

## GRAPHICAL ABSTRACTS

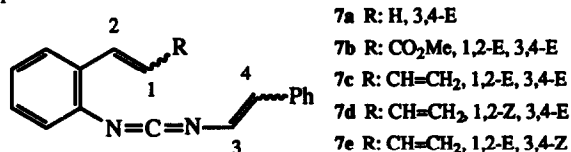
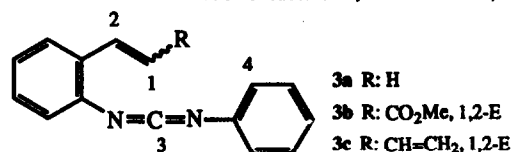
*Tetrahedron*, 1992, 48, 7425

### An AM1 And PM3 Molecular Orbital Study Of The Pericyclic Reactivity Of Aryl Carbodi-Imides.

Henry S. Rzepa,<sup>a\*</sup> Pedro Molina,<sup>b</sup> Mateo Alajarin<sup>b</sup> and Angel Vidal<sup>b</sup>

<sup>a</sup>Department of Chemistry, Imperial College of Science Technology and Medicine, London, SW7 2AY. <sup>b</sup>Departamento de Química Organica, Facultad de Ciencias, Universidad de Murcia, Campus de Espinardo, 30071-Murcia, Spain.

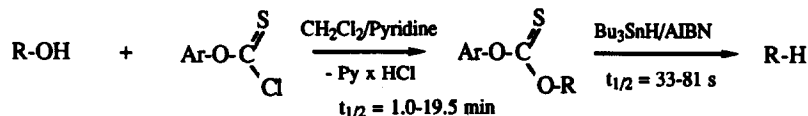
AM1 and PM3 SCF-MO calculated transition states for electrocyclisation and cycloadditions of a variety of carbodiimide intermediates (3 or 7) in the Aza-Wittig reaction between iminophosphoranes and isocyanates (2 or 6) reveal that the observed specificity of these reactions is due to a subtle combination of substituent, stereoelectronic, entropic and steric factors.



### THE INVENTION OF RADICAL REACTIONS. PART XXIV. RELATIVE RATES OF ACYLATION AND RADICAL DEOXYGENATION OF SECONDARY ALCOHOLS.

Derek H. R. Barton\*, Joseph Dorchak and Joseph Cs. Jaszberenyi  
Department of Chemistry, Texas A&M University, College Station, Texas, 77843

Secondary alcohols were transformed into various thionocarbonates with aryl chlorothionoformates and deoxygenated to the corresponding hydrocarbons. Half-life and competitive measurements revealed that both steps were fast.

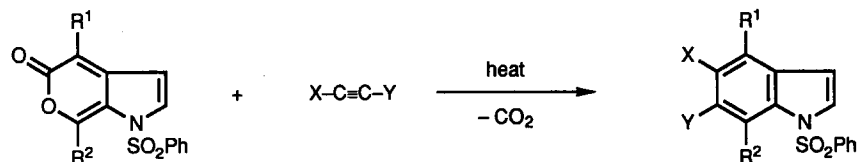


*Tetrahedron*, 1992, 48, 7435

### Diels-Alder Reactions of 1,5-Dihydropyrano[3,4-b]pyrrol-5(1H)-ones, Pyrrole-2,3-quinodimethane Analogues; a New Synthesis of Indoles

P. Mark Jackson and Christopher J. Moody

Department of Chemistry, Loughborough University of Technology, Loughborough, Leics. LE11 3TU, U.K.



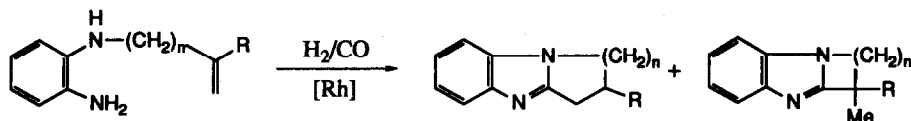
*Tetrahedron*, 1992, 48, 7447

A new route to indoles involving the Diels-Alder reaction of 1,5-dihydropyrano[3,4-b]pyrrol-5-ones with alkynes is described.

*Tetrahedron*, 1992, 48, 7467

**SYNTHESIS OF BENZIMIDAZOLES CONTAINING A FUSED  
ALICYCLIC RING BY RHODIUM CATALYSED HYDROFORMYLATION  
OF N-ALKENYL-1,2-DIAMINOENZES**

**Despina Anastasiou, Eva M. Campi, Hassan Chaouk and W. Roy Jackson\***  
*Department of Chemistry, Monash University, Clayton, Vic., Australia 3168*



*Tetrahedron*, 1992, 48, 7479

**A NEW METHOD FOR BROMINATION OF CARBAZOLES,  $\beta$ -CARBOLINES AND IMINODIBENZYL  
BY USE OF N-BROMOSUCCINIMIDE AND SILICA GEL**

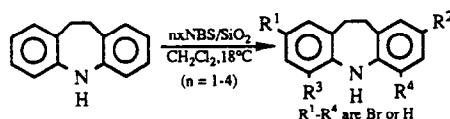
Keith Smith<sup>a</sup>, D.Martin James<sup>a</sup>, Anil G.Mistry<sup>a</sup>, Martin R.Bye<sup>b</sup> and D.John Faulkner<sup>c</sup>.

<sup>a</sup>Department of Chemistry, University College of Swansea, Swansea SA2 8PP, UK

<sup>b</sup>Amersham International plc, Cardiff Laboratories, Forest Farm, Whitchurch, Cardiff CF4 7YT, UK

<sup>c</sup>Scripps Institution of Oceanography, University of California at San Diego, La Jolla, CA92093-0212, USA

N-Bromosuccinimide in conjunction with an acidic silica is a useful reagent for bromination of the title heterocyclic systems. Sometimes the reactions are also highly selective.



*Tetrahedron*, 1992, 48, 7489

**NMR SPECTRA OF THE PORPHYRINS PART 41.**

**A MOLECULAR MECHANICS AND NMR INVESTIGATION OF  
STERIC EFFECTS IN LIGAND COMPLEXES**

**Raymond J. Abraham and Ian Marsden**

The geometries of the cobalt (III) porphyrin complexes of amines with the sterically hindered porphyrins were investigated by MM and NMR.

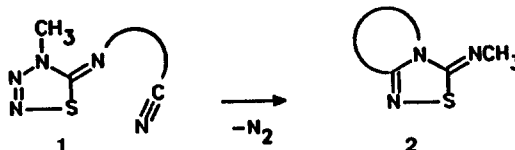
*Tetrahedron*, 1992, 48, 7505

# Synthesis of Fused 1,2,4-Thiadiazolines by Intramolecular Cycloaddition-Elimination Reactions of 4-Methyl-5-(cyano tethered)imino- $\Delta^2$ -1,2,3,4-thiadiazolines

Gerrit L'abbé and Stefan Leurs,

Department of Chemistry, University of Leuven,  
Celestijnenlaan 200F, 3001 Leuven (Heverlee), Belgium

Fused 1,2,4-thiadiazole derivatives **2** are obtained by thermolysis of 5-(cyano tethered)iminothiadiazolines **1** which react as masked 1,3-dipoles



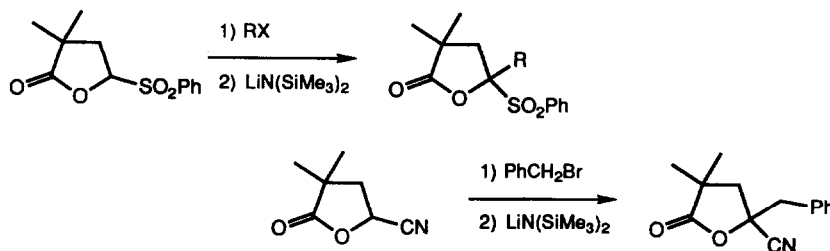
*Tetrahedron*, 1992, 48, 7519

# ALKYLATION AND ACYLATION OF 5-PHENYLSULFONYL-AND 5-CYANOBUTYROLACTONES

Jason Micklefield<sup>a</sup>, Michael H. Block<sup>b</sup> and Alan R. Battersby<sup>a\*</sup>

<sup>a</sup>University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, UK.

<sup>b</sup>ICI Pharmaceuticals Division, Mereside, Alderley Park, Macclesfield, Cheshire, SK10 4TG.

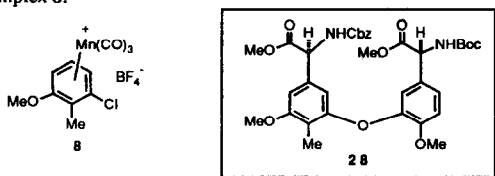


*Tetrahedron*, 1992, 48, 7527

# STUDIES ON RISTOCETIN A. A SYNTHESIS OF PROTECTED RISTOMYCINIC ACID USING ORGANOMANGANESE CHEMISTRY.

Anthony J. Pearson and Hunwoo Shin, Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, USA.

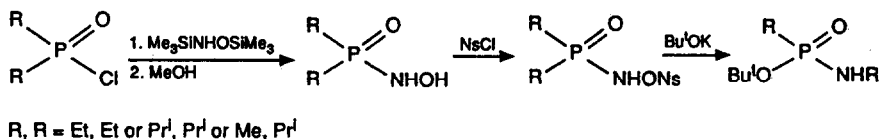
A synthesis of the protected ristomycinic acid derivative **28** was accomplished via consecutive nucleophilic addition reactions with the arene manganese complex **8**.



*Tetrahedron*, 1992, 48, 7539

***N*-(Dialkylphosphinoyl)hydroxylamines : Preparation using *N,O*-Bis-(trimethylsilyl)hydroxylamine and Migration of Simple Alkyl Groups in the Rearrangements of their *O*-*p*-Nitrobenzenesulphonates**

Martin J.P.Harger\* and P.Andrew Shimmin  
Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK



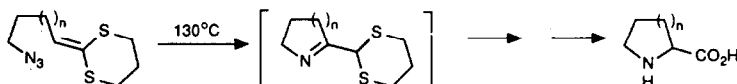
*Tetrahedron*, 1992, 48, 7551

**KETENE-S,S-ACETALS AS 1,3-DIPOLAROPHILES TOWARDS AZIDES. A NEW SYNTHETIC ENTRY INTO CYCLIC AMINO ACIDS.**

William O. Moss, Emma Wakefield, Mary F. Mahon, Kieran C. Molloy, Robert H. Bradbury, Neil J. Hales and Timothy Gallagher

School of Chemistry and X-Ray Crystallographic Unit, Bath University, Bath BA2 7AY and ICI Pharmaceuticals, Mereside, Alderley Park, Macclesfield SK10 4TG, U.K.

Intramolecular azide cycloaddition reactions of ketene-S,S-acetals can be utilised in the synthesis of 5- and 6-membered cyclic  $\alpha$ -amino acids ( $n=1,2$ ).

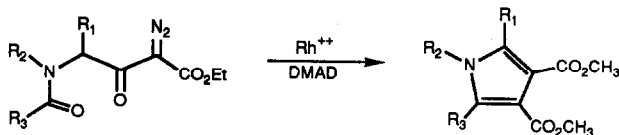


*Tetrahedron*, 1992, 48, 7565

**AZOMETHINE YLIDE GENERATION VIA THE DIPOLE CASCADE**

Albert Padwa\*, Dennis C. Dean, Donald L. Hertzog, William R. Nadler, and Lin Zhi  
Department of Chemistry, Emory University Atlanta, GA 30322 USA

A series of *N*-acyl 2-diazo-3-oxobutanoates, when treated with a catalytic quantity of a rhodium(II) carboxylate, were found to afford substituted pyrroles derived from an azomethine ylide intermediate.



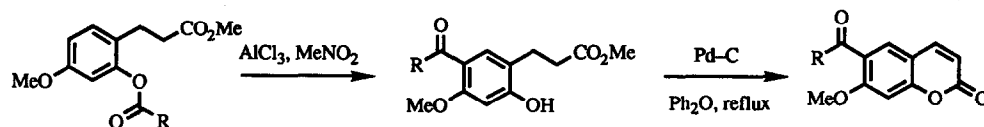
**SYNTHESES OF 6-ACYLCOUMARINS VIA HIGHLY REGIOSELECTIVE FRIES REARRANGEMENTS. TOTAL**

**SYNTHESES OF THE LINEAR ACYLATED COUMARINS GEIJERIN AND DEHYDROGEIJERIN.**

Nicholas Cairns,<sup>a</sup> Laurence. M. Harwood,<sup>a\*</sup> and David P. Astles<sup>b</sup>

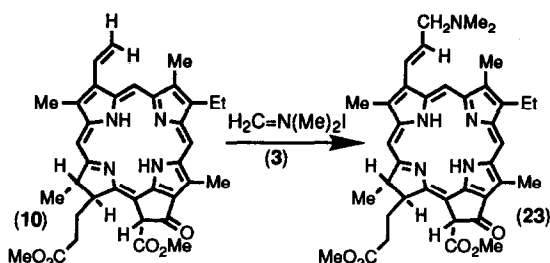
<sup>a</sup> Dyson Perrins Laboratory, University of Oxford, South Parks Road, OXFORD OX1 3QY, U.K.

<sup>b</sup> Shell, Sittingbourne Research Centre, SITTINGBOURNE ME9 8AG, U.K.



**SYNTHESES OF WATER-SOLUBLE CATIONIC PORPHYRINS AND CHLORINS. R.K. Pandey, F.-Y. Shiau, N.W. Smith, T.J. Dougherty and K.M. Smith,\*** Department of Chemistry, University of California, Davis, CA 95616, and Department of Radiation Medicine, Roswell Park Cancer Institute, Buffalo, NY 14263.

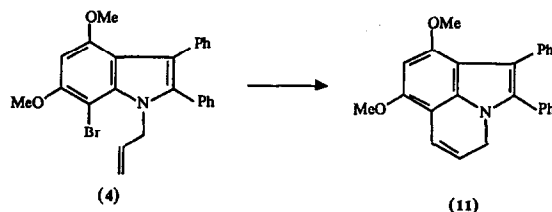
Treatment of vinylporphyrins and vinylchlorins with N,N-dimethylmethyleammonium iodide (3) gives trans-vinyl-substituted Mannich adducts (e.g. 23), and not meso-substituted products. Quaternization with MeI gives water-soluble cationic products.



**Palladium - catalysed Intramolecular Cyclisation of 7-Halo-N-allyl-indoles**

David St.C. Black, Paul A. Keller and Naresh Kumar, School of Chemistry, University of New South Wales, P. O. Box 1, Kensington, N.S.W., 2033, Australia.

N-Allyl-7-bromo-indoles undergo palladium-catalysed cyclisation to pyrroloquinoline derivatives, e.g. (4) to (11)



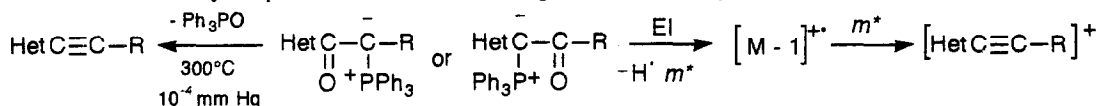
PHOSPHONIUM SALTS AND PHOSPHORANES. PART 5.<sup>1</sup>

## THERMAL AND ELECTRON-IMPACT INDUCED

## FRAGMENTATION OF HETEROAROYL METHYLENETRIPHENYLPHOSPHORANES.

Judith M. Brittain, R. Alan Jones,\* and (in part) Sayed Ali Naghi Taheri. School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, U.K.

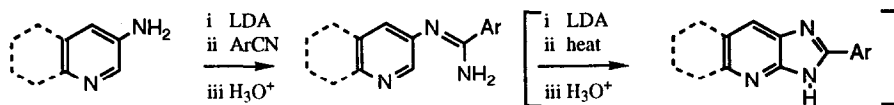
Thermal fragmentation of  $\pi$ -electron excessive heteroaroylmethylenephosphoranes at 300°C and  $10^{-4}$  mm Hg produce heteroarylethyne in good yield with the extrusion of triphenylphosphine oxide. Fragmentation of the phosphoranes under electron impact also yields the ions corresponding to the alkynes but *via* the initial extrusion of  $H^+$ , as confirmed by the presence of metastable ion signals in the mass spectra.



**SYNTHESIS OF AMIDINES AND ATTEMPTED  
SYNTHESIS OF IMIDAZOAZINES BY REACTION OF  
LITHIATED  $\beta$ -AMINOAZINES WITH NITRILES**

Alan D. Redhouse, Robin J. Thompson, Basil J. Wakefield\* and Jacklyn A. Wardell, Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, U.K.

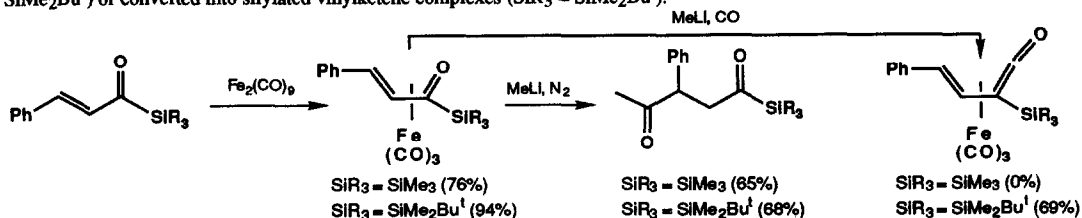
Amidines are prepared by deprotonation of  $\beta$ -aminoazines, followed by reaction with aromatic nitriles. Subsequent cyclisation to imidazoazines was achieved in only a few cases, .

SYNTHESIS AND REACTIVITY OF IRON CARBONYL COMPLEXES OF  $\alpha,\beta$ -UNSATURATED ACYL SILANES

Susan E. Thomas, Gary J. Tustin and A. Ibbotson

Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY; ICI Fine Chemicals Manufacturing Organisation, Hexagon House, Blackley, Manchester M9 3DA.

$\alpha,\beta$ -Unsaturated acyl silanes ( $\text{PhCH}=\text{CHCOSiR}_3$ ) form stable tricarbonyliron(0) complexes which can be acylated ( $\text{SiR}_3 = \text{SiMe}_3$ ,  $\text{SiMe}_2\text{Bu}^t$ ) or converted into silylated vinylketene complexes ( $\text{SiR}_3 = \text{SiMe}_2\text{Bu}^t$ ).



*Tetrahedron*, 1992, 48, 7641

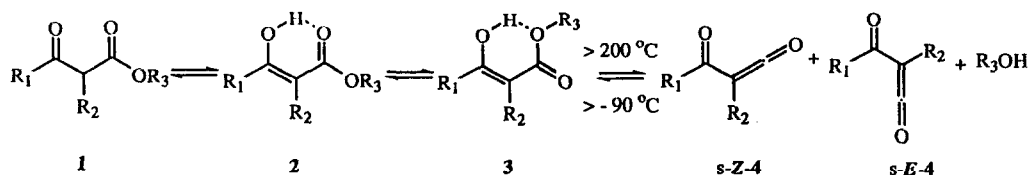
# Flash Vacuum Pyrolysis of *tert*-Butyl $\beta$ -Ketoesters:

## Sterically Protected $\alpha$ -Oxoketenes.

Regis Leung-Toung and Curt Wentrup\*

Department of Chemistry, The University of Queensland, Brisbane, Qld 4072, Australia

*tert*-Butylated ketenes (4;  $R_1$  and/or  $R_2 = t\text{-C}_4\text{H}_9$ ) and their reactions with methanol to enols have been investigated.

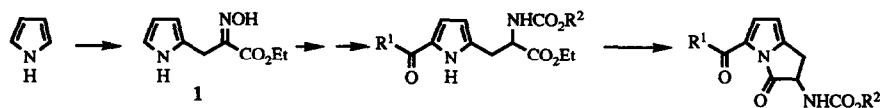


*Tetrahedron*, 1992, 48, 7655

# SYNTHESIS OF 2-ACYLAMINO-1,2-DIHYDROPYRROLIZIN-3-ONES FROM PYRROLE

Thomas L. Gilchrist and Américo Lemos, Chemistry Department, University of Liverpool, Liverpool L69 3BX

The synthesis of the title compounds is described by way of the oxime 1; the X-ray crystal structure of the pyrrolizinone with  $R^1 = \text{CF}_3$ ,  $R^2 = \text{CH}_2\text{Ph}$  is reported.



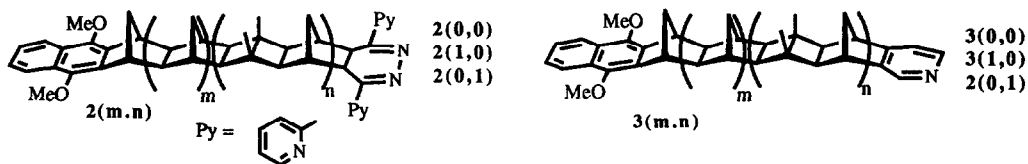
*Tetrahedron*, 1992, 48, 7663

# SYNTHESIS OF NOVEL RIGID NORBORNANOLOGOUS SPACERS BEARING HETEROCYCLIC LIGANDS FOR THE INVESTIGATION OF LONG-RANGE INTRAMOLECULAR ELECTRON TRANSFER INVOLVING METAL CENTRES

Anna Golka, Peter J. Keyte, and Michael N. Paddon-Row\*

Department of Organic Chemistry, University of New South Wales, PO Box 1, Kensington, NSW, 2033, Australia

The synthesis of some novel 1,4-dimethoxynaphthalene—bridge—heterocycle systems, 2(m,n) and 3(m,n), is described.

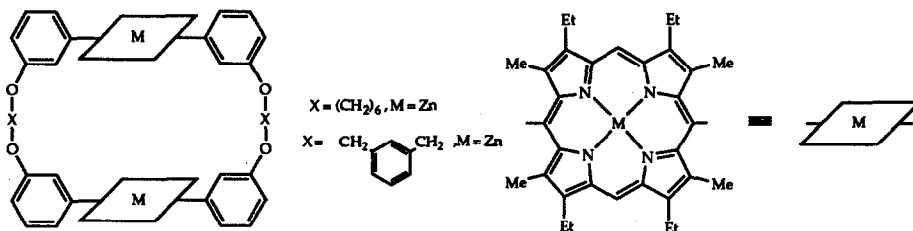


# FACE TO FACE PORPHYRINS AS SYNTHETIC HOST MOLECULES

Ian P. Danks, Trevor G. Lane, Ian O. Sutherland\*, and Maurice Yap

Department of Chemistry, University of Liverpool, PO Box 147, Liverpool, L69 3BX

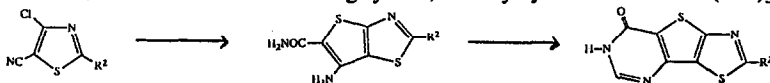
Bis zinc porphyrins form complexes in  $\text{CHCl}_3$  with amines and show a strong preference for diamines  $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$  and 4,4'-dipyridyl.



# AZOLES. PART 10. THIAZOLO[4',5';4,5]THIENO-[3,2-d]PYRIMIDINE; A NEW HETEROCYCLIC RING SYSTEM.

Salah Athmani and Brian Iddon\*, Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, U.K.

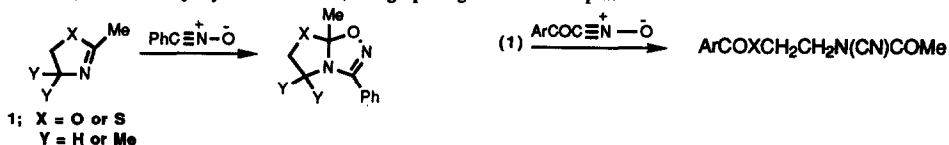
6-Aminothieno[2,3-d]thiazole-5-carboxamides were synthesised from 4-chlorothiazole-5-carbonitriles and converted into derivatives of the title ring system, initially by reaction with  $\text{HC}(\text{OEt})_3$  in  $\text{Ac}_2\text{O}$ .



# 1,3-DIPOLAR CYCLOADDITION REACTIONS OF NITRILE OXIDES WITH 4,5-DIHYDRO-OXAZOLE AND 4,5-DIHYDROTHIAZOLE DERIVATIVES

by David J. Miller, Richard M. Scrowston\* (School of Chemistry, The University, Hull HU6 7RX, U.K.), Peter D. Kennewell and Robert Westwood (Roussel Scientific Institute, Covingham, Swindon SN3 5BZ, U.K.)

4,5-Dihydro-2-methyl-oxazole and -thiazole derivatives undergo the expected cycloaddition reactions with benzonitrile  $N$ -oxide, but with aryl cyanide  $N$ -oxides, a ring-opening reaction takes place.

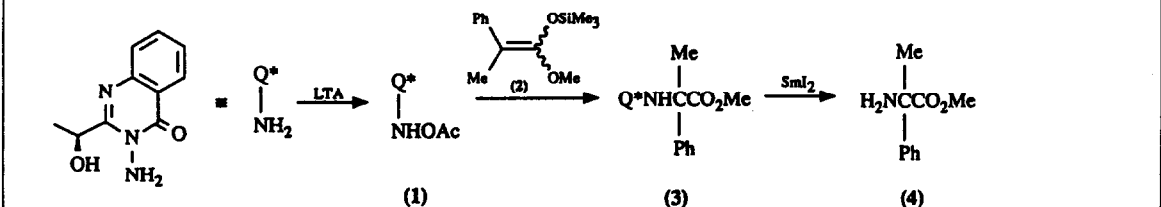




**AMINATION WITH 3-ACETOXYAMINOQUINAZOLIN-4(3H)-ONES: PREPARATION OF  $\alpha$ -AMINOACID ESTERS BY REACTION WITH SILYL KETENE ACETALS FOLLOWED BY N-N BOND CLEAVAGE.**

R.S. Atkinson, B. J. Kelly and J. Williams,

Department of Chemistry, Leicester University, Leicester, LE1 7RH, U. K.

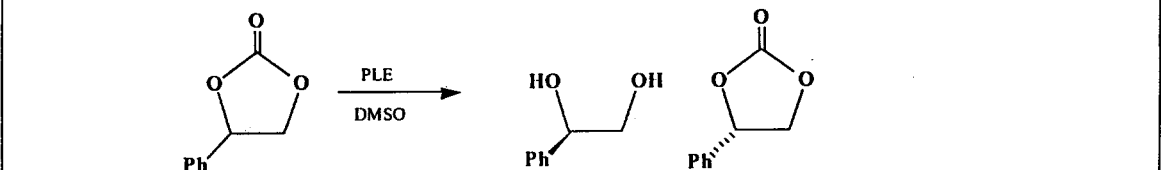


N-acetoxyaminoquinazolinones e.g. (1) aminate silyl ketene acetals e.g. (2) to give (3). Diastereoisomer separation and N-N bond reduction of (3) gives enantiopure  $\alpha$ -aminoacid ester (4).

THE RESOLUTION OF RACEMIC 1,2-DIOLS BY THE ESTERASE CATALYSED HYDROLYSIS OF THE CORRESPONDING CYCLIC CARBONATE.

M.I. Page\* and P.Barton

Department of Chemical Sciences, The University of Huddersfield, Queensgate,  
Huddersfield, HD1 3DH, England



*Tetrahedron*, 1992, 48, 7735

Amadeu F. Brigas and Robert A.W. Johnstone\*

Department of Chemistry, University of Liverpool, Liverpool L69 3BX, U.K.

The concentrations of substrate and hydrogen-donor in heterogeneous catalytic transfer reduction can be crucial to the success of the reaction because of their competitive adsorption onto the catalyst surface. Biphasic aqueous organic solvent systems can achieve control over effective donor concentration by separating the solid catalyst from the liquid phase containing the majority of the donor.

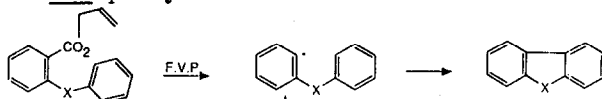
# GAS PHASE GENERATION AND CYCLISATION REACTIONS OF SOME *o*-SUBSTITUTED PHENYL RADICALS

J.I.G. Cadogan,\*<sup>a</sup> H. Susan Hutchison<sup>b</sup> and Hamish McNab\*<sup>b</sup>

<sup>a</sup>BP Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex, TW16 7LN, UK

<sup>b</sup>Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK

Flash vacuum pyrolysis of the *o*-substituted allyl ester shown below gives cyclised products via phenyl radical intermediates.



# PYROLYSIS OF QUINOLINE-3,4-DICARBOXYLIC ANHYDRIDES BEARING 2-PHENYL, 2-BENZYL AND 2-*o*-TOLYL SUBSTITUENTS: FORMATION OF PRODUCTS OF CARBENE INSERTION AND ADDITION

Roger F.C. Brown, Karen J. Coulston, Frank W. Eastwood and Mark R. Moffat  
Department of Chemistry, Monash University, Clayton, Vic. 3168 Australia

