

GRAPHICAL ABSTRACTS

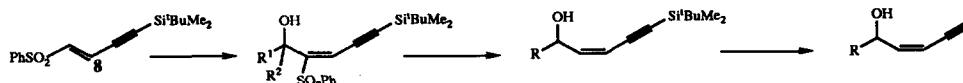
Tetrahedron, 1992, 48, 7775

A STEREOSELECTIVE *CIS*-ENYNE SYNTHESIS USING VINYL SULFONE CHEMISTRY

Andrew B. Holmes* and Guy R. Pooley

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

The enyne sulfone **8** was lithiated and then coupled with a variety of carbonyl compounds. Stereoselective desulfonylation and desilylation afforded terminal *cis*-enyne alcohols.

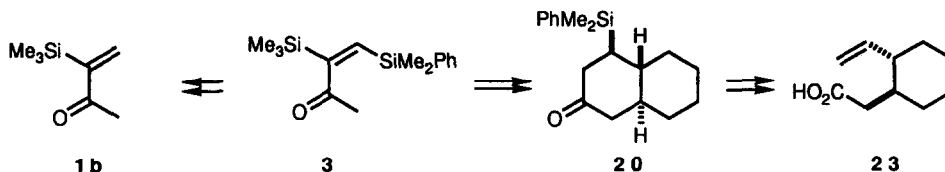


Tetrahedron, 1992, 48, 7793

THE SYNTHESIS OF 3-TRIMETHYLSILYL-4-DIMETHYL(PHENYL)-SILYLBUT-3-EN-2-ONE, A β -FUNCTIONALISED MICHAEL ACCEPTOR

Ian Fleming,* Trevor W. Newton, Verity Sabin and Françoise Zammattio,
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

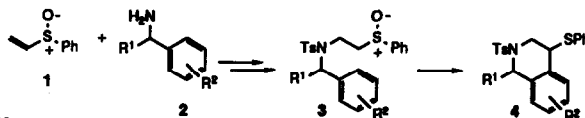
Silyl-cupration of trimethylsilylacetylene followed by acetylation gives the $\alpha\beta$ -disilylated enone **3**, which can be converted in 3 steps into **1b**. The enone **3** can be used in annulation reactions to make **20** or **23**.



Tetrahedron, 1992, 48, 7803

SYNTHESIS OF TETRAHYDROISOQUINOLINES *via* INTRAMOLECULAR ELECTROPHILIC AROMATIC SUBSTITUTION REACTIONS OF PUMMERER-DERIVED SUBSTITUTED *N*-BENZYL-*N*-TOSYL- α -AMINOTHIONIUM IONS

Donald Craig* and Kevin Daniels
Department of Chemistry
Imperial College of Science, Technology and Medicine
London SW7 2AY, U.K.
A. Roderick MacKenzie
Pfizer Central Research, Sandwich, Kent CT13 9NJ, U.K.

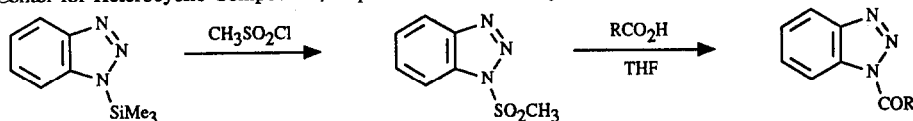


Substituted 1,2,3,4-tetrahydroisoquinolines **4** are synthesized in high overall yield via a three-step sequence starting from (phenylsulfinyl)ethene **1** and benzylic amines **2**.

**SULFONYL DERIVATIVES OF BENZOTRIAZOLE:
PART 1. A NOVEL APPROACH TO THE ACTIVATION OF CARBOXYLIC ACIDS**

Alan R. Katritzky,* N. Shobana, Juliusz Pernak, A. S. Afridi and Wei-Qiang Fan

Center for Heterocyclic Compounds, Department of Chemistry, University of Florida, Gainesville, FL 32611-2046

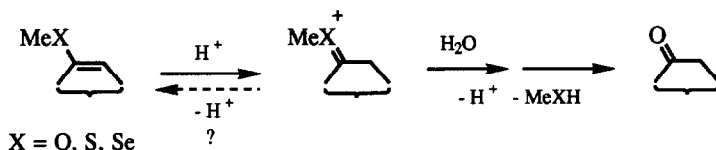


1-Acylbenzotriazoles are easily prepared from 1-(1-methanesulfonyl)benzotriazole and carboxylic acids as illustrated by the preparation of 1-(2-pyridoyl)-, 1-(3-pyridoyl)-, 1-(4-pyridoyl)-, 1-(2-pyrrolylcarbonyl)- and 1-(2-furoyl)-benzotriazole in yields of 80 - 95%.

**An Empirical Aromaticity Index (AIRT) Based on
"Reversion to Type" in the Hydrolysis of Methyl
Ethers, Methyl Thioethers, and Methyl Selenoethers
Derived from Some Heterocyclic and Homocyclic Polyenes**

Brian Capon* and Sing Quan Lew *Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong.*

The tendency for protonation to be reversible in the reactions of the following kind (Reversion to Type) is correlated with the aromaticity of the parent rings.

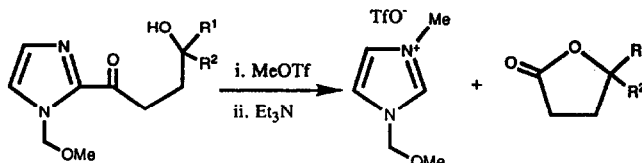


Synthesis of γ -Lactones from 2-(γ -Hydroxyacyl)-imidazoles by N-Methylation and Base-catalyzed C - C Bond Cleavage. Application to the Synthesis of (\pm) - Cavernosine.

D. Huw Davies,^a Nicholas A. Haire (in part),^b Jonathan Hall^b and Edward H. Smith^b

a. ICI Pharmaceuticals, Alderley Park, Macclesfield, Cheshire, SK10 4TG, UK

b. Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London, SW7 2AY, UK



HETEROAROMATICITY. 7. SOME QUANTITATIVE ASPECTS OF THE TAUTOMERISM
OF HYDROXY AND MERCAPTOAZINES

Clive W. Bird
Department of Chemistry, King's College, The Strand, London WC2R 2LS, U.K.

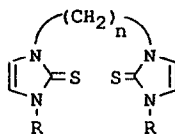
Aromaticity indices have been calculated from crystallographic data for a range of oxo tautomers of hydroxyazines and their thio counterparts. The differences between these indices and those for the hydroxyazines lead to values for changes in resonance energies accompanying tautomerisation. These values are closely parallel to those previously measured for the same process in aqueous solution.

THE SYNTHESIS AND LIGAND PROPERTIES OF *N,N'*-POLYMETHYLENE-BRIDGED
IMIDAZOLE-2-THIONES AND BENZIMIDAZOLE-2-THIONES

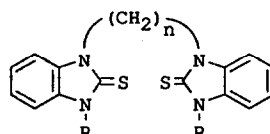
Lionel S Bark, N Chadwick and Otto Meth-Cohn*, Chemistry Department, Salford University, Salford M5 4WT.

(* Mailing address: Chemistry Department, Sunderland University, Sunderland SR1 3SD),

The title thiones were synthesised and shown to be effective ligands for transition metal salts



$n = 1-10$

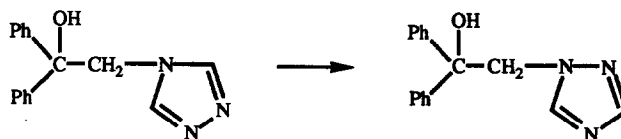


$n = 3-6$

REARRANGEMENT OF (1,2,4-TRIAZOL-4-YL)ETHANOLS
TO (1,2,4-TRIAZOL-1-YL)ETHANOLS

T. William Bentley*, Lisa M. Howle, Ray V. H. Jones and Peter J. Wareham
Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP, Wales, UK. and Imperial Chemical Industries, Fine Chemicals Manufacturing Organisation, Grangemouth FK3 8XG, Scotland, UK.

The mechanism of rearrangement of β -hydroxyethyl-(1,2,4-triazoles) has been shown using crossover experiments to be intermolecular and free energy profiles show that reactions are thermodynamically-controlled.

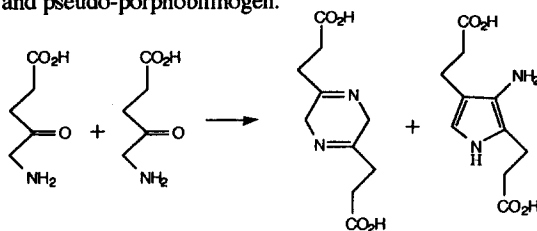


The Nonenzymatic Cyclic Dimerisation of 5-Aminolevulinic Acid

Anthony R Butler and Sharon George

Department of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland

In the absence of an enzyme the cyclic dimerisation of 5-aminolevulinic acid leads to the formation of a dihydropyrazine and pseudo-porphobilinogen.

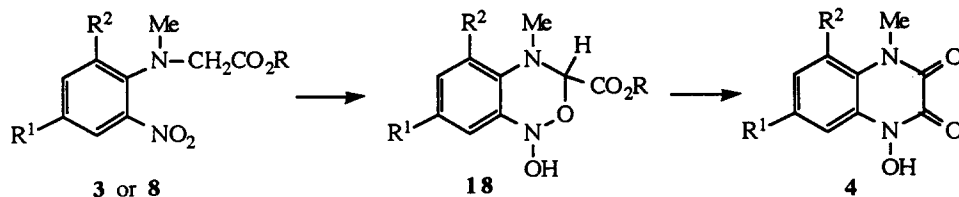


o-NITROANILINE DERIVATIVES - 13. REACTIONS OF N-(o-NITROARYL)SARCOSINE ESTERS WITH BASES

Pamela A. Collins, Michael D. McFarlane, Raymond K. Mackie, and David M. Smith*

Department of Chemistry, University of St. Andrews, Purdie Building, St. Andrews, Fife, KY16 9ST, Scotland

The title reactions give 1-hydroxy-4-methylquinoxaline-2,3-diones **4**, together with a variety of mono- and bi-cyclic by-products, possibly *via* benzoxadiazine intermediates of the type **18**.



TOTAL SYNTHESIS OF THE IONOPHORE ANTIBIOTIC CP-61,405 (ROUTIENNOCIN).

David Diez-Martin, Nikesh R. Kotecha, Steven V. Ley,* Sergio Mantegani,

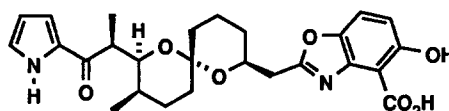
J. Carlos Menéndez, Helen M. Organ and Andrew D. White.

Dept. of Chemistry, Imperial College of Science, Technology and Medicine, London SW7 2AY, UK.

Bernard Banks.

Pfizer Ltd., Sandwich, Kent, CT13 9NJ, UK.

The total synthesis of the spiroketal ionophore antibiotic Routiennocin was achieved by employing π -allyltricarboxyl iron lactone complexes as precursors for 2-phenylsulfonyl pyrans, which in turn were coupled with iodoacetanilides to afford spiroketals.

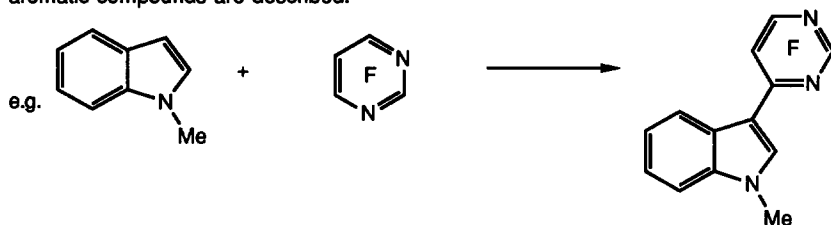


Polyhalogenoheterocyclic Compounds. Part 40.¹ Tertiary Aromatic Amines As Carbon-Nucleophiles With Activated Perfluorinated Aromatic Compounds

Richard D. Chambers^a, Stewart R. Korn^b, and Graham Sandford^a

^aDepartment of Chemistry, University of Durham, South Road, Durham, DH1 3LE, UK

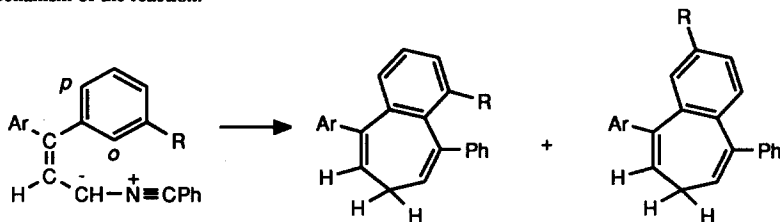
^bICI Specialities, North of England Works, P O Box A38, Leeds Road, Huddersfield, Yorkshire, HD2 1FF, UK
The first examples illustrating that aromatic amines may act as carbon nucleophiles with fluorinated aromatic compounds are described.



ELECTROCYCLIC AROMATIC SUBSTITUTION BY NITRILE YLIDES TO GIVE 3H-2-BENZAZEPINES: SUBSTITUENT EFFECTS AND MECHANISM.

John T. Sharp and Paul W. Groundwater, Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ.

The directive effects of substituents (R=Me, MeO, CF₃, Cl) have been determined and deuterium labelling has been used to investigate the mechanism of the reaction.

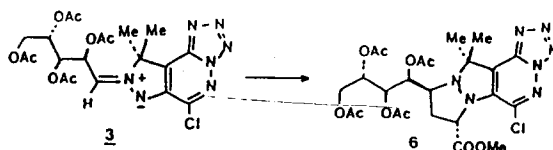


A NEW SYNTHESIS OF C-NUCLEOSIDES BY 1,3-DIPOLAR CYCLOADDITION OF CHIRAL AZOMETHINE IMINES TO METHYL ACRYLATE. THE STEREoselective SYNTHESIS OF FUSED PYRAZOLES.

Marko Žličar, Branko Stanovnik^{*} and Miha Tišler

Department of Chemistry, University of Ljubljana, 61000 Ljubljana, Slovenia

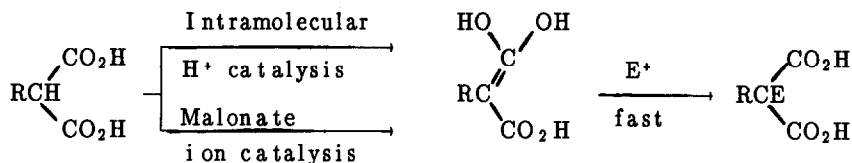
A stereoselective synthesis of fused pyrazoles from chiral azomethine imines is described.



Enols Derived from Malonic Acids as Intermediates in Nitrosation and Halogenation

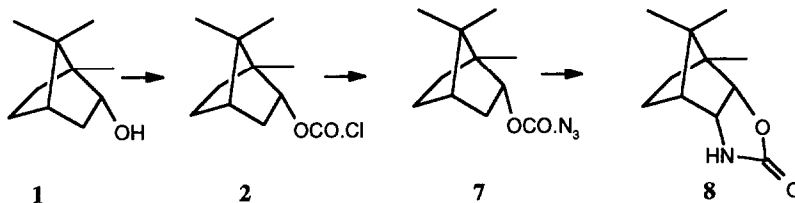
D. Lyn H. Williams* and Alan Graham

Department of Chemistry, University Science Laboratories, South Road, Durham DH1 3LE, UK.



Kinetic studies reveal two pathways for enolisation (a) which is intramolecularly H⁺ catalysed and (b) which is catalysed by malonate ion.

Enantiospecific Preparation of [(2R,6S)-endo]-5-Aza-1,10,10-trimethyl-3-oxatricyclo[5.2.1.0^{2,6}]decan-4-one by a Nitrene-mediated Route from [(1S)-endo]-(-)-Borneol and its Utility as a Chiral Auxiliary in Some Asymmetric Transformations; Malcolm R. Banks^a, Alexander J. Blake^a, J. I. G. Cadogan^b, Ian M. Dawson^a, Ian Gosney^a, Keith J. Grant^a, Suneel Gaur^a, Philip K. G. Hodgson^b, Kevin S. Knight^b, Glen W. Smith^b, and Dian E. Stevenson (nee Thomson)^a; ^aDepartment of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, Scotland; ^bBritish Petroleum Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex, TW16 7LN, England.

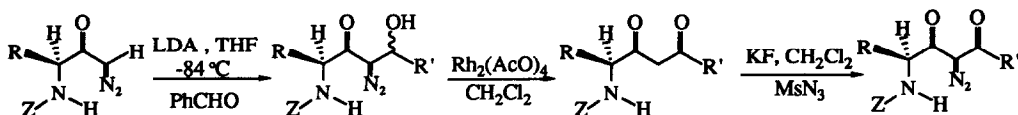


SYNTHESIS OF CHIRAL N-PROTECTED α -AMINO- β -DIKETONES FROM α -DIAZOKETONES DERIVED FROM NATURAL AMINO ACIDS

Tao Ye and M. Anthony McKervy*

School of Chemistry, The Queen's University, Belfast BT9 5AG, U.K.

Optically active α -amino- β -diketones were prepared *via* a diazo aldol reaction with subsequent rhodium-catalysed rearrangement



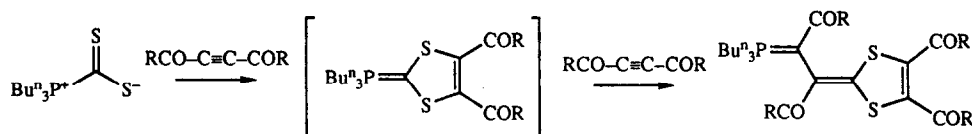
Formation of Novel 1:2 Adducts Between $\text{Bu}^n_3\text{P} \cdot \text{CS}_2$ and Electron-deficient Alkynes

R. Alan Aitken^{a*}, Swati V. Raut^a and George Ferguson^b

^a Department of Chemistry, University of St. Andrews, St. Andrews, Fife, KY16 9ST, U.K.

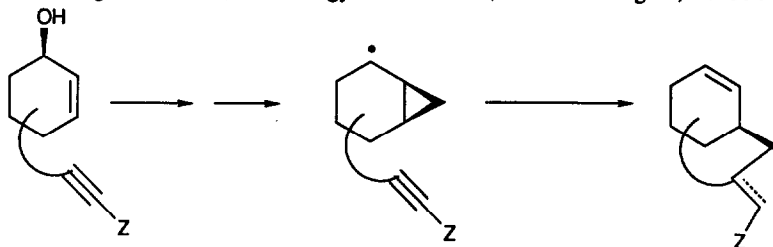
^b Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, N1G 2W1, Canada.

Addition of $\text{Bu}^n_3\text{P} \cdot \text{CS}_2$ to electron-deficient alkynes under neutral conditions occurs as shown to give the novel 1:2 adducts.



CONSTRUCTION OF BICYCLIC SYSTEMS VIA A TANDEM FREE RADICAL CYCLOPROPYLCARBINYL REARRANGEMENT-CYCLISATION STRATEGY

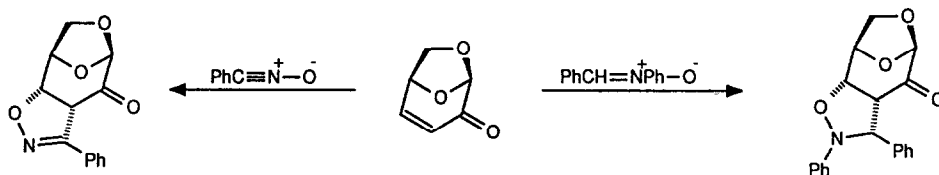
Robert A. Batey, John D. Harling and William B. Motherwell,* Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, U.K.



1,3-Dipolar Cycloaddition Reactions of Levoglucosenone

Alexander J. Blake, Tracey A. Cook, Angus C. Forsyth, Robert O. Gould and R. Michael Paton
Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK

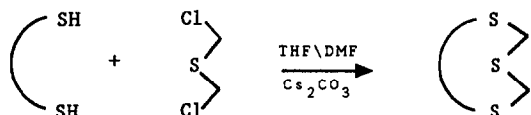
Levoglucosenone undergoes highly regio- and stereo-selective 1,3-dipolar cycloaddition reactions with nitrile oxides and nitrones; the major adducts result from reaction at the *exo*-face opposite the 1,6-anhydro bridge, with the oxygen of the 1,3-dipole attached to the β -carbon of the enone unit.



Synthesis of Thiocrown ethers Containing -SCH₂SCH₂S- Units.

Jilles J.H. Edema^{*}, Jan Buter, H. Thijs Stock, Richard M. Kellogg^{*}.

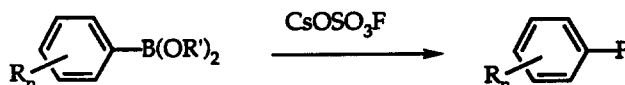
Department of organic and molecular inorganic chemistry University of Groningen, Nijenborgh 4 9747 AG Groningen, The Netherlands.



Application of thio(bischloromethane) in thia crownether chemistry allows the direct and selective incorporation of -SCH₂SCH₂S- units in the ring system

A New Synthesis of Aryl Fluorides: The Reaction of Caesium Fluoroxysulfate with Arylboronic Acids and Derivatives.

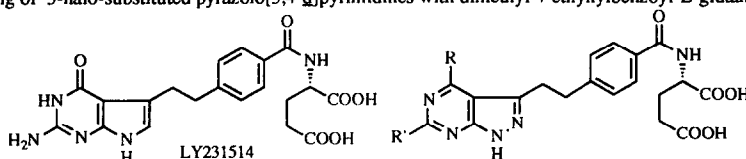
Louis J. Diorazio,^a David A. Widdowson^{*,a} and John M. Clough^b. ^aDepartment of Chemistry, Imperial College of Science, Technology and Medicine, London, SW7 2AY, UK. ^bICI Agrochemicals, Jealotts Hill Research Station, Bracknell, Berks., RG12 6EY, UK.



Synthesis of Pyrazolo[3,4-d]pyrimidine Analogues of the Potent Anti-tumor Agent N-{4-[2-(2-Amino-4(3H)-oxo-7H-pyrrolo[2,3-d]pyrimidin-5-yl)ethyl]benzoyl}-L-glutamic Acid (LY231514)

Edward C. Taylor^{*} and Hemantkumar H. Patel
Department of Chemistry, Princeton University, Princeton, NJ 08544

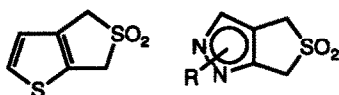
Several pyrazolo[3,4-d]pyrimidine analogues of the potent antitumor agent N-{4-[2-(2-amino-4(3H)-oxo-7H-pyrrolo[2,3-d]pyrimidin-5-yl)ethyl]benzoyl}-L-glutamic acid (LY231514) have been prepared by palladium-catalyzed C-C coupling of 5-halo-substituted pyrazolo[3,4-d]pyrimidines with dimethyl 4-ethynylbenzoyl-L-glutamate.



HETEROCYCLIC FUSED 2,5-DIHYDROTHIOPHENE S,S-DIOXIDES AS PRECURSORS TO HETEROCYCLIC o-QUINODIMETHANES

Lynne M. Chaloner, Andrew P.A. Crew, Paul M. O'Neill, Richard C. Storr, School of Chemistry, Liverpool University, P.O. Box 147, Liverpool L69 3BX
Michael Yelland, ICI Fine Chemicals Manufacturing Organisation, Hexagon House, Blackley, Manchester M9 3DA

Thiophene and pyrazole fused
2,5-dihydrothiophene dioxides
have been prepared by a variety
of routes.



On heating in solution at 200°C
these sulfones lose sulfur dioxide and the
resulting o-quinodimethane can be
trapped by dienophiles.

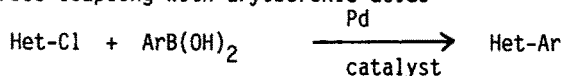
PALLADIUM-CATALYSED CROSS-COUPLING REACTIONS OF ARYLBORONIC ACIDS WITH π -DEFICIENT HETERO- ARYL CHLORIDES

N.M. Ali,^a A. McKillop,^{*a} M.B. Mitchell,^{*b} R.A. Rebelo^a and P.J. Wallbank^b

^aSchool of Chemical Sciences, University of East Anglia, Norwich, NR4 7TJ, England.

^bSynthetic Chemistry Department, SmithKline Beecham Pharmaceuticals, Old Powder Mills, Nr. Leigh, Tonbridge, Kent, TN11 9AN.

Heteroaryl chlorides, rather than bromides or iodides, undergo smooth high yield palladium-catalysed cross-coupling with arylboronic acids



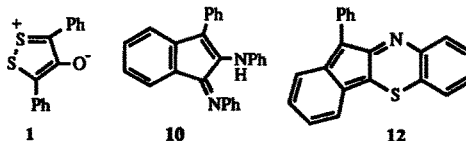
Het = pyridine, pyrimidine, pyrazine, quinoline

Cyclic Meso-ionic Heterocycles. Part 24. The Reaction of 1,2-Dithiolium-4-olates with Aniline. The Formation of 11-Phenylbenzene[b]indeno[2,1-e]-1,4-thiazine

Christopher G. Newton, W. David Ollis*, and Graham P. Rowson
Department of Chemistry, The University, Sheffield S3 7HF, UK

Margaret J. Hamor and Thomas A. Hamor
School of Chemistry, The University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

Reaction of the type B meso-ionic
heterocycle (1) with aniline yields the
products (10) and (12) by an
unexpected mechanism.



Synthetic, Structural and Electrochemical Studies on the 1,2-Dithiole-3-thione System: Preparation and Reactions of the 5,6-Dihydro-1,2-dithiolo[4,5-*b*][1,4]dithiin-3-ium Cation

Martin R. Bryce,^{a,*} Gordon R. Davison,^a Adrian J. Moore,^a Michael B. Hursthouse^b and K. M. Abdul Malik^b

^a Department of Chemistry, University of Durham, Durham, DH1 3LE, U.K

^b School of Chemistry and Applied Chemistry, University of Wales College of Cardiff, PO Box 912, Cardiff, CF1 3TB, U.K.

The synthesis, X-ray crystal structure and some reactions of 1,2-dithiole-3-thione derivative **8** are reported. Notably, cation salt **11** and isothiazole derivative **18** have been prepared.

