GRAPHICAL ABSTRACTS

A ß,ß-Shielded Vinyllithium Example for a Quantification of Structure, Monomer-Dimer Equilibrium, and some Reactivity Parameters

Tetrahedron, **1994**, *50*, 5845

Rudolf Knorr*, Johannes Freudenreich and Kurt Polborn
Institut für Organische Chemie der Universität München,
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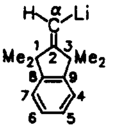
Institut für Anorganische Chemie der Universität
München, Meiserstrasse 1, D-80333 München

2-(Lithiomethylene)-1,1,3,3-tetramethylindan (3) is a dimeric etherate in the crystal (11) and in *tert*-butyl methyl ether solution, but partially monomeric in THF. Its synthesis, equilibrium parameters, charge polarization, and reactivity are reported.



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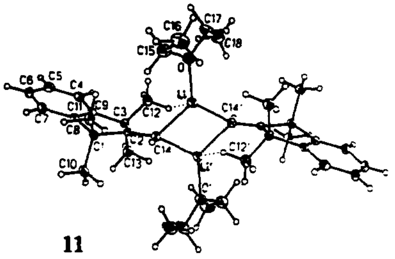

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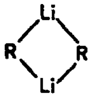
THE AGGREGATION BEHAVIOR OF BUTYLLITHIUM, PHENYLLITHIUM,AND LITHIUM DIISOPROPYLAMIDE IN DIMETHOXY- AND DIETHOXYMETHANE

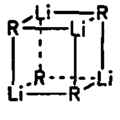
Tetrahedron, **1994**, *50*, 5861

Klaus Bergander, Runxi He, Narayanan Chandrakumar, Oswald Eppers,and Harald Günther*
University of Siegen, Fachbereich 8, OC II, D-57068 Siegen, Germany

The aggregation behaviour of butyllithium (BuLi), phenyllithium (PhLi), and lithium diisopropylamide (LDA) in dimethoxy- and diethoxymethane (methylal and ethylal, respectively) has been studied by NMR spectroscopy. In both solvents, LDA exists as a dimer, while BuLi forms a tetramer. PhLi forms a dimer in methylal, whereas two major aggregates exist in ethylal.



R = $N[CH(CH_3)_2]_2$
C_6H_5



R = CH_2-CH_2-CH_2-CH_3

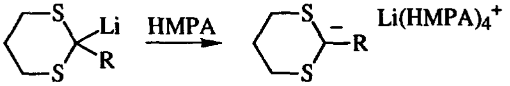
SOLUTION ION PAIR STRUCTURE OF 2-LITHIO-1,3-DITHIANES IN THF AND THF-HMPA

Tetrahedron, **1994**, *50*, 5869

Hans J. Reich,*, Joseph P. Borst and Robert R. Dykstra

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

An NMR study of 2-lithio-1,3-dithiane and various 2-substituted analogues reveals that all are contact ion pair species in THF and all become separated ions with excess HMPA. The ease of ion pair separation varies greatly with substitution.

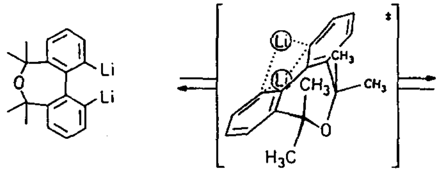


R = H, *t*-Bu, $SiMe_2Ph$, $SiMe_3$, Ph

How Advantageous is the Intramolecular Aggregation of 1,4-Organodilithio Compounds ?

Tetrahedron, **1994**, *50*, 5881

O. Desponds and Manfred Schlosser *
Institut de Chimie organique, Université de Lausanne, Switzerland

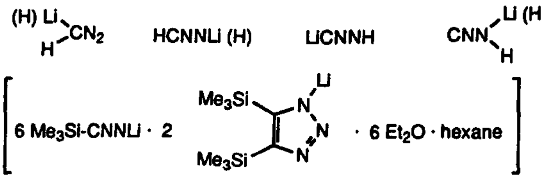


The barrier to torsional planarization of the dilithio species is approximately 2 kcal/mol lower than that of the corresponding hydrocarbon.

Tetrahedron, **1994**, *50*, 5889

Lithio-diazomethane and Lithio-(trimethylsilyl)diazomethane: Theoretical and Experimental Studies of Their Structures, Reactions and Reaction Products

Gernot Boche*, John C.W. Lohrenz, Frank Schubert
Fachbereich Chemie der Philipps-Universität Marburg, D-35032 Marburg, Germany

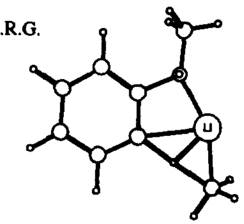


Ab initio calculations and X-ray structure analysis

Tetrahedron, **1994**, *50*, 5903

Mechanisms of Aromatic Lithiation. Influence of Aggregation and Directing Groups.

Nicolaas J.R. van Eikema Hommes and Paul von Ragué Schleyer
Institut für Organische Chemie, Universität Erlangen-Nürnberg, Henkestraße 42, D-91054 Erlangen, F.R.G.

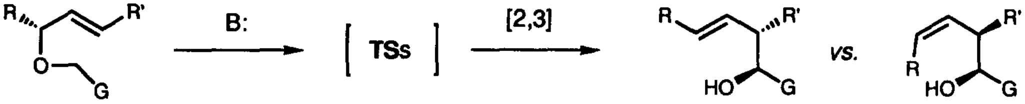


High level ab initio calculations (MP2/6-31+G*//MP2/6-31G*+ΔZPE//6-31G*) on the reaction of benzene, fluorobenzene, anisole and dimethylaniline with methyllithium monomer and model aggregates with lithium hydride are presented. A mixed CH_3Li-LiH dimer is predicted to be more reactive towards benzene than CH_3Li monomer. The accelerating and ortho-directing effect of Lewis base substituents is due to stabilization of the "active" lithium in the transition state by intramolecular coordination and favorable electrostatic interactions.

Tetrahedron, **1994**, *50*, 5917

DIFFERENT TRANSITION STRUCTURES FOR [2,3]-WITTIG REARRANGEMENTS OF STABILIZED AND UNSTABILIZED ALLYLOXY METHYL ANIONS: RATIONALE FOR THE DICHOTOMOUS SENSE OF STEREOSELECTION

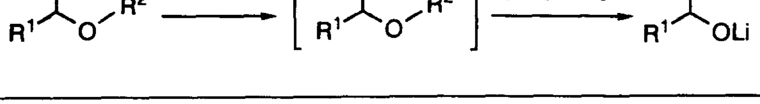
Koichi Mikami[a)]*, Tomoya Uchida[b)], Tsuneo Hirano[b)], Yun-dong Wu[c)], and Ken N. Houk[c)]*
a) Department of Chemical Technology, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan
b) Department of Industrial Chemistry, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan
c) Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, CA90024, U.S.A.



Tetrahedron, **1994**, *50*, 5927

[1,2]-Wittig Rearrangement of Enantio-defined α-Alkoxyalkyllithiums: Structural Requirement and Steric Course at the Li-Bearing Terminus.

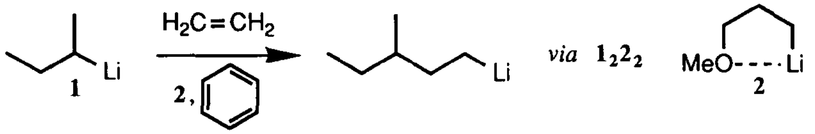
Katsuhiko Tomooka, Tatsuya Igarashi, and Takeshi Nakai*,
Department of Chemical Technology, Tokyo Institute of Technology, Meguro-ku, Tokyo, Japan



MIXED TETRAMERS OF *S*-BUTYLLITHIUM AND 3-METHOXYPROPYLLITHIUM; DEGREE OF INTRACLUSTER ETHERATION AND REACTIVITY OF *S*-BUTYLLITHIUM TOWARDS ETHYLENE

Tetrahedron, **1994**, *50*, 5933

Robert F. Schmitz, Franciscus J.J. de Kanter, Marius Schakel, Gerhard W. Klumpp*
Scheikundig Laboratorium Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

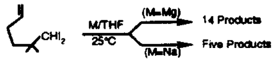


Tetrahedron, **1994**, *50*, 5945

CONCERNING THE PREPARATION OF GEMINAL DIGRIGNARD REAGENTS. THE MECHANISM OF REACTION OF GEMINAL DIHALIDES WITH MAGNESIUM AND SODIUM

Fabio Doctorovich, Abhay K. Deshpande, and E.C. Ashby*
School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332, USA

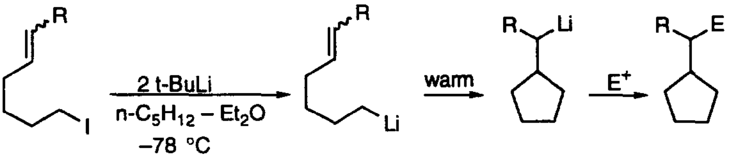
Mechanistic studies of the reactions of geminal dihalides with magnesium and sodium have been carried out and the possibility of preparing geminal DiGrignard Reagents for use in situ has been explored.



ANIONIC CYCLIZATION OF OLEFINIC ALKYLLITHIUMS: RING CLOSURE OF TERMINALLY SUBSTITUTED 5-HEXENYLLITHIUMS

Tetrahedron, **1994**, *50*, 5957

William F. Bailey* and Kaustubh V. Gavaskar
Department of Chemistry, University of Connecticut, Storrs, Connecticut 06269-3060



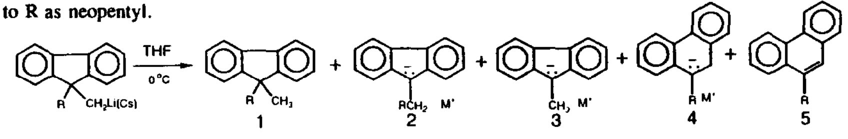
R= Ph, TMS, c-C_3H_5

CARBANIONS 27. REARRANGEMENTS OF (9-ALKYL-9-FLUORENYL)METHYLLITHIUM (OR CESIUM) AND 2,2-DIPHENYL-3,3-DIMETHYLBUTYLLITHIUM[1]

Tetrahedron, **1994**, *50*, 5971

Erling Grovenstein, Jr.*, Jagvir Singh, Bhalchandra B. Patil, and Don VanDerveer
School of Chemistry, Georgia Institute of Technology, Atlanta, GA 30332, U.S.A.

The products are primarily **1** when R is ethyl or 1-norbornyl, some **2** but mostly **3** when R is *tert*-Bu, and **4** plus **5** when R is neopentyl. 2,2-Diphenyl-3,3-dimethylbutyllithium undergoes [1,2]-aryl migration analogous to R as neopentyl.

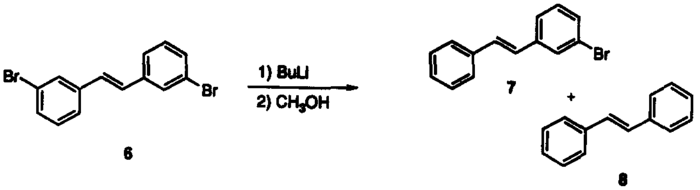


R = Et, *t*-Bu, neopentyl, 1-norbornyl

EVIDENCE FOR BROMINE-LITHIUM EXCHANGE IN A LOCAL HIGH CONCENTRATION GRADIENT

Tetrahedron, **1994**, *50*, 5999

Peter Beak and Chao Liu, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801

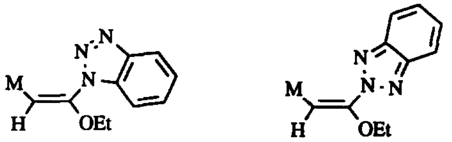


The bromine lithium exchange of **6** is shown to give a higher ratio of **8**:**7** then would be expected if all bromines had equal reactivity; this result is consistent with accelerated dilithiation in a local concentration gradient.

BENZOTRIAZOLE-ASSISTED β-LITHIATION OF VINYL ETHERS

Tetrahedron, **1994**, *50*, 6005

Alan R. Katritzky, Alexey V. Ignatchenko, Xiangfu Lan, Hengyuan Lang and Christian V. Stevens
Department of Chemistry, University of Florida, P.O. Box 117200, Gainesville, FL 32611-7200, USA.
Andreas Opitz, Rainer Koch and Ernst Anders
Institut für Organische Chemie der Universität, Henkestrasse 42, D-91054 Erlangen, Germany.



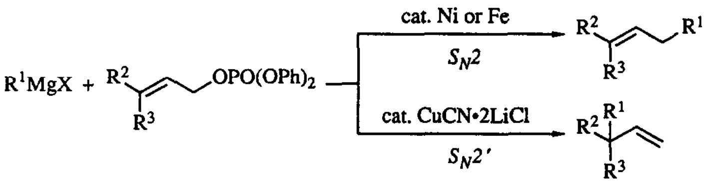
$$\boxed{M = H \xrightarrow{BuLi} M = Li}$$

TRANSITION METAL-CATALYZED SUBSTITUTION REACTION OF ALLYLIC PHOSPHATES WITH GRIGNARD REAGENTS

Tetrahedron, **1994**, *50*, 6017

Akira Yanagisawa, Nobuyoshi Nomura, and Hisashi Yamamoto*
School of Engineering, Nagoya University, Chikusa, Nagoya 464-01, Japan

S_N2-selective Grignard coupling with primary allylic diphenylphosphates was successfully achieved using Ni or Fe catalyst. In sharp contrast, a catalytic amount of CuCN•2LiCl promoted a S_N2'-selective coupling reaction.

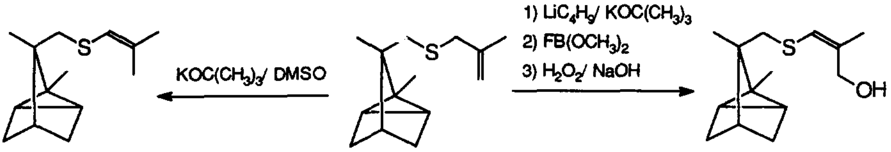


THE SYNTHESIS OF 4'-THIA-α-SANTALENE AND 4'-THIA-α-SANTALOL THROUGH AN ORGANOMETALLIC APPROACH

Tetrahedron, **1994**, *50*, 6029

*Alessandro Mordini *, Sabina Pecchi and Giuseppe Capozzi*
Centro CNR Composti Eterociclici, Dipartimento di Chimica Organica dell?Università, via G. Capponi 9, I-50121 Firenze, Italy

The 4'-thia analogues of α-santalene and α-santalol are prepared in a very convenient, regio- and stereocontrolled manner by using allyl type organometallic intermediates.

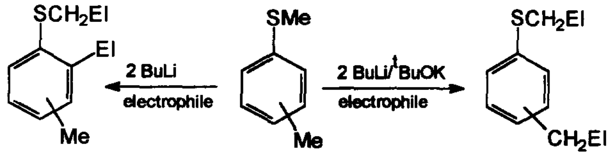


METALLATION REACTIONS. XXI. METALLATION OF ALKYL(ALKYLTHIO)BENZENES BY SUPERBASES *VERSUS* ORGANOLITHIUM COMPOUNDS

Tetrahedron, **1994**, *50*, 6037

Salvatore Cabiddu*, Claudia Fattuoni, Costantino Floris*, Stefana Melis and Alessandro Serci
Dipartimento di Scienze Chimiche, Università, Via Ospedale 72, I-09124 Cagliari (Italy)

Superbases bimetallate the methylic and thiomethylic carbon while butyllithium attacks the thiomethylic and arylic carbon *ortho* to the thioethereal group.

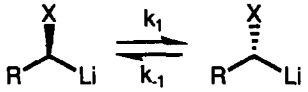


CONFIGURATIONAL STABILITY OF CHIRAL ORGANOLITHUM COMPOUNDS ON THE TIME SCALE OF THEIR ADDITION TO ALDEHYDES

Tetrahedron, **1994**, *50*, 6049

Reinhard W. Hoffmann, Manfred Julius, Fabrice Chemla, Thomas Ruhland, and Gerlinde Frenzen
Fachbereich Chemie der Philipps-Universität, D-35032, Marburg, Germany

Trapping of the organolithium compounds 1 with X = Br, SPh, SePh by aldehydes occurs faster than racemisation

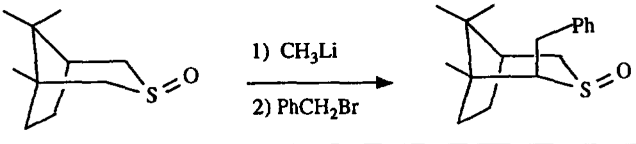


Unusual Stereochemical Results in the Reaction of Alpha-Lithio Derivatives of Bicyclic Sulfoxides

Tetrahedron, **1994**, *50*, 6061

Robert N. Ben, L. Breau, C. Bensimon and T. Durst*

Ottawa-Carleton Chemistry Institute
Department of Chemistry, University of Ottawa
Ottawa, Ontario, Canada, K1N 6N5

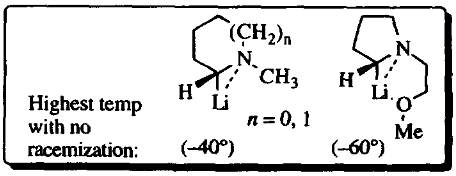


SEARCH FOR CONFIGURATIONALLY STABLE, ARACEMIC α-AMINO ORGANOLITHIUMS.

Tetrahedron, **1994**, *50*, 6077

Robert E. Gawley* and Qianhui Zhang
Department of Chemistry, University of Miami, Coral Gables, Florida 33124-0431

α-Lithio *N*-alkylpyrrolidines and piperidines exhibit remarkable chemical and configurational stability. Based on comparisons of three related α-amino-organolithium classes and based on recent structural work from other laboratories, a hypothesis explaining the stability of these species is presented. Previous work in the area is reviewed.

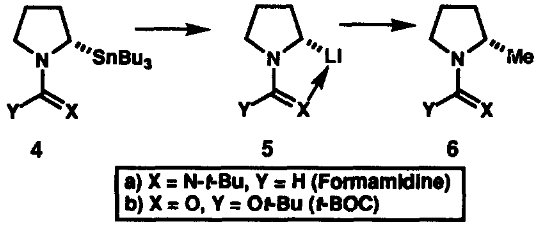


Tetrahedron, **1994**, *50*, 6089

The Configurational Stability of Chiral Lithio α-Amino Carbanions. The Effect of Li-O *vs.* Li-N Complexation.

Todd R. Elworthy and A. I. Meyers*
Department of Chemistry, Colorado State University,
Fort Collins, Colorado 80523 U.S.A.

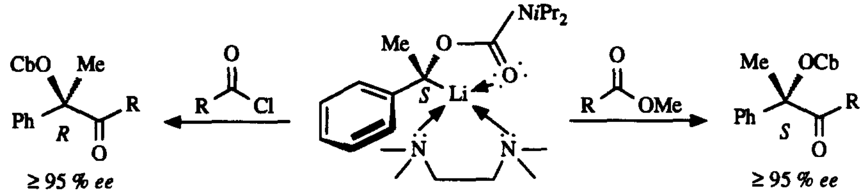
Transmetallation of optically active **4a**, **4b** gave methyl derivatives **6a**, **6b** with the former retaining optical activity.



Tetrahedron, **1994**, *50*, 6097

GENERATION OF A CONFIGURATIONALLY STABLE, ENANTIOENRICHED α-OXY-α-METHYLBENZYLLITHIUM: STEREODIVERGENCE OF ITS ELECTROPHILIC SUBSTITUTION

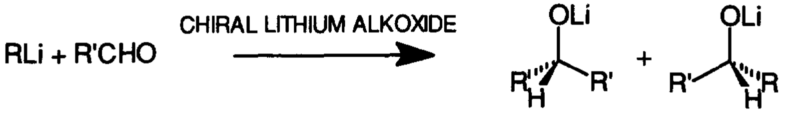
Axel Carstens and Dieter Hoppe, Institut für Organische Chemie der Universität Kiel
Olshausenstr. 40-60, D-24118 Kiel, Germany



Tetrahedron, **1994**, *50*, 6109

Enantioselective Addition of Alkyllithium Reagents to Aldehydes Induced by Chiral Lithium Alkoxides.

Maochun Ye,[a] Sundaram Logaraj,[a] Lloyd M. Jackman,[a]* Kevin Hillegass,[a]
Keith A. Hirsh,[a] Amy M. Bollinger,[a] Alice L. Grosz,[a] Venkatachalam Mani.[b]
[a] Department of Chemistry, The Pennsylvania State University, University Park, PA 16803.
[b] Supelco Inc., Supelco Park, Bellefonte, PA 16823



MIXED AGGREGATE FORMATION LEADS TO AN EXCESS OF ONE ENANTIOMER

Tetrahedron, **1994**, *50*, 6117

HIGHLY ENANTIOSELECTIVE ADDITION OF PRIMARY ALKYL GRIGNARD REAGENTS TO CARBOCYCLIC AND HETEROCYCLIC ARYLKETONES IN THE PRESENCE OF MAGNESIUM TADDOLATE - PREPARATIVE AND MECHANISTIC ASPECTS

Beat Weber and Dieter Seebach*, Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule,
ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich, Switzerland.

Primary alkyl-*Grignard* reagents add to ketones in a TADDOL (1) mediated reaction with high enantioselectivity (up to >99% ee). Three tentative models of the stereochemical course of the addition are discussed.