^1 = Ph or *p*-AcOPh; R^2 = OMe, OCMe$_3$ or NHCMe$_3$