

GRAPHICAL ABSTRACTS

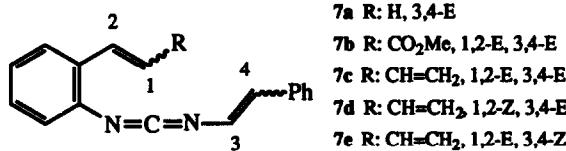
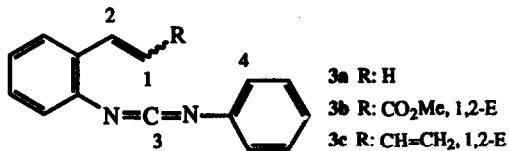
Tetrahedron, 1992, 48, 7425

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

Henry S. Rzepa,^{a*} Pedro Molina,^b Mateo Alajarín^b and Angel Vidal^b

^aDepartment of Chemistry, Imperial College of Science Technology and Medicine, London, SW7 2AY. ^bDepartamento de Química Orgánica, 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.

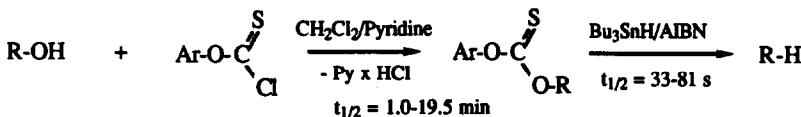


THE INVENTION OF RADICAL REACTIONS. PART XXIV. RELATIVE RATES OF ACYLATION AND RADICAL DEOXYGENATION OF SECONDARY ALCOHOLS.

Tetrahedron, 1992, 48, 7435

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.

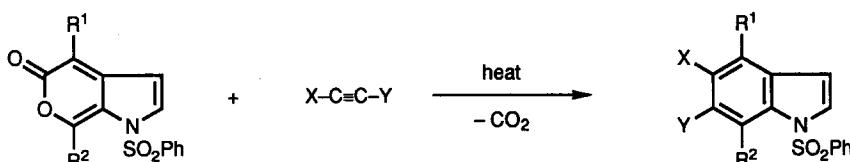


Diels–Alder Reactions of 1,5-Dihydropyrano[3,4-b]pyrrol-5(1H)-ones, Pyrrole-2,3-quinodimethane Analogues; a New Synthesis of Indoles

Tetrahedron, 1992, 48, 7447

P. Mark Jackson and Christopher J. Moody

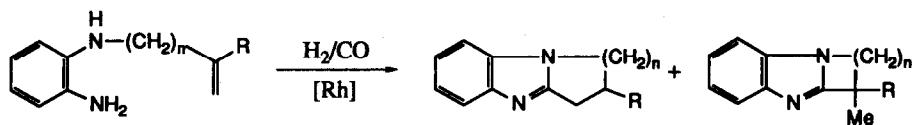
Department of Chemistry, Loughborough University of Technology, Loughborough, Leics. LE11 3TU, U.K.



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

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

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



A NEW METHOD FOR BROMINATION OF CARBAZOLES, β -CARBOLINES AND IMINODIBENZYLs
BY USE OF N-BROMOSUCCINIMIDE AND SILICA GEL

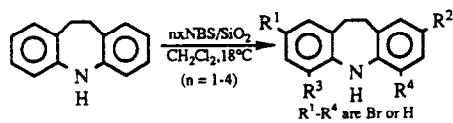
Keith Smith^a, D. Martin James^a, Anil G. Mistry^a, Martin R. Bye^b and D. John Faulkner^c.

^aDepartment of Chemistry, University College of Swansea, Swansea SA2 8PP, UK

^bAmersham International plc, Cardiff Laboratories, Forest Farm, Whitchurch, Cardiff CF4 7YT, UK

^cScripps 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.



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

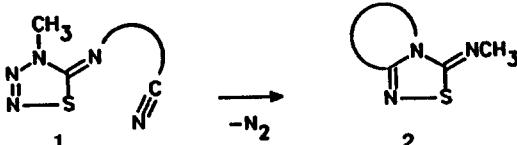
The geometries of the cobalt (III) porphyrin complexes of amines with the sterically hindered porphyrins were investigated by MM and NMR.

Synthesis of Fused 1,2,4-Thiadiazolines by Intramolecular Cycloaddition-Elimination Reactions of 4-Methyl-5-(cyano tethered)imino- Δ^2 -1,2,3,4-thatriazolines

Gerrit L'abbé and Stefan Leurs,

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

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

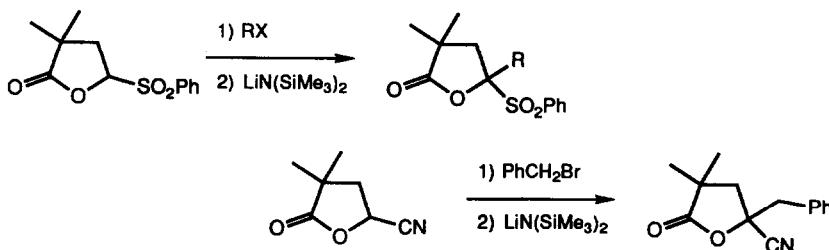


ALKYLATION AND ACYLATION OF 5-PHENYLSULPHONYL-AND 5-CYANOBUTYROLACTONES

Jason Micklefield^a, Michael H. Block^b and Alan R. Battersby^{a*}

^aUniversity Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, UK.

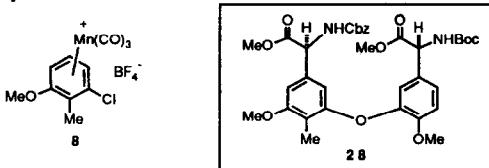
^bICI Pharmaceuticals Division, Mereside, Alderley Park, Macclesfield, Cheshire, SK10 4TG.



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.

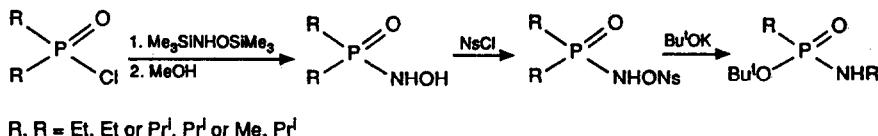
A synthesis of the protected ristomycinic acid derivative **28** was accomplished via consecutive nucleophilic addition reactions with the arene manganese complex **8**.



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

Tetrahedron, 1992, 48, 7539

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



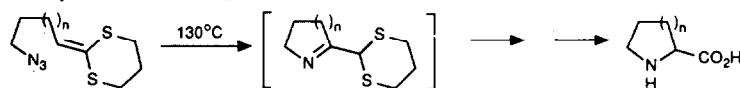
**KETENE-S,S-ACETALS AS 1,3-DIPOLAROPHILES TOWARDS AZIDES.
A NEW SYNTHETIC ENTRY INTO CYCLIC AMINO ACIDS.**

Tetrahedron, 1992, 48, 7551

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 α -amino acids (n=1,2).



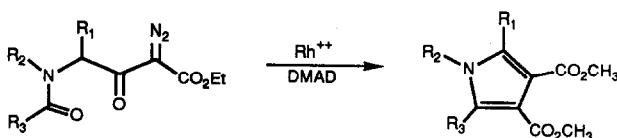
AZOMETHINE YLIDE GENERATION VIA THE DIPOLE CASCADE

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.

Tetrahedron, 1992, 48, 7565



SYNTHESSES OF 6-ACYLCOUMARINS VIA HIGHLY

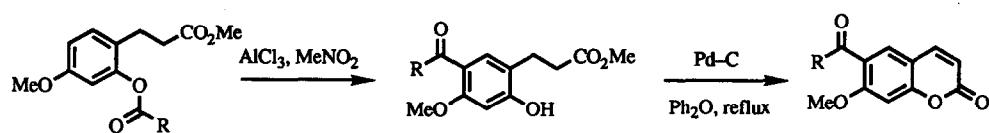
REGIOSELECTIVE FRIES REARRANGEMENTS. TOTAL

SYNTHESSES OF THE LINEAR ACYLATED COUMARINS GEIJERIN AND DEHYDROGEIJERIN.

Nicholas Cairns,^a Laurence. M. Harwood,^{a*} and David P. Astles^b

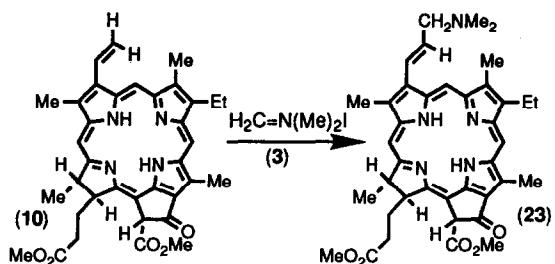
^a Dyson Perrins Laboratory, University of Oxford, South Parks Road, OXFORD OX1 3QY, U.K.

^b Shell, Sittingbourne Research Centre, SITTINGBOURNE ME9 8AG, U.K.



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

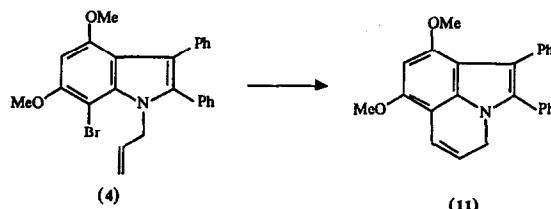
Treatment of vinylporphyrins and vinylchlorins with N,N -dimethylmethylenearmmonium iodide (3) gives trans-vinyl-substituted Mannich adducts (e.g. 23), and not meso-substituted products. Quaternization with MeI gives water-soluble cationic products.



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)



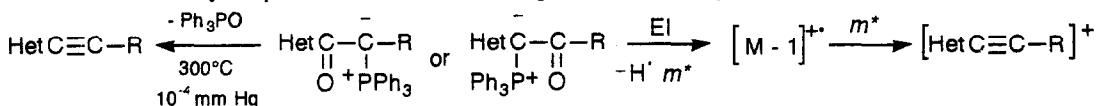
PHOSPHONIUM SALTS AND PHOSPHORANES. PART 5.¹

THERMAL AND ELECTRON-IMPACT INDUCED

FRAGMENTATION OF HETEROAROYLMETHYLENETHIOPHOSPHORANES.

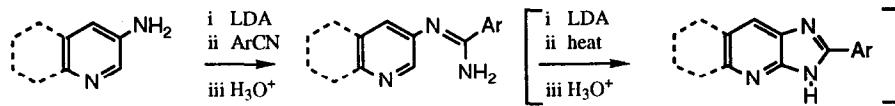
Judith M. Brittain, R. Alan Jones,* and (in part) Sayed Ali Naghi Taheri. School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, U.K.

Thermal fragmentation of π -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 β -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.

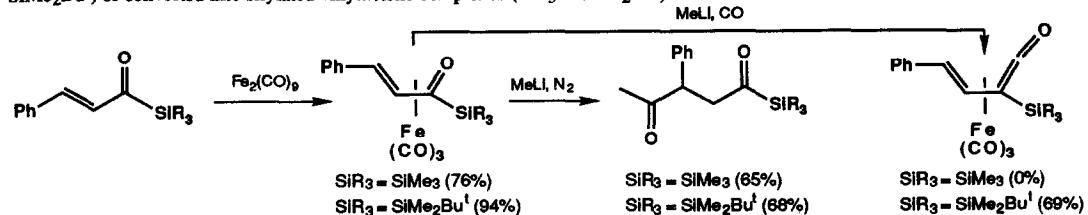
Amidines are prepared by deprotonation of β -aminoazines, followed by reaction with aromatic nitriles. Subsequent cyclisation to imidazoazines was achieved in only a few cases.

SYNTHESIS AND REACTIVITY OF IRON CARBONYL COMPLEXES OF α,β -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.

α,β -Unsaturated acyl silanes (PhCH=CHCOSiR_3) form stable tricarbonyliron(0) complexes which can be acylated ($\text{SiR}_3 = \text{SiMe}_3$, SiMe_2Bu^1) or converted into silylated vinylketene complexes ($\text{SiR}_3 = \text{SiMe}_2\text{Bu}^1$).



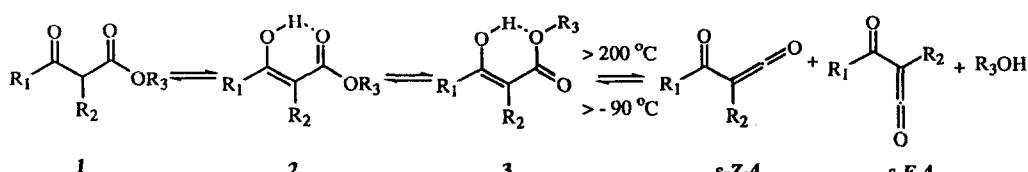
Flash Vacuum Pyrolysis of *tert*-Butyl β -Ketoesters:

Sterically Protected α -Oxoketenes.

Regis Leung-Toung and Curt Wentrup*

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

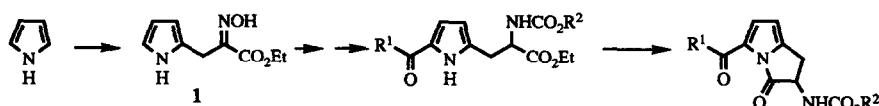
tert-Butylated ketenes (4; R_1 and/or $R_2 = t\text{-C}_4\text{H}_9$) and their reactions with methanol to enols have been investigated.



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.

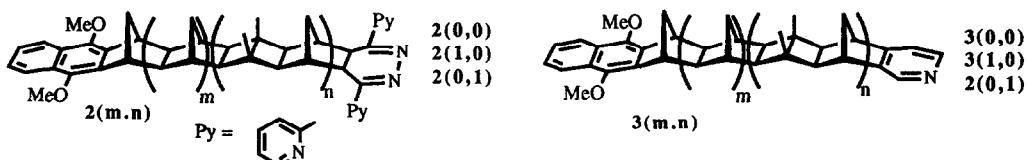


SYNTHESIS OF NOVEL RIGID NORBORNYLOGOUS SPACERS BEARING
HETEROCYCLIC LIGANDS FOR THE INVESTIGATION OF LONG-RANGE
INTRAMOLECULAR ELECTRON TRANSFER INVOLVING METAL CENTRES

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.

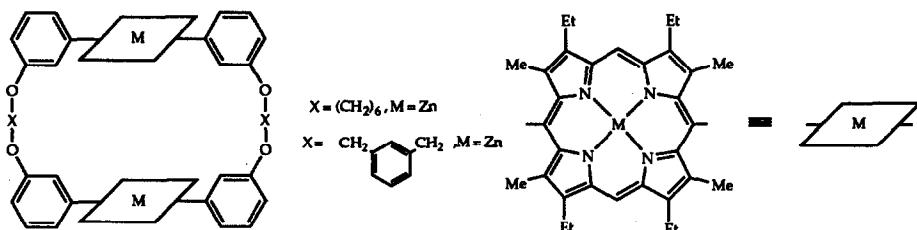


FACE TO FACE PORPHYRINS AS SYNTHETIC HOST MOLECULES

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

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

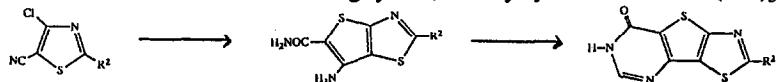
Bis zinc porphyrins form complexes in CHCl_2 with amines and show a strong preference for diamines $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$ and 4,4'-dipyridyl.



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.

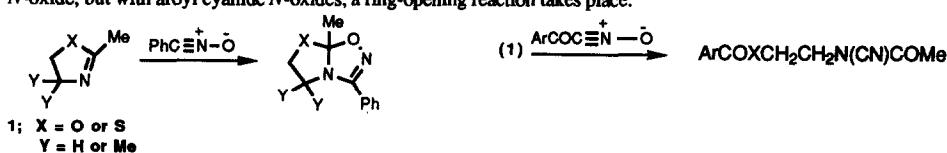
6-Aminothieno[2,3-*d*]thiazole-5-carboxamides were synthesised from 4-chlorothiazole-5-carbonitriles and converted into derivatives of the title ring system, initially by reaction with $\text{HC}(\text{OEt})_3$ in Ac_2O .



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.)

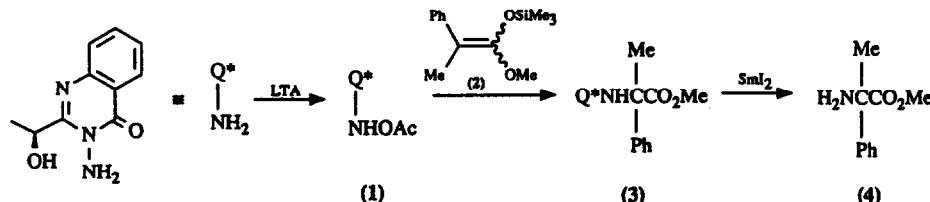
4,5-Dihydro-2-methyl-oxazole and -thiazole derivatives undergo the expected cycloaddition reactions with benzonitrile *N*-oxide, but with aryl cyanide *N*-oxides, a ring-opening reaction takes place.



AMINATION WITH 3-ACETOXYAMINOQUINAZOLIN-4(3H)-ONES: PREPARATION OF α -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.

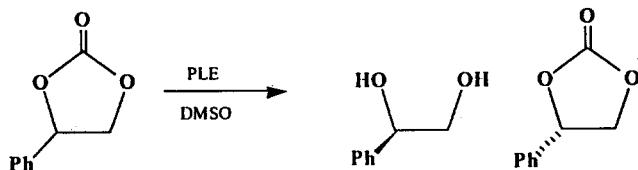


N-acetoxyaminoquinazolinones e.g. (1) aminate silyl ketene acetals e.g. (2) to give (3). Diastereoisomer separation and N-N bond reduction of (3) gives enantiopure α -aminoacid ester (4).

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



METAL-ASSISTED REACTIONS. Part 24¹. THE IMPORTANCE OF SOLVENT IN LIQUID-PHASE HETEROGENEOUS CATALYTIC TRANSFER REDUCTION

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.

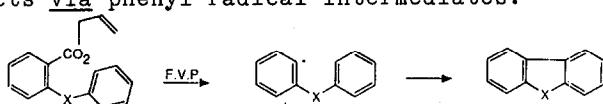
GAS PHASE GENERATION AND CYCLISATION
REACTIONS OF SOME *o*-SUBSTITUTED PHENYL
RADICALS

J.I.G. Cadogan,*^a H. Susan Hutchison^b and Hamish McNab*^b

^aBP Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex, TW16 7LN, UK

^bDepartment 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

