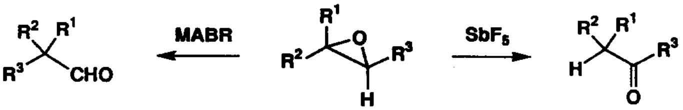
GRAPHICAL ABSTRACTS

Tetrahedron, **1994**, *50*, 3663

Lewis Acid-Promoted Selective Rearrangement of Trisubstituted Epoxides to Aldehydes or Ketones

Keiji Maruoka, Noriaki Murase, Ronan Bureau, Takashi Ooi, and Hisashi Yamamoto*
School of Engineering, Nagoya University Chikusa, Nagoya 464-01, Japan

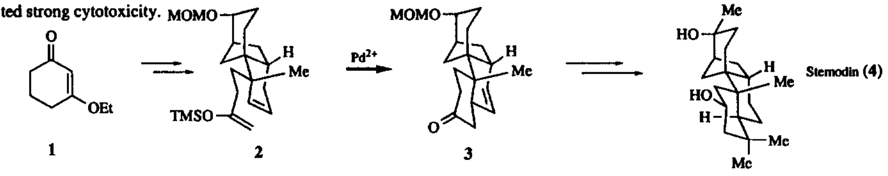


Tetrahedron, **1994**, *50*, 3673

Stemodin Synthesis (II)——Highly Diastereoselective Formal Total Synthesis of (±)-Stemodin *via* Pd^{2+}-Promoted Cycloalkenylation Reaction

Msahiro Toyota, Takashi Seishi, and Keiichiro Fukumoto*, Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980, Japan

Beginning with 1, diastereoface-selective Pd^{2+}-promoted cycloalkenylation reaction (2 → 3) has been employed as the key step for a conceptually new and highly diastereocontrolled formal total synthesis of (±)-stemodin (4). Interestingly, some synthetic intermediates exhibited strong cytotoxicity.

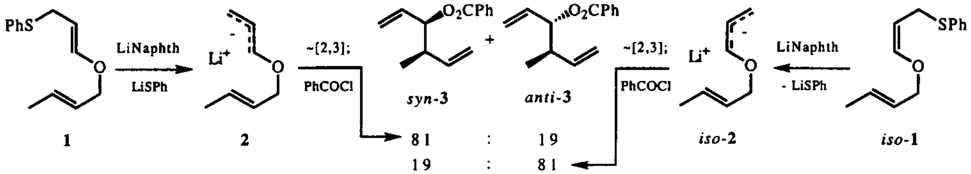


Tetrahedron, **1994**, *50*, 3687

THE GEOMETRY OF THE CARBANIONIC MOIETY INFLUENCES THE NON-INDUCED DIASTEREOSELECTIVITY OF THE [2,3]-WITTIG REARRANGEMENT OF LITHIATED DIALLYL ETHERS

Dirk Goeppel#), Ingo Münster§), and Reinhard Brückner#)*
#) Institut für Organische Chemie der Georg-August-Universität, Tammannstr. 2, D-37077 Göttingen, Germany; §) Fachbereich Chemie der Philipps-Universität, Hans-Meerwein-Str., D-35043 Marburg, Germany.

Lithium naphthalenide and enol ethers 1 and *iso*-1 give lithioethers 2 and *iso*-2, respectively, which rearrange with opposite *syn,anti*-selectivity.

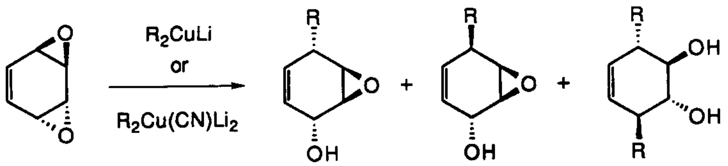


Tetrahedron, **1994**, *50*, 3709

Concerning the Reaction of *anti*-Benzene Dioxide with Various Nucleophiles

Thomas Esser, Frédéric Farkas, Sissi Mangholz, Urs Séquin*
Institut für Organische Chemie, Universität Basel, St. Johanns-Ring 19, CH-4056 Basel, Switzerland

Reaction of *anti*-benzene dioxide with *C*-nucleophiles leads to 1,4-addition products: addition occurs to the vinyloxirane part of the benzene dioxide rather than to the diepoxide unit.



DONOR SUBSTITUTED SULFONYL CARBENES, 2: ORGANOTHIO SULFONYL CARBENES

Tetrahedron, **1994**, *50*, 3721

K. Schank[a], A.A. Abdel-Wahab[b], S. Bügler[a], P. Eigen[a], J. Jager[a], K. Jost[a]

a) Department of Organic Chemistry, University of Saarbrücken, D-66041 Saarbrücken
b) Chemistry Department, Faculty of Science, University of Assiut, Assiut/Egypt

Generation and reactions of electrophilic organothio sulfonyl carbenes are described, sulfinate-sulfone Pummerer rearrangement and carbene (carbenoid) trapping methods (dimers, cyclopropanes a.s.o.) are presented.

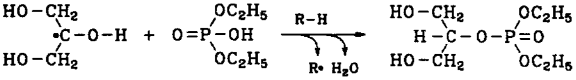
$$R^1SO_2—\bar{C}—SR^2$$

GLYCEROL-2-DIETHYL PHOSPHATE BY PHOTOCHEMICAL REACTION OF DIHYDROXY ACETONE WITH DIETHYL PHOSPHORIC ACID

Tetrahedron, **1994**, *50*, 3743

J. Schole and Ch . Schole,
Institut für Physiologische Chemie der Tierärztlichen Hochschule Hannover, Bünteweg 17, D-30559 Hannover, Germany.

Photochemically excited dihydroxy acetone reacts in 1,2-dimethoxy-ethane - presumably under H abstraction from the solvent and elimination of water - with diethyl phosphoric acid to form glycerol-2-diethyl phosphate, which may be very important for the cellular energy production:



SYNTHESIS OF PEPTIDE DERIVATIVES OF 5-FLUOROURACIL

Marieta Nichifor and Etienne Schacht*, Department of Organic Chemistry, Biomaterial Research Group, University of Ghent, 9000 Ghent, Belgium

Tetrahedron, **1994**, *50*, 3747

The preparation of some peptides carrying 5-fluorouracil as an α-substituent of a C-terminal glycine moiety is described.

$$\text{Z-A-CONH}_2 + \text{O=CHCOOEt} \rightarrow \text{Z-A-CONH-CH(OH)COOEt} \xrightarrow[\text{Py}]{\text{Ac}_2\text{O}} \text{Z-A-CONH-CH(OAc)COOEt} \xrightarrow[\text{DMF/TEA}]{\text{FU}} \text{Z-A-CONH-CH(FU)COOEt}$$

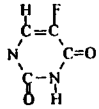
$$\text{Z-A-CONH-CH(FU)COOEt} \xrightarrow[\text{Pd/C}]{\text{1,4-cyclohexadiene}} \text{H-A-CONH-CH(FU)COOEt}$$

$$\text{H-(A-CO)}_{x+1}\text{-NH-CH(FU)COOEt} \xleftarrow[\text{DMF}]{\text{DEA}} \text{Fmoc-(A-CO)}_{x+1}\text{-NH-CH(FU)COOEt} \xleftarrow[\text{DMF/HOBt}]{\text{Fmoc-(A-CO)}_x\text{-OPFF}} \text{H-A-CONH-CH(FU)COOEt}$$

A = NHCH(R) [Gly,Ala,Phe,Leu]

PFF = pentafluorophenyl

FU =



Z = benzyloxycarbonyl

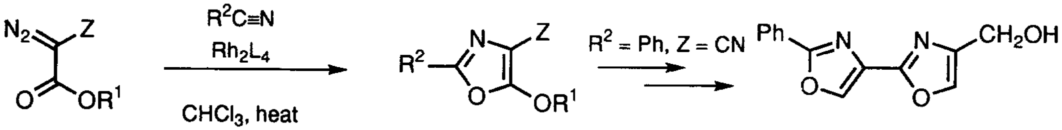
x = 2-3

Fmoc = 9-fluorenyloxycarbonyl

Tetrahedron, **1994**, *50*, 3761

THE RHODIUM CARBENOID ROUTE TO OXAZOLES. SYNTHESIS OF 4-FUNCTIONALISED OXAZOLES; THREE STEP PREPARATION OF A BIS-OXAZOLE

Kevin J. Doyle and Christopher J. Moody
Department of Chemistry, Loughborough University of Technology, Loughborough, Leicestershire LE11 3TU, U.K.



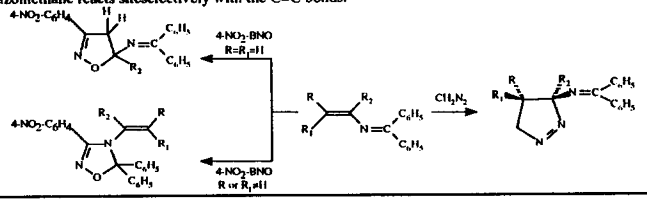
Oxazole-4-sulfones,-phosphonates, and -nitriles are prepared by rhodium(II) catalysed addition of diazocarbonyl compounds to nitriles; a 4-cyanooxazole is readily converted into a bis-oxazole.

Substituent Effects on 1,3-Dipolar Cycloadditions to Some 1,1-Diphenyl-2-Aza-1,3-Butadiene Derivatives.

Tetrahedron, **1994**, *50*, 3773

Cesarino Balsamini*[a] , Annalida Bedini[a], Marina Burdisso[b], Anna Maria Capelli[c], Gilberto Spadoni[a].
a: Istituto di Chimica Farmaceutica - Università degli Studi - Piazza del Rinascimento 6, 61029 - Urbino - Italy.
b: Dipartimento di Chimica Organica - Università degli Studi - Via Taramelli 10, 27100 - Pavia - Italy
c: Glaxo Research Laboratories - Via Fleming, 4 - 37100 Verona - Italy.

1,1-Diphenyl-2-aza-1,3-butadiens cycloadd selectively 1,3-dipoles. p-Nitrobenzonitrile oxide attacks either the C=C or C=N depending on the presence of C4 substituents; differently, diazomethane reacts siteselectively with the C=C bonds.

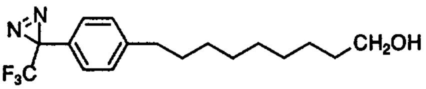


SYNTHESIS OF A PHOTOACTIVATABLE 9-Z-OLEIC ACID FOR PROTEIN KINASE C LABELING

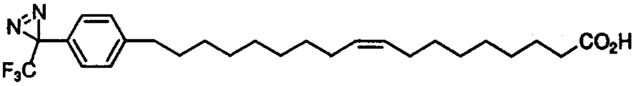
Tetrahedron, **1994**, *50*, 3785

A. Rühmann and Curt Wentrup, Department of Chemistry, The University of Queensland, Brisbane, QLD 4072, Australia

A convenient synthesis of (Z)-18-[4-[3-(trifluoromethyl)diazirinyl]phenyl]-9-octadecenoic acid (13) for photoaffinity labeling is described. Photochemical experiments on 13 and its precursor 11 in ethanol solution as well as in an argon matrix at 12 K demonstrate the formation of diazo compounds and ultimately carbene-derived products.



11



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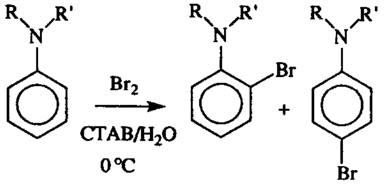
SURFACTANT CONTROL OF THE ORTHO/PARA RATIO IN THE BROMINATION OF ANILINES. 2. Giorgio Cerichelli, Giovanna Mancini; Centro CNR di Studio sui Meccanismi di Reazione, Dipartimento di Chimica, Universita' degli Studi di Roma "La Sapienza", P.le A. Moro 2 00185 Roma (Italy). Luciana Luchetti; Dipartimento di Scienze e Tecnologie Chimiche, Universita' degli Studi di Roma "Tor Vergata" Via della Ricerca Scientifica 00133 Roma (Italy). The presence of surfactant strongly affects the regioselectivity of the bromination of anilines 1, 2, 3, 4 and 5. The regioselectivity depends on the nature of the substituents on the nitrogen and on the temperature.

Tetrahedron, **1994**, *50*, 3797



1	$R=CH_3$, $R'=CH_2CH_3$	*ortho* 50%, *para* 50%
2	$R,R'=CH_2CH_3$	*ortho* 50%, *para* 50%
3	$R=CH_3$, $R'=(CH_2)_3CH_3$	*ortho* 50%, *para* 50%
4	$R,R'= -(CH_2)_2-$	*ortho* 85%, *para* 15%
5	$R= -(CH_2)_2-$, $R'= -(CH_2)_3-$	*ortho* 20%, *para* 80%

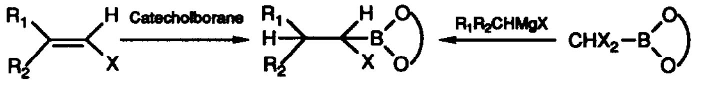
FACILE ROUTES TO 1-HALO-1-ALKYL BORONIC ESTERS AS PRECURSORS FOR NOVELTHROMBIN INHIBITORS

Tetrahedron, **1994**, *50*, 3803

Said Elgendy*, Goran Claeson, Vijay V. Kakkar, Donovan Green, Geeta Patel, Christopher A. Goodwin, Jehan Baban, Michael Scully, John Deadman

Thrombosis Research Institute, Emmanuel Kaye Building, Manresa Road, Chelsea, London SW3 6LR, UK.

Methods of synthesis are described of α-halo boronic esters by hydroboration of 1-halo-1-alkene with catecholborane and reaction of pinanediol (dichloromethyl) boronate with organometallic reagents

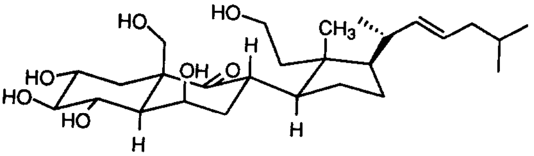


EURYSPONGIOLS: TEN NEW HIGHLY HYDROXYLATED 9,11-SECOSTEROIDS WITH ANTIHISTAMINIC ACTIVITY FROM THE SPONGE *EURYSPONGIA* SP. STEREOCHEMISTRY AND REDUCTION

Tetrahedron, **1994**, *50*, 3813

José Dopeso[1], Cécile Debitus[2], Patricia R. Bergquist[3], Emilio Quiñoá[1], Ricardo Riguera[1]*
[1]Departamento de Química Orgánica, Facultad de Química, Universidad de Santiago de Compostela, 15706 Santiago de Compostela, Spain. [2]Centre Orstom, B. P. A5, Nouméa Cedex, New Caledonia. [3]School of Biological Sciences, University of Auckland, Auckland, New Zealand.

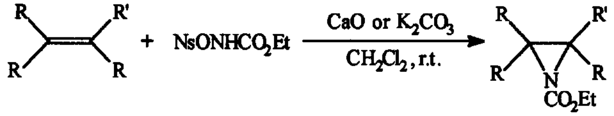
Ten novel polyhydroxylated 9,11-secosterols, **1-10**, with strong antihistaminic activity, have been isolated from the sponge *Eurysponga* sp., and their structures elucidated by spectroscopic studies and chemical transformations, including stereospecific reduction of the C-9 ketone.



IMPROVED AMINATION BY ETHYL *N*-{[(4-NITROPHENYL)SULPHONYL]OXY}CARBAMATE IN THE PRESENCE OF INORGANIC OXIDES OR CARBONATES

Tetrahedron, **1994**, *50*, 3829

Marco Barani, Stefania Fioravanti,* M. Antonietta Loreto, Lucio Pellacani,* and Paolo A. Tardella
Dipartimento di Chimica, Università "La Sapienza", P.le Aldo Moro 2, I-00185 Roma, Italy



R= H, alkyl   R' = alkyl, $-OSiMe_3$, $-O(CH_2)_2OSiMe_3$, $-CH_2SiMe_3$

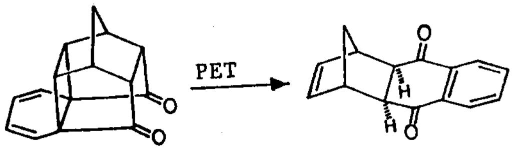
The reaction does not require either catalyst or ultrasounds. Good yields were obtained in short times.

STUDIES ON CYCLOBUTYL BOND CLEAVAGE BY ADJACENT KETYL RADICAL GENERATED UNDER PET CONDITIONS

Tetrahedron, **1994**, *50*, 3835

Bipin Pandey*, Ashok T. Rao, Pramod V Dalvi and Pradeep Kumar
National Chemical Laboratory, Pune 411 008, India

Generality and limitations of the cleavage of cyclobutyl ketones have been examined under PET conditions. The cleavage of cyclopentane ring is proposed during efficient endo to exo isomerization.



Tetrahedron, **1994**, *50*, 3843

EFFICIENT CLEAVAGE OF CYCLOPROPYL BOND BY ADJACENT KETYL RADICAL GENERATED UNDER PET CONDITIONS

Bipin Pandey*, Ashok T. Rao, Pramod V. Dalvi and Pradeep Kumar
National Chemical Laboratory, Pune 411 008, India.

Irradiation of conjugated cyclopropyl and epoxy ketones either at 254 nm or at 300 nm under PET conditions leads to efficient regioselective cleavage. Interesting wavelength dependance phenomenon is observed.