GRAPHICAL ABSTRACTS

Tetrahedron, **1992**, *48*, 1539

A NEW STERIC SUBSTITUENT CONSTANT Ω_S. CHARACTERISTIC FEATURE AND COMPARISON WITH SOME OTHER STERIC CONSTANTS

Tamiki Komatsuzaki, Ikuo Akai, Kazuhisa Sakakibara, and Minoru Hirota*
Department of Synthetic Chemistry, Division of Materials Science and Chemical Engineering, Faculty of Engineering, Yokohama National University, Yokohama 240, Japan.

$\log (k/k_0) = \rho_S \Omega_S + a'$ A new steric substituent constant, Ω_S, was proposed in order to evaluate the kinetic steric effect. Ω_S is isotropic and dependent most significantly on the number of α-carbon atoms. The rates of several reactions were shown to be correlated with Ω_S better than with Es.

Tetrahedron, **1992**, *48*, 1557

AIR OXIDATION OF *P*-SUBSTITUTED BENZOIN TO THE CORRESPONDING BENZIL CATALYZED BY FE(II)-CYSTEINE PEPTIDE COMPLEXES

Wei-Yin Sun, Norikazu Ueyama and Akira Nakamura*
Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

Catalytic air oxidation of benzoin was carried out in the presence of a variety of Fe(II)-cysteine peptide complexes.

X = Br, H, CH_3, OCH_3

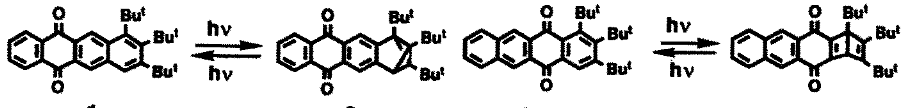
Catalyst: $[Fe(Z\text{-cys-Gly-Val-OMe})_4]^{2-}$, $[Fe(Z\text{-cys-Pro-Val-cys-OMe})_2]^{2-}$, $[Fe(Z\text{-cys-Pro-Leu-cys-Gly-Val-OMe})_2]^{2-}$ *etc.*

Tetrahedron, **1992**, *48*, 1567

NOVEL NAPHTHACENEQUINONE DERIVATIVES UNDERGOING PHOTOVALENCE ISOMERIZATION: A NEW PHOTOCHROMIC MOLECULE

Sadao Miki,* Hiroyuki Kagawa, Kohji Matsuo, Osamu Kobayashi, Masahiro Yoshida and Zen-ichi Yoshida*
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606, Japan

7,8,9-Tri-t-butyl-5,12-naphthacenequinone (1) and 1,2,3-tri-t-butyl-5,12-naphthacenequinone (2) were synthesized. Upon irradiation, 1 and 2 undergo photovalence isomerization to give the *valene* isomer (3) and the *Dewar* isomer (4), respectively. Interconversions between the naphthacenequinones and their valence isomers were photochemically reversible.

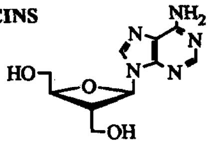


1 3 2 4

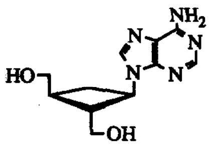
Tetrahedron, **1992**, *48*, 1573

A FACILE ENANTIOSELECTIVE SYNTHESIS OF (1*R*,2*R*,3*S*)-1-AMINO-2,3-BISHYDROXYMETHYLCYCLOBUTANE DERIVATIVES, A KEY SYNTHETIC INTERMEDIATE OF CARBOCYCLIC OXETANOCINS

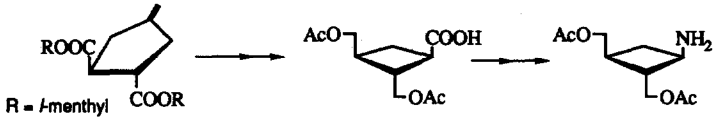
T. Izawa[1], Y. Ogino[1], S. Nishiyama[1], S. Yamamura[1], K. Kato[2],and T. Takita[2]
1. Dept. of Chem., Faculty of Science and Technology, Keio Univ., Hiyoshi, Yokohama 223, Japan
2. Research Laboratories, Pharmaceuticals Group, Nippon Kayaku Co.Ltd. Shimo, Tokyo 115, Japan.



Oxetanocin-A



COXT-A

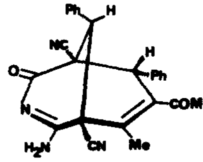


Tetrahedron, **1992**, *48*, 1581

A NOVEL BRIDGEHEAD AZOCINE. THE END OF A CONTROVERSY.

N. Martín[a], M. Quinteiro[a], C. Seoane[a]*, A. Albert[b], F. H. Cano[b] and R. A. Abramovitch[c]
[a]Departamento de Química Orgánica, Facultad de Química, Universidad Complutense, 28040-Madrid, Spain.
[b]U.E.I. de Cristalografía, Instituto Rocasolano, CSIC, Serrano 116, 28006-Madrid, Spain.
[c]Department of Chemistry, Clemson University, Clemson 223, Hunter Labs, SC 29634-1905, USA.

A novel bridgehead azocine has been obtained and the structure confirmed by X-ray diffraction.

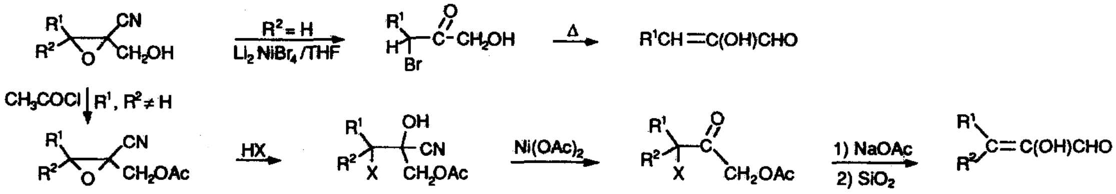


4

Tetrahedron, **1992**, *48*, 1585

SYNTHESES DE CETONES α-α'-FONCTIONNALISEES PUIS D'ALDEHYDES α-ENOLS PAR OUVERTURE DES α-CYANO α-HYDROXYMETHYL EPOXIDES.

K. Layachi[a], I. Ariès-Gautron[b], M. Guerro[b], A. Robert[b] a) Faculté des Sciences de El Jadida. b) Groupe de Chimie Structurale, URA CNRS 704, Université de Rennes I, Campus de Beaulieu, 35042 Rennes Cédex, France.

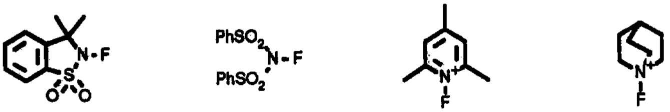


Tetrahedron, **1992**, *48*, **1595**

ELECTROCHEMICAL REDUCTION OF N-F BONDS: RELEVANCE TO THE REACTIVITY OF ELECTROPHILIC FLUORINATING AGENTS.

Edmond Differding* and Pierre M. Bersier, Central Research and Central Analytical Laboratories, Ciba-Geigy AG, CH-4002-Basel, Switzerland

The cyclovoltammetric and polarographic behaviour of nitrogen-fluorine bond containing compounds including the electrophilic fluorinating agents shown below is described.

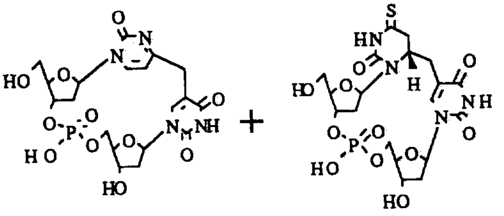


Tetrahedron, **1992**, *48*, **1605**

NMR and Molecular Modelling studies of two Photoproducts of 2'-Deoxy-4- thiouridylyl-(3',5')-thymidine.

Pascale Clivio, Alain Favre, Catherine Fontaine, Jean-Louis Fourrey, Jeannette Gasche, Eric Guittet and Philippe Laugâa
I. C.S. N., C.N.R.S., 91190 Gif sur Yvette Cedex, France.

Preparation, spectroscopic analysis and molecular modelling of photoproducts 3 and 4 are described.



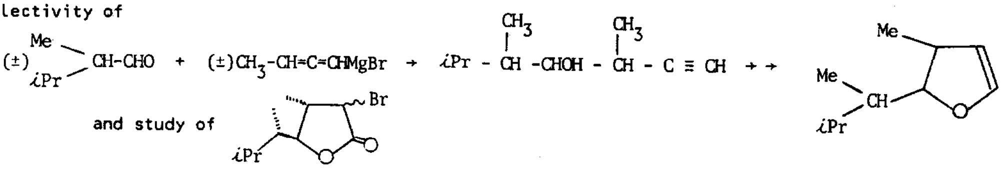
dYo(4- α;p)dT 3 **dhs4U(6- α;p)dT 4**

Tetrahedron, **1992**, *48*, **1617**

REMOTE STEREOCHEMICAL CONTROL OF THE RING CONFORMATION OF 2-BROMO-3-METHYL-4-ALKYL-BUTYROLACTONES

Gilbert DANA*, Estera TOUBOUL and Mariam MELLOT-SROUR
Lab. de Stéréochimie Réactionnelle, Bât. F. Université P & M. Curie, 4 Pl. Jussieu, 75252 PARIS Cedex 05 FRANCE

Stereoselectivity of

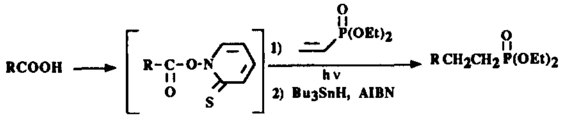


Tetrahedron, **1992**, *48*, 1627

New Synthesis of Sugar, Nucleoside and α-Amino Acid Phosphonates.

Derek H.R. Barton,[a] Stephane D. Géro,[b] Béatrice Quiclet-Sire*[b] , Mohammad Samadi [b].[a]*Department of Chemistry, Texas A&M University, College Station, Texas 77843, U.S.A.* [b] *Institut de Chimie des Substances Naturelles, C.N.R.S., 91198 Gif-sur-Yvette, France.*

Photolysis of N-hydroxy-2-thiopyridone esters derived from uronic acids or α-amino acids in presence of vinyl phosphonate affords the corresponding phosphonate derivatives.



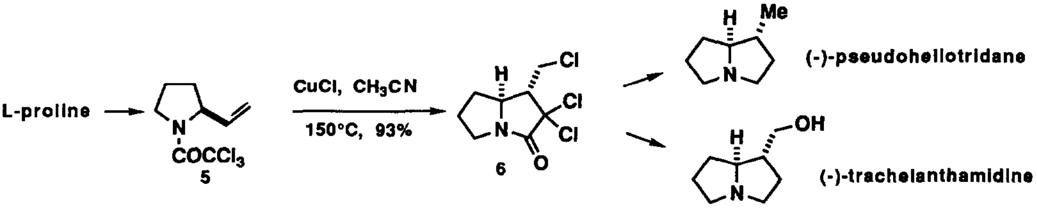
R= sugar, amino-acid, nucleoside

Tetrahedron, **1992**, *48*, 1637

Synthesis of Pyrrolizidines via Copper(I) Catalyzed Radical Atom Transfer Cyclization

Julio A. Seijas, M. Pilar Vázquez-Tato, Luis Castedo, Ramón J. Estévez, M. Gabriela Ónega and María Ruiz.
Departamento de Química Orgánica. Facultad de Ciencias. Universidad de Santiago. Aptdo. 280, 27080-Lugo. Spain.

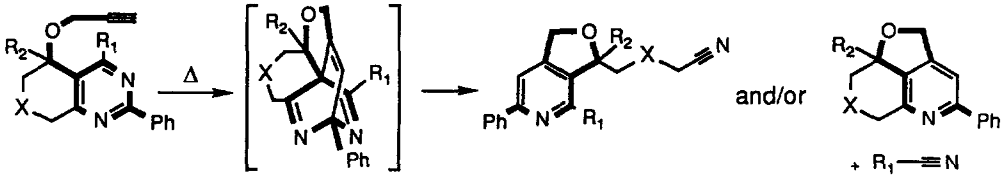
Trachelanthamidine and pseudoheliotridane are synthesized from (2S)-N-trichloroacetyl-2-vinylpyrrolidine (5) by a 5-exo-trig radical cyclization.



Tetrahedron, **1992**, *48*, 1643

SYNTHESIS OF 5-PROPYNYLOXYCYCLOALKANE-PYRIMIDINES AND THEIR SELECTIVITY AND REACTIVITY IN INTRAMOLECULAR DIELS-ALDER REACTIONS .

W.A. W. Stolle, J. M. Veurink, A. T. M. Marcelis and H. C. van der Plas*; Laboratory of Organic Chemistry, Agricultural University , Dreyenplein 8, 6703 HB Wageningen, The Netherlands.

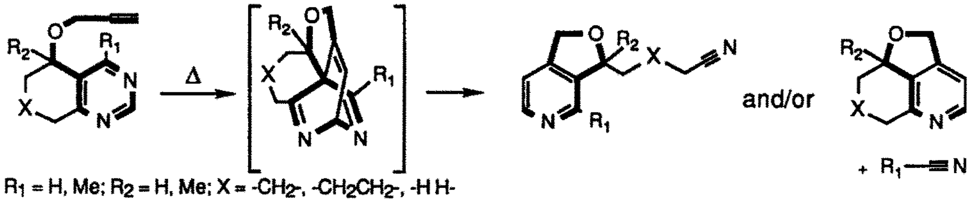


R_1 = H, Me; R_2 = H, Me, Et, Ph; X = -CH_2-, -CH_2CH_2-, -H H-

Tetrahedron, **1992**, *48*, 1657

COMPUTATIONAL STUDIES TOWARDS THE SELECTIVITY AND REACTIVITY OF 5-PROPYNYLOXY-CYCLOALKANEPYRIMIDINES IN INTRAMOLECULAR DIELS-ALDER REACTIONS.

W. A. W. Stolle, A. T. M. Marcelis and H. C. van der Plas*; Laboratory of Organic Chemistry, Agricultural University Wageningen, Dreyenplein 8, 6703 HB Wageningen, The Netherlands.

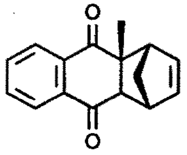


R_1 = H, Me; R_2 = H, Me; X = -CH_2-, -CH_2CH_2-, -H H-

Tetrahedron, **1992**, *48*, 1667

SOLVENT EFFECT AS THE RESULT OF FRONTIER MOLECULAR ORBITAL INTERACTION. VII. THE RETRO DIELS-ALDER REACTION.

G. Desimoni, G. Faita, D. Pasini, and P.P. Righetti; Dipartimento di Chimica Organica dell'Università, V.le Taramelli 10, 27100 Pavia, Italy.



1

The solvent effect on the retro-Diels-Alder reaction giving 2-methyl-1,4-naphthoquinone and cyclopentadiene from **1** was investigated kinetically in 16 solvents. The hyperbolic correlation with the electrophilic properties of the solvent and the linear relationship with the kinetic data of an analogous Diels-Alder reaction strongly suggest that the solvent effect is the result of the electrophilic coordination of the medium with the solvatable reaction product.

Tetrahedron, **1992**, *48*, 1675

HETEROAROMATICITY. 6. THE EFFECT OF MOLECULAR DISTORTION ON AROMATICITY.

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

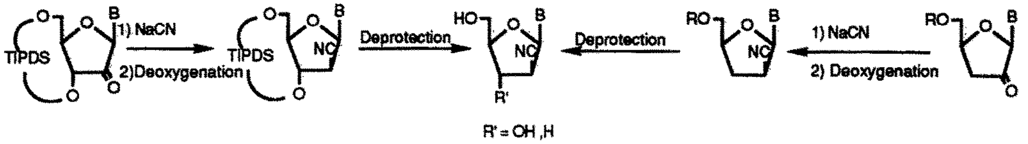
The application of a recently described aromaticity index is shown to provide a convenient means of assessing the extent of change in aromaticity of a benzenoid or heterocyclic ring occasioned by steric overcrowding or restrictive ring bridging.

Tetrahedron, **1992**, *48*, 1683

SYNTHESIS OF 2'-*C*-CYANO-2'-DEOXY- AND 2'-*C*-CYANO-2',3'-DIDEOXY-β-D-ARABINOFURANOSYL NUCLEOSIDES.

Sonsoles Velázquez and María-José Camarasa
Instituto de Química Médica, Juan de la Cierva 3, 28006-Madrid, Spain

2'-*C*-Cyano-2'-deoxy- and 2'-*C*-cyano-2',3'-dideoxy nucleosides have been prepared from the corresponding 2'-ketonucleosides by reaction with NaCN, followed by deoxygenation of the cyanohydrins formed and removal of the protecting groups of the sugar moiety.



Tetrahedron, **1992**, *48*, 1695

ELECTRONIC EFFECTS IN THE REGIOSELECTIVITY OF NUCLEOPHILIC ATTACKS ON CATIONIC 1,3-DIARYL-π-ALLYLPALLADIUM COMPLEXES

M. Prat, J. Ribas, M. Moreno-Mañas;* Department of Chemistry. Universitat Autònoma de Barcelona. Bellaterra. 08193-Barcelona. Spain

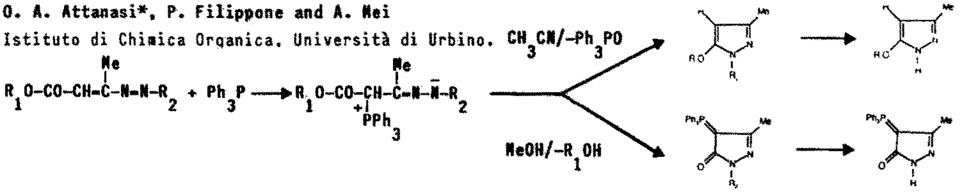
Nucleophilic attacks on π-allylpalladium complexes derived from $O_2NPh{-}(CH{-}CH{-}CH){-}PhX$ (X = OMe, Cl) occur with high regioselectivity at the allylic terminus remote from the electron-withdrawing group (NO_2).

$$\underset{\text{or allylic isomer}}{O_2NPh{-}CH{=}CH{-}CH(OAc){-}PhX} + Nu^- \xrightarrow{Pd(0)} \underset{\text{Major}}{O_2NPh{-}CH{=}CH{-}CH(Nu){-}PhX} + \underset{\text{Minor}}{O_2NPh{-}CH(Nu){-}CH{=}CH{-}PhX}$$

Tetrahedron, **1992**, *48*, 1707

CONJUGATED AZOALKENES. PART XI. DIRECT SYNTHESIS OF SUBSTITUTED PYRAZOLES AND 4-TRIPHENYLPHOSPHORANYLIDENE-4,5-DIHYDROPYRAZOL-5-ONES BY HETEROCYCLIZATION OF SOME ZWITTERIONIC 1,4-ADDUCTS BETWEEN CONJUGATED AZOALKENES AND TRIPHENYLPHOSPHINE

O. A. Attanasi*, P. Filippone and A. Mei
Istituto di Chimica Organica, Università di Urbino.



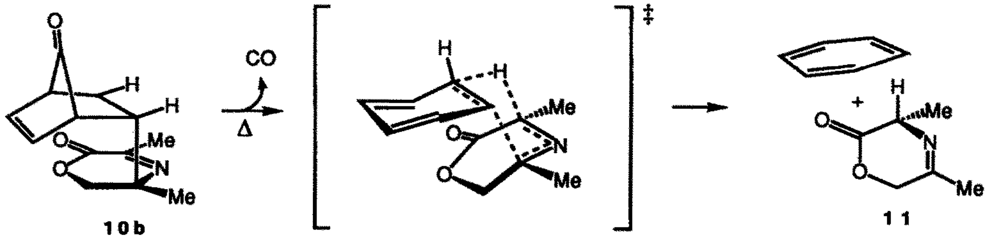
$$R_1O{-}CO{-}CH{=}\overset{\overset{Me}{|}}{C}{-}N{=}N{-}R_2 + Ph_3P \longrightarrow R_1O{-}CO{-}\underset{\underset{PPh_3}{+|}}{CH}{-}\overset{\overset{Me}{|}}{C}{=}N{-}\bar{N}{-}R_2 \quad \xrightarrow{CH_3CN/-Ph_3PO} \quad \xrightarrow{MeOH/-R_1OH}$$

Tetrahedron, **1992**, *48*, 1715

A NEW RETRO-AZA-ENE REACTION: FORMAL REDUCTIVE AMINATION OF AN α-KETO ACID TO AN α-AMINO ACID

David B. Berkowitz* and W. Bernd Schweizer, Laboratorium für Organische Chemie, ETH, CH-8092, Zürich, SWITZERLAND

Pyruvate derivatives **10a** and **10b** undergo a tandem cheleotropic elimination/retro-aza-ene reaction to produce **11**, CO and benzene. This is the first instance of the formal reductive amination of an α-keto acid to a protected α-amino acid via a thermal rearrangement.

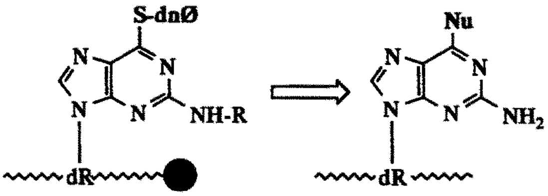


Tetrahedron, **1992**, *48*, 1729

SYNTHESIS BY POST-SYNTHETIC SUBSTITUTION OF OLIGOMERS CONTAINING GUANINE MODIFIED AT THE 6-POSITION WITH S-, N, O-DERIVATIVES

Yao-Zhong Xu*, Qinguo Zheng and Peter F. Swann
Cancer Research Campaign
Nitrosamine-Induced Cancer Research Group
Department of Biochemistry and Molecular Biology
University College London
Gower Street, London WC1E 6BT, England

The phosphoramidite of N^2-protected 6-(2,4-dinitrophenyl)-thioguanine was incorporated into oligodeoxynucleotides. Post-synthetic conversion gave DNA containing 6-thioguanine, 2,6-diaminopurine, 2-amino-6-methylaminopurine, O^6-methyl-guanine or guanine in high yield and purity.



Nu: SH, NH_2, NHMe, OMe, OH