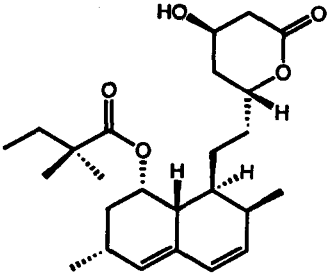
GRAPHICAL ABSTRACTS

Tetrahedron, 1993, 49, 4447

AUTOOXIDATION OF SIMVASTATIN

George B. Smith*, Lisa DiMichele*, Lawrence F. Colwell, Jr., George C. Dezeny, Alan W. Douglas, Robert A. Reamer, and Thomas R. Verhoeven, Department of Process Research, Merck Research Laboratories, Division of Merck & Co., Inc., Rahway, N.J.

Autooxidation of the cholesterol-lowering agent simvastatin in ethylene dichloride solution with an azo-type free-radical initiator was investigated in kinetic studies using HPLC. The primary products were oligomers, with peroxide groups within the backbone chain, and some monomeric epoxides. These and several secondary products were isolated chromatographically and identified spectroscopically. A reaction scheme was proposed in which the oligomers arise from competitive hydrogen abstraction and addition reactions of oligomeric free radicals with simvastatin while the epoxides arise from homolytic peroxide cleavage.



Tetrahedron, 1993, 49, 4463

CONCERNING THE MECHANISM OF DISPLACEMENT OF NITRO GROUPS FROM ACTIVATED AROMATIC SYSTEMS

Donald B. Denney*, Dorothy Z. Denney and Airan Jun Perez
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P.O. Box 939, Piscataway, NJ 08855-0939

The displacement of nitro groups from various activated aromatic systems by a variety of nucleophiles are subject to inhibition. It is concluded that the aromatic systems are converted to nondissociating radical anions which then react with the nucleophile.

Tetrahedron, 1993, 49, 4477

SOME NOVEL CONCEPTS IN AROMATIC REACTIVITY

Joseph F. Bunnett, Thimann Laboratories, University of California, Santa Cruz, CA 95064

Proposals by Denney & Denney that $S_{RN}1$ reactions occur instead by the $S_{RN}2$ mechanism, and that alkoxide hydrodehalogenations likewise involve reaction directly with $ArX^{\bullet -}$, raise serious problems.

$S_{RN}1$ key steps: $ArX^{\bullet -} \longrightarrow Ar^{\bullet} + X^-$

$Ar^{\bullet} + Nu^- \longrightarrow ArNu^{\bullet -}$

$S_{RN}2$ proposal: $ArX^{\bullet -} + Nu^- \longrightarrow ArNu^{\bullet -} + X^-$

Tetrahedron, **1993**, *49*, 4485

On the $S_{RN}1$ - $S_{RN}2$ Mechanistic Possibilities

Roberto A. Rossi* and Sara M. Palacios
Dpto. de Química Orgánica and CEQUIMAP, Fac. de Ciencias Químicas, Universidad Nacional de Córdoba, Suc. 16, C.C. 61, Córdoba, Argentina.

The $S_{RN}1$ and $S_{RN}2$ mechanistic possibilities are discussed taking into consideration kinetic data , nucleophilic reactivity and reactions of substrates with different leaving groups.

$$S_{RN}1:\quad (RX)^{\cdot -} \xrightarrow{-X^-} R^{\cdot} \xrightarrow{\overset{-}{Nu}} (RNu)^{\cdot -} \xrightarrow{ET} RNu$$

$$S_{RN}2:\quad (RX)^{\cdot -} + \overset{-}{Nu} \longrightarrow X^- + (RNu)^{\cdot -} \xrightarrow{ET} RNu$$

Tetrahedron, **1993**, *49*, 4495

THE $S_{RN}1$ REACTIONS OF ARYL HALIDES WITH CARBANIONS INITIATED BY SODIUM AMALGAM IN LIQUID AMMONIA

Eduardo Austin, Carlos G. Ferrayoli, Rubén A. Alonso and Roberto A. Rossi
Dpto. Química Orgánica - Fac. Cs. Químicas - U.N.C. - C.C.61 - 5016 Córdoba - Argentina

$$ArX + {}^{-}CH_2COR \xrightarrow[NH_3]{Na(Hg)} Ar\text{-}CH_2COR$$

ArX: 1-chloronaphthalene, 2-chloroquinoline
2-chloropyridine, 4-bromobenzophenona

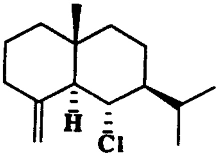
Tetrahedron, **1993**, *49*, 4503

ACANTHENES A TO C: A CHLORO, ISOTHIOCYANATE, FORMAMIDE SESQUITERPENE TRIAD ISOLATED FROM THE NORTHEASTERN PACIFIC MARINE SPONGE *ACANTHELLA* SP. AND THE NUDIBRANCH *CADLINA LUTEOMARGINATA*

D.L. Burgoyne, E.J. Dumdei and R.J. Andersen*, Departments of Chemistry and Oceanography, University of British Columbia, Vancouver, B.C. CANADA V6T 1Z1

Acanthenes A (1), B (2) and C (3), three new eudesmane sesquiterpenoids, have been isolated from the nudibranch *Cadlina luteomarginata* and the sponge *Acanthella* sp., a predator-prey pair. Acanthene A (1) appears to represent the first example of the co-occurrence a chloro sesquiterpenoid analog of sponge isothiocyanate, formamide or isonitrile sesquiterpenoids.

1

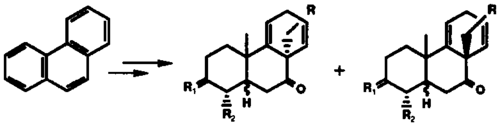


Tetrahedron, **1993**, *49*, 4511

STEREOSELECTIVE ROUTE TO HIGHLY FUNCTIONALIZED 4a,8a-SUBSTITUTED- 1,2,3,4,4a,6,8a,9,10,10a-DECAHYDROPHENANTHRENES, A NEW ENTRY TO THE QUASSINOID AND FUSIDANE FRAMEWORKS.

Alejandro J. Vila, Raquel M. Cravero and M. González Sierra*Instituto de Química Orgánica de Síntesis (IQUIOS), Facultad de Ciencias Bioquímicas y Farmacéuticas, Suipacha 531, 2000 Rosario, ARGENTINA.

The title compounds had been prepared, in a stereospecific way from the corresponding benzylic ketones, by a sequence involving a reductive Birch alkylation. The use of oxigenated alkylating agents allowed the introduction of protected alcoholic functions at the angular positions.

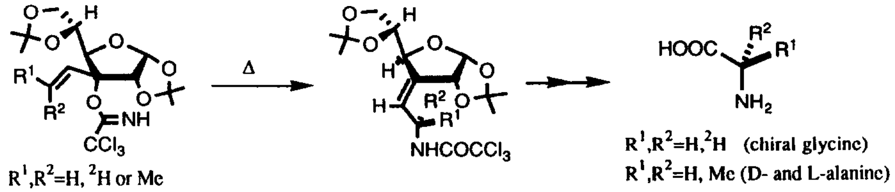


Tetrahedron, **1993**, *49*, 4527

The Overman Rearrangement on a Diacetone-D-Glucose Template: Kinetic and Theoretical Studies on the Chirality Transcription

Tadashi Eguchi , Takashi Koudate, and Katsumi Kakinuma*
Department of Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

Kinetic and theoretical studies on the chirality transcription using the Overman rearrangement leading to chiral amino acids on a diacetone-D-glucose template were described.



R^1,R^2=H,^{2}H or Me

R^1,R^2=H,^{2}H (chiral glycine)

R^1,R^2=H, Me (D- and L-alanine)

Tetrahedron, **1993**, *49*, 4541

LIPASE-CATALYZED PEPTIDE SYNTHESIS USING Z-AMINO ACID ESTERS AS ACYL DONORS IN AQUEOUS WATER-MISCIBLE ORGANIC SOLVENTS

Katsuhiro Kawashiro*, Kohji Kaiso, Daisuke Minato, Shigeru Sugiyama, and Hiromu Hayashi
Department of Chemical Science and Technology, Faculty of Engineering, The University of Tokushima, Minamijosanjima, Tokushima 770, Japan

Influence of an added organic cosolvent, pH of buffer, concentration of a nucleophile, and reaction temperature on lipase-catalyzed peptide synthesis was studied .

$$\text{Z-Phe-OEt} + \text{Phe-NH}_2 \xrightarrow{\text{PPL}} \text{Z-Phe-Phe-NH}_2 + \text{EtOH}$$

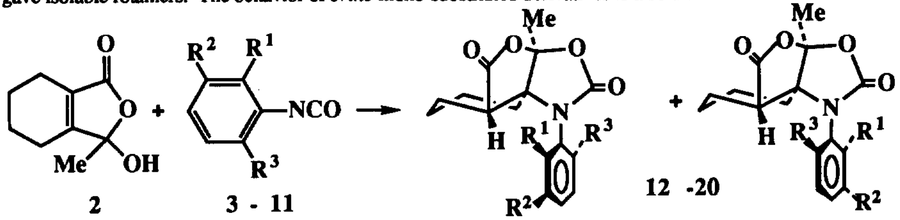
Z : Benzyloxycarbonyl , Et : Ethyl , PPL : Porcine pancreas lipase

Tetrahedron, **1993**, *49*, 4549

SYNTHESIS AND STEREOCHEMICAL BEHAVIOR OF 1-ARYLOCTAHYDROISOBENZOFURO[7a,1-*d*]OXAZOLE RING SYSTEM: NEW EXAMPLES OF ISOLABLE ROTAMERS.

Kenji Saito, *,[1] Makoto Yamamoto, Kazutoshi Yamada.
Graduate School of Science and Technology, Chiba University, 1-33 Yayoi-cho, Chiba-shi, 260 Japan
[1] Present Address: Organic Synthesis Laboratory, Nippon Soda Co. LTD., 345, Takada, Odawara-shi, Kanagawa, 250-02 Japan.

Reaction of hydroxylactone **2** with isocyanates **3** - **11** gave the corresponding **12** - **20** in good yields. Among them, *ortho* di-substituted ones gave isolable rotamers. The behavior of *ortho* mono-substituted derivatives is also discussed.

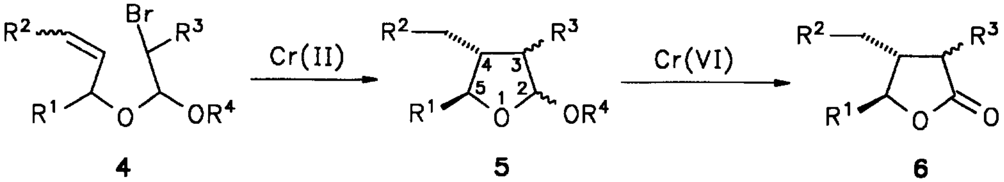


Tetrahedron, **1993**, *49*, 4559

NEW METHODS FOR REDUCTIVE FREE-RADICAL CYCLIZATIONS OF α-BROMOACETALS TO 2-ALKOXYTETRAHYDROFURANS WITH ACTIVATED CHROMIUM(II)-ACETATE

Claus Hackmann and Hans J. Schäfer*
Organisch-Chemisches Institut der Universität Münster, Correnstraße 40, D-4400 Münster, Germany

The tetrahydrofurans **5** (75-93 %) are oxidized to the γ-butyrolactones **6** (71-97 %). The diastereoselectivity of the cyclization depends on the substitution pattern of **4** and ranges between 30.4 : 1 to 1 : 54.8.

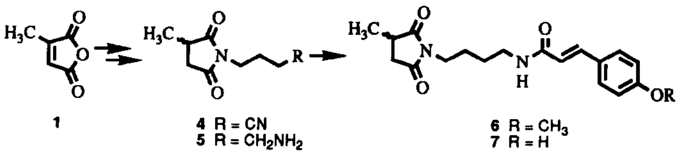


Tetrahedron, **1993**, *49*, 4575

Simple Synthesis of (±)-(*E*)-3-(4-Hydroxyphenyl)-*N*-[4-(3-methyl-2,5-dioxo-1-pyrrolidinyl)butyl]-2-propenamide, a Novel Phenolic Amide Derivative from the Bulbs of *Lilium regale* WILSON

Paul Kuehne and Manfred Hesse*
Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland

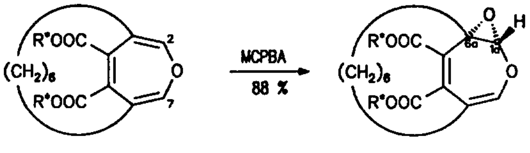
A preparation of (±)-(*E*)-3-(4-hydroxyphenyl)-*N*-[4-(3-methyl-2,5-dioxo-1-pyrrolidinyl)butyl]-2-propenamide (7) is described. Overall yield was 45%.



Tetrahedron, **1993**, *49*, 4581

STEREOSELECTIVE EPOXIDATION OF DI-[3-*O*-(1,2:5,6-DIISOPROPYLIDENE)-α-D- AND α-L-GLUCOFURANOSYL]-3,6-HEXANOOXEPINE-4,5-DICARBOXYLATE

Werner Tochtermann*, Brigitta Popp und Frank Ott,
Institut für Organische Chemie der Universität
Olshausenstr. 40, D-2300 Kiel 1, FRG
Eva-Maria Peters, Karl Peters und H.G. von Schnering,
Max-Planck-Institut für Festkörperforschung
Heisenbergstr. 1, D-7000 Stuttgart 80, FRG



1a R*OH = Diacetone-D-glucose 2a

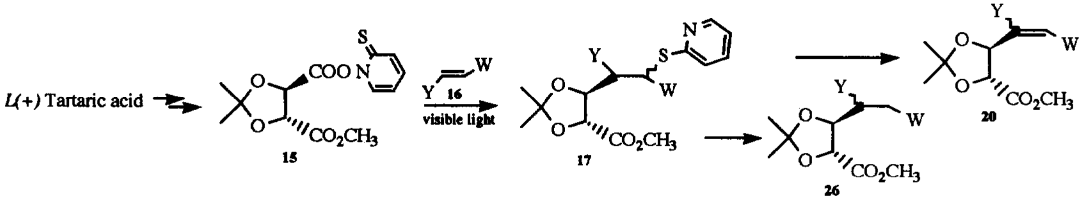
The stereoselective epoxidation of (−)-**1a** and its enantiomer (+)-**1b** is described.

Tetrahedron, **1993**, *49*, 4589

RADICAL DECARBOXYLATIVE ALKYLATION OF TARTARIC ACID

Derek H. R. Barton*[a], Alice Gateau-Olesker[b], Stephan D. Géro[b], Brigitte Lacher[b], Catherine Tachdjian[a] and Samir S. Zard[c].
a) Department of Chemistry, Texas A&M University, College Station, Texas 77843.b) Institut de Chimie des Substances Naturelles, C.N.R.S., 91198 Gif-sur-Yvette, France.c) Laboratoire de Synthèse Organique, Ecole Polytechnique, 92128 Palaiseau, France.

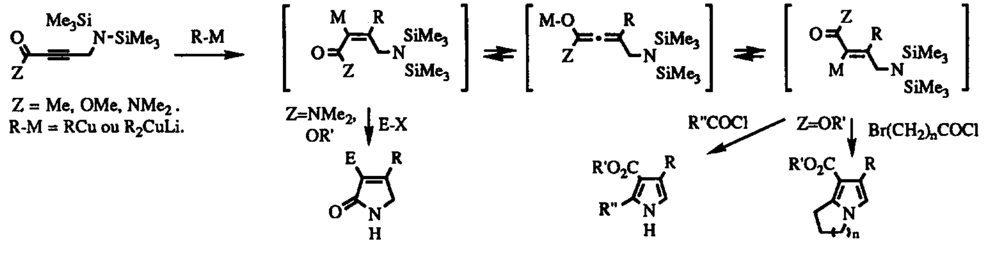
*Carbon radicals generated by the photolysis of **15** add stereoselectively to the olefin **16** to give the addition product **17** with retention of configuration at the dioxolane ring. Oxidation-elimination and reduction of the thiopyridyl group gave the derivatives **20** and **26**.*



Tetrahedron, **1993**, *49*, 4603

AMINOSILANES IN ORGANIC SYNTHESIS. ADDITION OF ORGANOCOPPER REAGENTS ON γ-BIS(TRIMETHYLSILYL)AMINO-α-ACETYLENIC AMIDES, ESTERS AND KETONES. STEREOCHEMISTRY AND SOME SYNTHETIC USES.

Robert J.P. Corriu*, Geng Bolin, Javed Iqbal, Joël J.E. Moreau* and Claude Vernhet - Université de Montpellier II, F-34095 Montpellier Cedex 05- France.

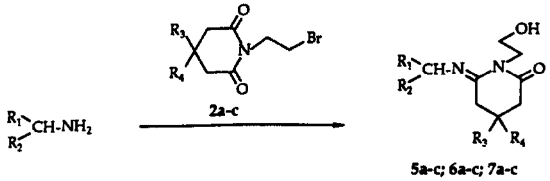


Z = Me, OMe, NMe$_2$.
R-M = RCu ou R$_2$CuLi.

Tetrahedron, **1993**, *49*, 4619

Synthèse de N-(2-Hydroxyéthyl)iminoglutarimides à partir de N-(2-Bromoéthyl)glutarimides

Tchao Podona, Saïd Lazar, Gérard Coudert, Gérald Guillaumet.
Laboratoire de Chimie Bioorganique et Analytique, URA CNRS n°499, Université d'Orléans, BP. 6759, 45067 Orléans Cedex 2, France.



Conditions : K_2CO_3, DMF, 60°C (68-82%)

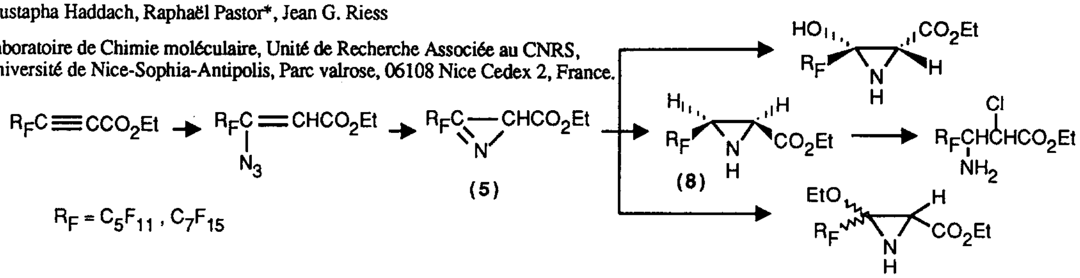
Une synthèse générale de N-(2-hydroxyéthyl)iminoglutarimides est décrite.

Tetrahedron, **1993**, *49*, 4627

SYNTHESE ET REACTIVITE DE NOUVEAUX SYNTHONS PERFLUOROALKYLES. COMPORTEMENT ATYPIQUE DES AZIRINES ET AZIRIDINES *F*-ALKYLEES

Mustapha Haddach, Raphaël Pastor*, Jean G. Riess

Laboratoire de Chimie moléculaire, Unité de Recherche Associée au CNRS,
Université de Nice-Sophia-Antipolis, Parc valrose, 06108 Nice Cedex 2, France.



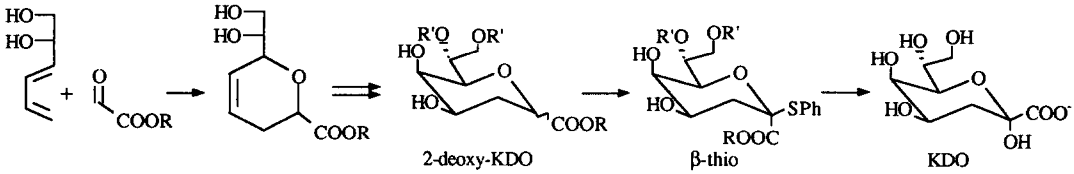
The reactivity of *F*-alkyl substituted azirines (5) and aziridines (8) is different from that of their hydrocarbon analogues.

Tetrahedron, **1993**, *49*, 4639

New Strategy in the Synthesis of 3-Deoxy-D-manno-2-octulosonic acid (KDO), 2-Deoxy-KDO and Thioglycoside of KDO

A. Lubineau, J. Augé*, N. Lubin
Laboratoire de Chimie Organique Multifonctionnelle associé au CNRS, Institut de Chimie Moléculaire d'Orsay, Bât. 420, 91405 ORSAY Cedex, France

This strategy lies on an aqueous hetero Diels-Alder reaction with a water-soluble diene derived from D-glyceraldehyde, followed by dihydroxylation, bis-inversion and oxidation. This synthesis leads to 2-deoxy-KDO, thioglycoside of KDO and KDO.

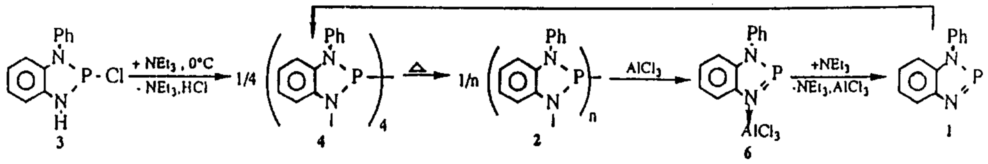


Tetrahedron, **1993**, *49*, 4651

IS THE PREVIOUSLY DESCRIBED N-PHENYL 4,5-BENZO 1,3,2 DIAZAPHOSPHOLE A DICOORDINATED PHOSPHORUS COMPOUND ?

Serge Kaji Nitcheu and Christian Malavaud
Laboratoire de Synthèse, Structure et Réactivité des Molécules Phosphorées, Université Paul Sabatier, 118 Route de Narbonne,
31062 TOULOUSE Cedex - FRANCE

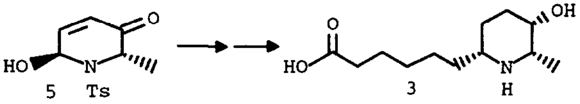
A synthesis of the N-phenyl cyclotetraphosphazane 4 and the N-phenyl cyclophosphazane 2 via the 1-phenyl 2-chloro 1,3,2-diazaphospholine 3 One have characterized the complexed dicoordonated phosphorus compound 6 obtained by complexation of 2 with AlCl$_3$.



Tetrahedron, **1993**, *49*, 4659

A NEW CONCISE STEREOSELECTIVE TOTAL SYNTHESIS OF (+)-AZIMIC ACID

Zhi-Hui Lu and Wei-Shan Zhou* Shanghai Institute of Organic Chemistry,
Chinese Academy of Sciences,345 Lingling Lu, Shanghai 200032, China

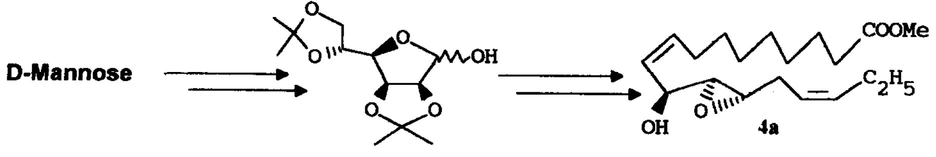


A new concise stereoselective total synthesis of (+)-azimic acid, which is the immediate precursor of macrocyclic dilactone azimine, has been achieved in eleven steps from (2S, 6S)-6-hydroxy-2-methyl-N-tosyl-Δ^4-piperidone-3 (5) with an high overall yield (36%).

Tetrahedron, **1993**, *49*, 4665

STEREOSELECTIVE SYNTHESIS OF METHYL (11*S*,12*S*,13*S*)-(9*Z*,15*Z*)-11-HYDROXY-12,13-EPOXY OCTADECADIENOATE FROM D-MANNOSE

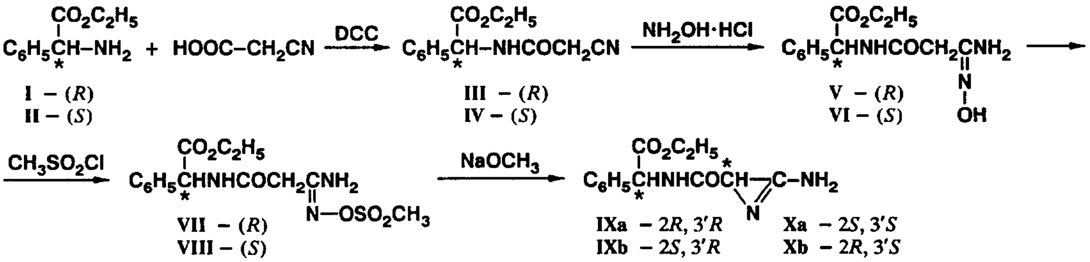
Wen-Lian Wu and Yu-Lin Wu*
State Key Laboratory of Bio-organic and Natural Products Chemistry
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, CHINA



SYNTHESIS AND STRUCTURE OF OPTICALLY ACTIVE 3-AMINO-2H-AZIRINES

Tetrahedron, **1993**, *49*, 4671

I.P. Piskunova, A.V. Eremeev, A.F. Mishnev, I.A. Vosekalna; Institute of Organic Synthesis, Latvian Academy of Sciences, Aizkraukles 21, 226006 Riga, LATVIA



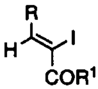
NEW SYNTHETIC APPLICATIONS OF ORGANOTIN COMPOUNDS: SYNTHESIS OF STEREODEFINED 2-IODO-2-ALKENONES, 2-SUBSTITUTED (*E*)-2-ALKENONES AND 2-METHYL-2-CYCLOALKENONES

Tetrahedron, **1993**, *49*, 4677

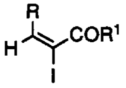
Fabio Bellina, Adriano Carpita, Donatella Ciucci, Massimo De Santis and Renzo Rossi*.
Dipartimento di Chimica e Chimica industriale – University of Pisa. – Via Risorgimento 35, I-56126 Pisa, Italy.

Compounds (*Z*)- and (*E*)-**8**, which have been prepared from compounds **10**, undergo Pd-catalyzed reaction with organostannanes to give the cross-coupled products, **13**, having in general E-stereochemistry.

Compounds **18** also undergo Pd-catalyzed reaction with $SnMe_4$, to give 2-methyl-2-cycloalkenones, **19**.



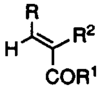
(*Z*)-**8**



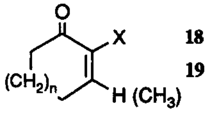
(*E*)-**8**

$R-\equiv-COR^1$

10



13



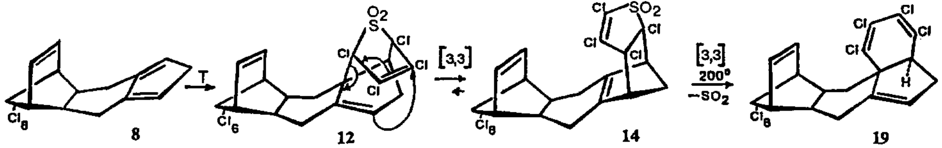
18: X = I ; n = 0, 1

19: X = CH_3 ; n = 0, 1

SEQUENTIAL CYCLOADDITION-CYCLOREVERSION-CYCLOADDITION-COPE REARRANGEMENT WITH AN ANNELATED NORBORNADIENE AND ELECTROPHILIC DIENES. UNUSUAL [$\pi^2_s + \pi^2_a + \sigma^2_a$] TRANSFORMATION OF A PENTACYCLO-[11.4.0.1^{7,10}.0^{4,13}.0^{6,11}]OCTADECA-3,8,14,17-TETRAENE.

Tetrahedron, **1993**, *49*, 4699

Edward C. Gravett, Judith A. K. Howard,* Kenneth Mackenzie,* Liu Shi-Xiong and Peter B. Karadakov.
School of Chemistry, The University, Bristol BS8 1TS UK.

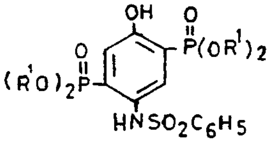


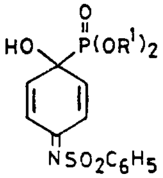
At 25-60°C, Tetrachlorothiophenedioxide as diene captures 8 ($\xrightarrow{T}$) giving in 1:1 ratio *syn-endo* adduct 12 (and *anti-endo* isomer 13) which Cope rearrange into sulphones 14 (and 15); at ≈200°C retro- Cope sigmatropy with concomitant loss of SO_2 gives from 14 (and 15) isomers of decachloropentacyclotetraenes, e.g. 19 (and 20). Tetracyclone also captures 8 giving an arylated carbonyl-bridge adduct which extrudes CO, the product undergoing an unusual [$\pi^2_s + \pi^2_a + \sigma^2_a$] transformation.

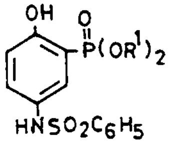
Tetrahedron, **1993**, *49*, 4711

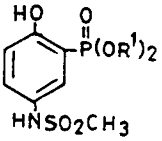
THE NOVEL BEHAVIOUR OF DIALKYL PHOSPHITES TOWARD 1,4- BENZOQUINONE MONOIMINES

Leila Sadek Boulos and Mona Hizkial Nasr Arsanious
National Research Centre, Dokki, Cairo, Egypt









Tetrahedron, **1993**, *49*, 4721

REDUCTIVE QUENCHING OF EXCITED STATES OF CHROMIUM(III)-POLYPYRIDYL COMPLEXES WITH ALKYL ARYL SULPHIDES

GEORGE ALLEN GNANARAJ[a], SEENIVASAN RAJAGOPAL*[a], CHOCKALINGAM SRINIVASAN[b] and KASI PITCHUMANI[a]
[a]School of Chemistry, [b]Department of Materials Science
Madurai Kamaraj University, Madurai-625 021 India

The change of quenching rate constant, k_q, with the structure of organic sulphides for the photoreduction of $^*Cr(NN)_3{}^{3+}$ (NN=bpy, phen) is explained in terms of Marcus model and electron transfer distance. The oxidised products, sulphoxides in aerated solutions, are accounted for by the formation of singlet oxygen.

Tetrahedron, **1993**, *49*, 4741

SYNTHESIS OF [a]ANNULATED CARBAZOLES FROM INDOL-2,3-DIONES

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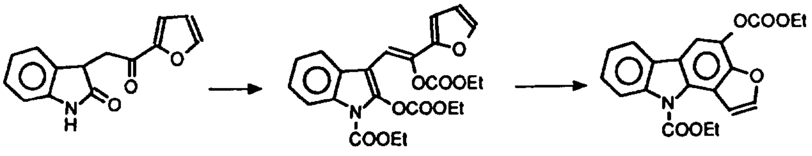
Photoelectrocyclization of 3-(2-aryl-2-ethoxycarbonyloxy)ethenyl]-2-(ethoxycarbonyloxy)indole-1-carboxylates **6**, prepared from 3-aroylmethylindol-2(3H)-ones **5**, affords the corresponding [a]annulated carbazoles **10**. E.g. for furo[3,2-a]carbazole:



5d **6d** **10d**