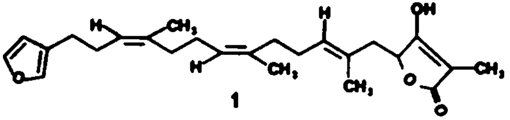
GRAPHICAL ABSTRACTS

Tetrahedron **1990**, *46*, 1119

PALOMININ, A NOVEL FURANOSESTERTERPENE FROM A CARIBBEAN SPONGE *IRCINIA SP*.

Miriam Ortiz Garcia and Abimael D. Rodríguez*
Department of Chemistry, University of Puerto Rico, Rio Piedras, P.R.

A new linear monofuranosesterterpene, palominin, has been isolated from the Caribbean sponge *Ircinia sp*. On the basis of physical and chemical evidence, structure 1 is suggested for palominin.



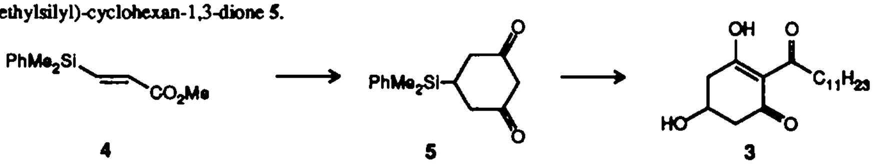
1

Tetrahedron **1990**, *46*, 1125

SYNTHESIS OF 2-DODECANOYL-3,5-DIHYDROXY-2-CYCLOHEXEN-1-ONE

James E. Oliver*, Rolland M. Waters, and William R. Lusby
USDA, ARS, Beltsville, MD

The title compound, 3 (isolated from the lace bug *Stephanitis takeyai*) has been synthesized via 5-(phenyldimethylsilyl)-cyclohexan-1,3-dione 5.



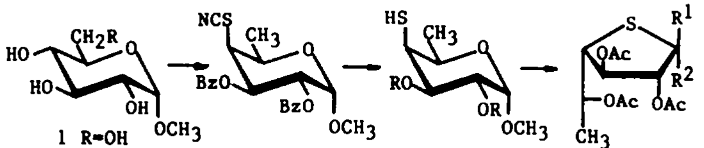
4 5 3

Tetrahedron **1990**, *46*, 1131

SYNTHESIS OF FURANOID AND PYRANOID DERIVATIVES OF 6-DEOXY-4-THIO-D-GALACTOSE

Daniel CICERO, Oscar VARELA and Rosa M. de LEDERKREMER.

Dep. Quím. Orgánica, Fac. Ciencias Exactas y Naturales, Univ. Buenos Aires, C. Universitaria, Pab. II, 1428, Buenos Aires, Argentina.



1 R=OH
5 R=Br
9 R=H

14

15 R=Bz
16 R=H

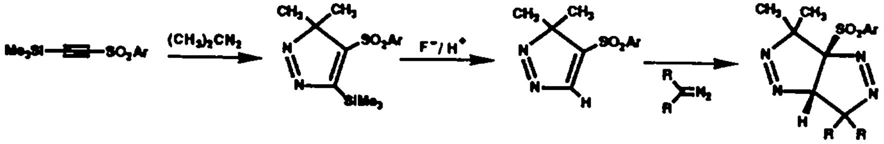
18 R^1=H, R^2=OAc
19 R^1=OAc, R^2=H

Tetrahedron **1990,** *46,* 1145

DIPOLAR CYCLOADDITION REACTION OF DIAZOALKANES WITH TRIMETHYLSILYL SUBSTITUTED ALKYNES. STERIC CONTROL OF REGIOCHEMISTRY BY THE TRIMETHYLSILYL GROUP

Albert Padwa and M. Woods Wannamaker*
Department of Chemistry, Emory University, Atlanta, GA 30322 USA

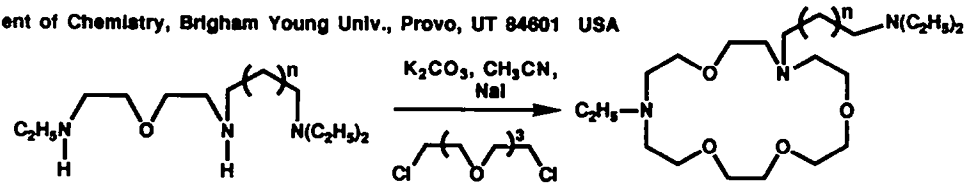
Dipolar cycloaddition of a 2-(trimethylsilyl) substituted alkyne led to the unexpected 5-trimethylsilyl substitued 3H-pyrazole which was desilylated and further reacted with 2-diazopropane.



Tetrahedron **1990,** *46,* 1163

THE SYNTHESIS OF NEW DIAZA-N-PIVOT LARIAT 15-CROWN-5 AND 18-CROWN-6 MACROCYCLES

J. S. Bradshaw*, K. E. Krakowiak, H. An and R. M. Izatt
Department of Chemistry, Brigham Young Univ., Provo, UT 84601 USA

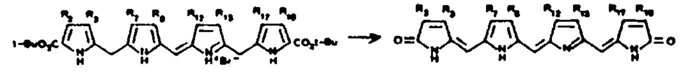


Tetrahedron **1990,** *46,* 1171

CONCERNING THE MECHANISM OF FORMATION OF BILIVERDINS FROM b-BILENES.

Josefina Awruch. Facultad de Farmacia y Bioquímica. Universidad de Buenos Aires, Junín 956, Buenos Aires, Argentina

The oxidation of 1,19-di-t-butoxy-carbonyl-b-bilenes with bromine affords not only a major biliverdin, but also minor biliverdins.



1. $R_2=R_8=R_{12}=R_{17}=Me$; $R_{13}=R_{18}=Et$; $R_3=R_7=P^{Me}$
4. $R_3=R_8=R_{12}=R_{18}=Me$; $R_2=R_{17}=Et$; $R_7=R_{13}=P^{Me}$
7. $R_2=R_8=R_{13}=R_{18}=Me$; $R_{12}=R_{17}=Et$; $R_3=R_7=P^{Me}$
$Me=CH_3$; $Et=C_2H_5$; $P^{Me}=CH_2CH_2CO_2CH_3$

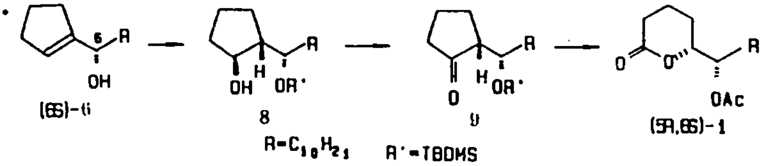
2. $R_2=R_8=R_{12}=R_{17}=Me$; $R_{13}=R_{18}=Et$; $R_3=R_7=P^{Me}$
3. $R_2=R_8=R_{12}=R_{18}=Me$; $R_3=R_7=R_{13}=R_{17}=P^{Me}$
5. $R_3=R_8=R_{12}=R_{18}=Me$; $R_2=R_{17}=Et$; $R_7=R_{13}=P^{Me}$
6. $R_2=R_8=R_{12}=R_{18}=Me$; $R_3=R_{17}=Et$; $R_7=R_{13}=P^{Me}$
8. $R_2=R_8=R_{13}=R_{18}=Me$; $R_{12}=R_{17}=Et$; $R_3=R_7=P^{Me}$
$Me=CH_3$; $Et=C_2H_5$; $P^{Me}=CH_2CH_2CO_2CH_3$

Tetrahedron **1990**, *46*, 1191

Stereoselective Synthesis of (-)-(5R,6S)-6-Acetoxy-5-Hexadecanolide, The Mosquito Oviposition Attractant Pheromone

Zhi-Min Wang[a] Xin-Hua Qian[b] Wei-Shan Zhou*[c]
a. Xingjiang Institute of Chemistry, Academia Sinica, 40 Beijing Lu, Wulumuqi 830011, China; b. Department of Chemistry, Fudan University, Shanghai 200433, China; c. Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032, China.

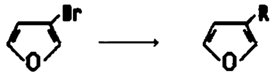
The mosquito oviposition attractant pheromone was synthesized from 1,2-cyclohexanediol.

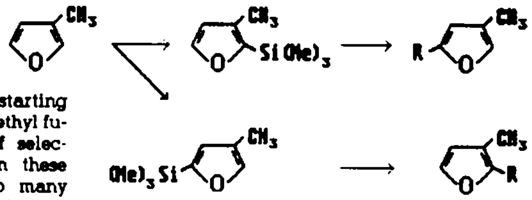


Tetrahedron **1990**, *46*, 1199

NEW ASPECTS IN THE SYNTHESIS OF MONO- AND DIALKYLFURANS

I. Bock, H. Bornowski*, A. Ranft and H. Theis
Institut für Organische Chemie der Technischen Universität Berlin, Straße des 17. Juni 135, D-1000 Berlin 12





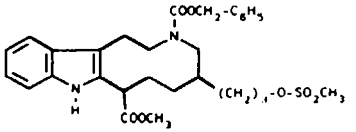
Some regiospecific syntheses of mono- and dialkylfurans, starting from easily available precursors like 3-bromo- and 3-methyl furan, were studied. Regiospecific lithiation and blocking of selected positions of the furan ring are the key reactions in these few-step syntheses, which represent a simple approach to many naturally occurring furan compounds, as is demonstrated in the synthesis of the terpenoid s ursinanolide and longifolin.

Tetrahedron **1990**, *46*, 1211

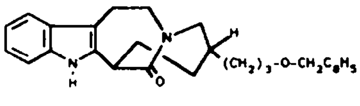
EINE NEUE SYNTHESE VON VINBLASTIN-DERIVATEN V. KONZEPT UND UNTERSUCHUNGEN ZUR SYNTHESE VON 20'-DESETHYL-20'-DESOXY- C'-HOMOVINBLASTIN.- OCTAHYDRO-3H-AZECINO[5,4-B]INDOL-DERIVATE

Gottfried Schill*, Claus Ulrich Priester, Udo Frank Windhövel und Hans Fritz*
Institut für Organische Chemie und Biochemie der Universität Freiburg,
*Albertstr. 21, D-7800 Freiburg und *Ciba-Geigy AG, CH-4002 Basel*

Starting from tryptamine compounds 1 and 2 are synthesised in a multi-step reaction sequence.



1



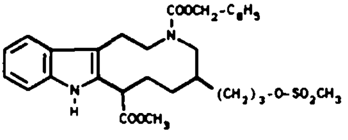
2

Tetrahedron **1990**, *46*, 1221

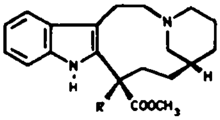
EINE NEUE SYNTHESE VON VINBLASTIN-DERIVATEN VI. SYNTHESE VON 20'-DESETHYL-20'-DESOXY-C'-HOMOVINBLASTIN

Gottfried Schill*, Claus Ulrich Priester, Udo Frank Windhövel und Hans Fritz •
Institut für Organische Chemie und Biochemie der Universität Freiburg, Albertstr. 21, D-7800 Freiburg und • Ciba-Geigy AG, CH-4002 Basel

Starting from 1 the title compound 2 is synthesised.



1

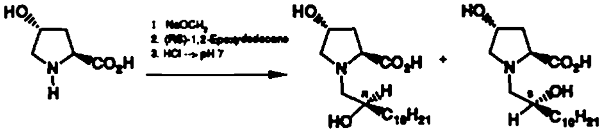


2: R = 10-vindolinyl

Tetrahedron **1990**, *46*, 1231

SYNTHESIS OF STERICALLY UNIFORM CHIRAL SELECTORS FOR TLC ENANTIOMERIC RESOLUTION

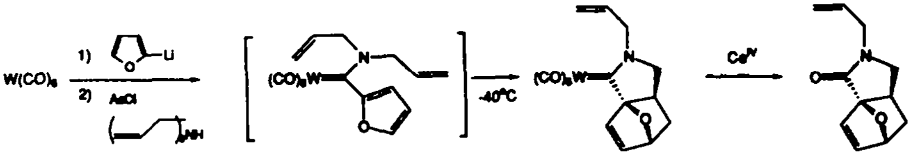
JÜRGEN MARTENS* AND STEFAN LÜBBEN
Fachbereich Chemie, Universität Oldenburg, D-2900 Oldenburg i. O., Germany



Tetrahedron **1990**, *46*, 1235

CARBENE COMPLEXES IN INTRAMOLECULAR DIELS-ALDER REACTIONS

K.H. Dötz*, R. Noack, K. Harms, and G. Müller
Fachbereich Chemie der Philipps-Universität, D-3550 Marburg, and
Anorg.-chem. Institut der Technischen Universität München, D-8046 Garching

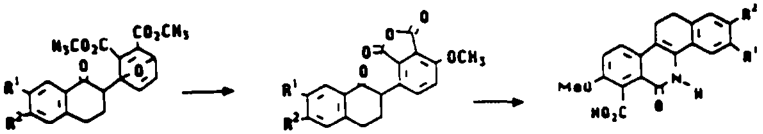


Tetrahedron **1990**, *46*, 1253

A NEW SYNTHETIC ROUTE TO 7-CARBOXY BENZO (c)PHENANTHRIDONES

O. Duval, L. Mavoungou Gomès
Laboratoire de Chimie organique
U.F.R de Médecine et Pharmacie, 16 Bd Daviers 49100 ANGERS, FRANCE

A convenient carboxy-7 benzo(c)phenanthridone synthesis is described, starting from (Furyl-2)-2 tetralones and dimethyl acetylenedicarboxylate.

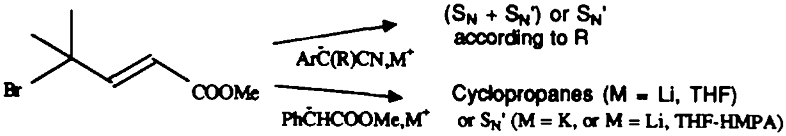


Tetrahedron **1990**, *46*, 1263

ALLYLIC SUBSTITUTION BY CARBON NUCLEOPHILES, ON 4-BROMO-4-METHYL-2-PENTENOATE : ANTI-MICHAEL REGIOSELECTIVITY.

M.-C. ROUX-SCHMITT, A. PETIT, A. SEVIN, J. SEYDEN-PENNE
I.C.M.O., Unité Associée au CNRS, Bât. 420, Université de Paris-Sud, 91405 ORSAY CEDEX (France)

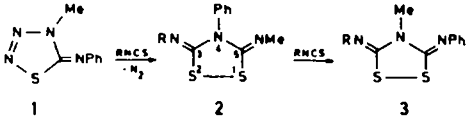
and NGUYEN TRONG ANH
Laboratoire des Mécanismes Réactionnels, Unité Associée au CNRS
DCRM, Ecole Polytechnique, 91128 PALAISEAU (France)



Tetrahedron **1990**, *46*, 1281

CYCLOADDITION-ELIMINATION REACTIONS OF 4-METHYL-5-PHENYLIMINO-Δ^2-1,2,3,4-THIATRIAZOLINE WITH STRONG ELECTROPHILIC ISOTHIOCYANATES. MECHANISM OF THE ISOMERIZATION PROCESS.

Gerrit L'abbé and Karin Buelens
Department of Chemistry, University of Leuven, Belgium.



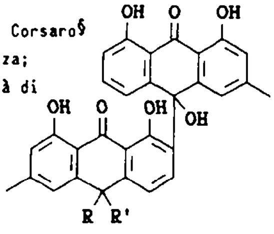
The rearrangement of 3,5-bisimino-1,2,4-dithiazolidines (2) into isomeric dithiazolidines (3) under the influence of isothiocyanates occurs by a cycloaddition-elimination process and not by a Dimroth rearrangement.

Tetrahedron **1990, *46*,** 1287

BIANTHRONE C-GLYCOSIDES. 2. THREE NEW COMPOUNDS FROM ASPHODELUS RAMOSUS TUBERS.

R. Lanzetta*, M. Parrilli*, M. Adinolfi§, T. Aquila§, M. Corsaro§
*Istituto di Chimica, Università della Basilicata, Potenza;
§Dipartimento di Chimica Organica e Biologica, Università di Napoli, Napoli, Italy.

The structures of three further members (a-c) of the new class of bianthrone C-glycosides were elucidated by spectral analysis (^{1}H-, ^{13}C-NMR, FAB-MS, CD).



a R = OH
R' = C-β-D-xylp

b R = OH
R' = β-D-glup(1→4)-C-β-D-glup

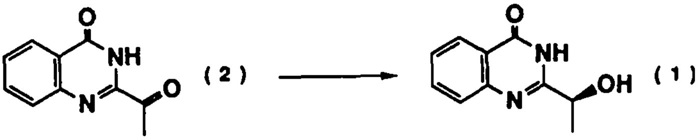
c R = H
R' = C-β-D-glup

Tetrahedron **1990, *46*,** 1295

Synthesis of Chrysogine, a Metabolite of *Penicillium chrysogenum* and some related 2-substituted 4-(3H)-quinazolines

J. Bergman , A. Brynolf, Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, SWEDEN

Syntheses of both enantiomers of chrysogine (2-(α-hydroxyethyl)-4(3H)-quinazolinone) 1 from 2-aminobenzamide are described. The enantiomeric purity of 1 was determined by NMR. Reduction of 2 with baker's yeast gave the S-enantiomer of 1.



Tetrahedron **1990, *46*,** 1311

CONFORMATIONAL STUDIES OF d(CACGTG)$_2$ AND d(CACCGTG), (CACGGTG) BY TWO-DIMENSIONAL ^{1}H, ^{31}P NMR AND CIRCULAR DICHROISM SPECTRA.

K.N.Ganesh*, Division of Organic Chemistry, National Chemical Laboratory, Pune-411 008, India, amd G.V.Rajendrakumar, Centre for Cellular & Molecular Biology, Hyderabad, 7

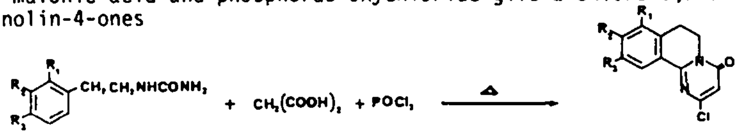
The conformational studies of titled DNA sequences by 2D ^{1}H NMR (COSY and NOESY), ^{31}P NMR and CD methods are reported. These duplexes adopt B-form with significant conformational heterogeneity at C3 of hexamer and C3, C10 of heptamer. They fail to exhibit B to Z transition in solution, though d(CACGTG)$_2$ is reported to crystallise in a left handed form.

Tetrahedron **1990, *46*,** 1323

A CONVENIENT ONE-POT ENTRY INTO NOVEL 2-SUBSTITUTED-6,7-DIHYDRO-4H-PYRIMIDO(2,1-a)ISOQUINOLIN-4-ONES.

Bansi Lal*, A. S. D'Sa, B. K. Kulkarni, N. J. de Souza
Department of Chemistry, Centre for Basic Research, Hoechst India Limited, Mulund, Bombay 400 080, India.

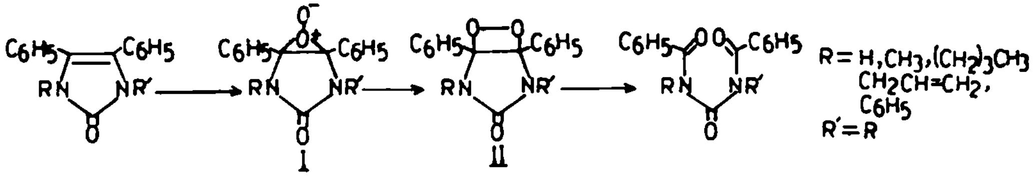
1-(2-Arylethyl)ureas, malonic acid and phosphorus oxychloride give 2-Chloro-6,7-dihydro-4H-pyrimido(6,1-a)isoquinolin-4-ones



Tetrahedron **1990, *46*,** 1331

DYE SENSITIZED PHOTOOXYGENATION OF N-SUBSTITUTED-4,5-DIPHENYLIMIDAZOLIN-2-ONES

H. Mohindra Chawla and Manisha Pathak, Department of Chemistry, Indian Institute of Technology, New Delhi-110016, India.

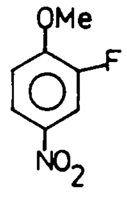


Tetrahedron **1990, *46*,** 1343

THE PHOTOSUBSTITUTION OF 2-FLUORO-4-NITROANISOLE WITH n-HEXYLAMINE. EVIDENCE OF TWO DIFFERENT TRIPLET EXCITED STATES IN A DUAL MECHANISTIC PATHWAY.

R.Pleixats and J.Marquet*
Department of Chemistry. Universitat Autònoma de Barcelona.
08193 Bellaterra. Barcelona. Spain.

The photoreaction of 2-fluoro-4-nitroanisole with n-hexylamine gives rise to fluoride (major) and methoxy (minor) substitution. A continuous irradiation mechanistic study suggest that the first is produced through a $S_N2^3Ar^*$ mechanism that involves a π-π^* triplet excited state whereas the second comes from a n-π^* triplet excited state via an electron transfer mechanism.

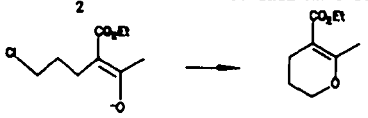


Tetrahedron **1990**, *46*, 1353

METAL ION EFFECT ON THE RATE OF INTRAMOLECULAR O-ALKYLATION OF THE ANION OF ETHYL(3-CHLOROPROPYL)ACETOACETATE

R. Cacciapaglia and L. Mandolini*
Università La Sapienza 00185 Roma, Italy

The retarding effect of alkali-metal and alkaline-earth-metal ions on the rate of intramolecular O-alkylation of the title compound has been thoroughly investigated in 99% aqueous Me_2SO at 25° C. Rate data have been dissected into contributions of free ions and ion pairs. The present results, when combined with analogous data related to intramolecular C-alkylation, are apparently at variance with widely accepted views on metal ion effects on the regiochemical course of enolate alkylations.

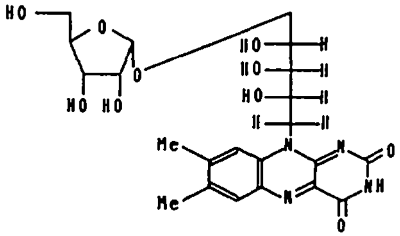


Tetrahedron **1990**, *46*, 1367

Lampteroflavin, the First Riboflavinyl Alpha Ribofuranoside as Light Emitter in the Luminous Mushroom, L. japonicus

Duangchan Uyakul, Minoru Isobe and Toshio Goto
School of Agriculture, Nagoya University,
Chikusa 464, Japan

Structure was elucidated to be:



Tetrahedron **1990**, *46*, 1379

A NEW APPROACH TO THE SYNTHESIS OF 2-SUBSTITUTED INDOLES: REACTION OF DI-METALLATED *ORTHO* - TRIMETHYLSILYLMETHYLANILIDES WITH ESTERS

Giuseppe Bartoli*[a], Gianni Palmieri[a], Marino Petrini[a], Marcella Bosco[b], Renato Dalpozzo[b]
a.Dipartimento di Scienze Chimiche, via S.Agostino 1, I-62032 Camerino (Mc), Italy
b.Dipartimento di Chimica Organica, viale Risorgimento 4, I-40136 Bologna, Italy