Oxidative Coupling of 7,7-Dilithionorbornane; 7,7'-Dilithio-7,7'-dinorbornyl, a New *vic*-Dilithioalkane Prone to a New Mode of Decomposition[#]

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Abstract: 7,7-Dilithionorbornane reacts with butyl halides at -100° C to give 7,7'-dilithio-7,7'-dinorbornyl (30%), which is easily oxidized to 7,7'-dinorbornylidene.

"Simple" vic-dilithioalkanes are "difficult" because of their limited accessibility and their high reactivity. They cannot be prepared from the corresponding halogen compounds, often the most effective starting materials for organolithiums: vic-dihaloalkanes initially form β -halolithioalkanes which usually eliminate lithium halide much faster than they exchange the remaining halogen for lithium.¹ Other methods of carbanion generation (deprotonation, reduction of π -systems) can be applied for the preparation of a few "special" dilithium compounds² but are incapable of generating two directly neighboring negative charges in a "normal" environment lacking special carbanion stabilizing features. "Simple" vic-dilithioalkanes are expected to be more reactive towards ether solvents³ and have higher propensities for loss of lithium hydride than "normal" alkyllithiums. In accordance with calculations, 1,2-dilithioethane (I) generated in THF eliminates lithium hydride at temperatures below -10 °C.⁴

Two novel low temperature approaches to I and some of its derivatives have been explored in our laboratory. (1) On addition of CH_2I_2 to three equivalents of lithium p_sp' -di-*tert*-butylbiphenyl (LiDBB) in THF at -100 °C the main product, CH_2Li_2 (ca. 50%), is accompanied by I which is formed in a low (ca. 0.5%) steady state concentration (since it is formed as well as destroyed by CH_2I_2).⁴ In similar vein, mixtures (e.g. 1:10) of 7,7-dilithionorcarane and 7,7'-dilithio-7,7'-dinorcaryl (II) were obtained by addition of LiDBB to 7,7-dihalonorcaranes,⁵ while, under the same conditions, 7,7-dibromonorbornane (III) led to 7,7-dilithionorbornane (IV), exclusively.^{6,7} (2) I can be prepared in about 28% yield together with 1,4-dilithiobutane (28%) by reaction of solid ethylene at -195° C with lithium vapour in a Kündig-Perret apparatus.⁸

Unfortunately, the latter method seems not to be applicable to other olefins. Even the strained double bond of 7,7'-dinorbornylidene (V) proved unreactive towards lithium vapour. We now report that the product

#Dedicated to Professor R.W. Hoffmann on the occasion of his 60th birthday.

expected from V, 7,7'-dilithio-7,7'-dinorbornyl (VI) could be generated via a third route to vicdilithioalkanes: oxidative coupling of a gem-dilithioalkane. Our recent observation that tetraphenylethylene dilithium (ca. 18%) was one of the products of oxidation of diphenyldilithiomethane with various organic halides was seminal.⁹



When one equivalent of a butyl halide dissolved in a small amount of ether was added at -100 °C to a stirred solution (ether-THF, 5:1) of a mixture of IV (85-90%) and 7-lithionorbornane (VII, 10-15%) the color of the solution turned from dark green (residual LiDBB from the preparation of IV + VII) to red after about 5 minutes. Subsequent quenching with CH₃OD(CH₃OH), followed by aqueous work-up, gaschromatography and analysis by NMR and mass spectrometry indicated that before the quench the reaction mixture had contained V, VI, VII and 7-butyl-7-lithionorbornane (VIII) in varying proportions (see Table 1).

 Table 1. Yields of V-VIII from a 9:1-Mixture of 7,7-Dilithionorbornane (IV) and 7-Lithionorbornane

 (VII) and Butyl Halides (%, based on IV+VII, internal standard: cycloheptane).

Butyl halide	V	VI	VП	VIII
t-BuCl	5	31	53	-
n-BuCl	5	27	36	16
n-BuBr	3	27	15	38

VI could arise from coupling of a pair of 7-lithio-7-norbornyl radicals (IX) formed by single electron transfer from IV to the butyl halide. Alternatively, VI could arise from reaction of IV with 7-halo-7-lithionorbornane (X, Hal = Br or Cl), formed by halogen-lithium exchange or two consecutive one-electron transfer reactions from IV to butyl halide. V most probably originates from VI (see below). Coupling of IX with a butyl radical and hydrogen atom abstraction by IX could be sources of VIII and of part of VII, respectively. In the preparation of IV by LiDBB reduction of carbenoïd X (Hal = Br), the initial product formed by LiDBB and III, occurrence of IX is indicated by the formation of 10-15% VII.⁶ Deprotonation of the butyl halides by IV and S_N^2 reaction between *n*-butyl halides and IV constitute other routes to VII and VIII, respectively. In fact, the increase of the proportion of VIII at the cost of VII, observed on going from *t*-BuCl to *n*-BuBr, argues for these modes, as does the formation of 7,7-dimethylnorbornane (XI) from IV and dimethyl sulfate.⁶ For steric reasons only monoalkylation appears possible with a butyl halide.

The ratio of (V+VI):(VII+VIII) is about 3:5 for each of the three halides. It seems unlikely to us that a single species IV would partition into derivatives of dinorbornyl and of norbornane with each of the three butyl

halides in the same ratio. Therefore, we speculate that the proportion of dinorbornyl to norbornane derivatives found, reflects the proportion in which two different species of IV are present in the solution reacted, each yielding its own typical product with a butyl halide. In this view about 40% of IV would exist (ether-THF, 5:1, -100 °C) as a sterically hindered aggregate (LiBr-complexed dimer?) that upon reaction with butyl halide would engage in single electron transfer (SET) processes creating juxtaposed pairs of IX (or IV+X) that collapse to give VI. About 60% of IV would be present as LiBr-complexed monomer that on butyl halides would either perform deprotonation and nucleophilic substitution, respectively, or produce "unpaired" IX by SET. "Unpaired" IX is deemed unable to yield VI, but should give VII (and possibly VIII). Evidence suggesting that symmetrical vic-dilithium compounds $(R_2LiC)_2$, like VI, arise within aggregates, whereas lithium compounds containing a single R_2C moiety are formed from precursors that themselves contain only one R_2C unit was also obtained in our previous studies.^{5,9}

Loss of lithium hydride, which severely limits the stabilities of "simple" vic-dilithioalkanes, 4,8 is impossible in VI. In order to study the stability of this organolithium containing two vicinal tertiary carbanions, the reaction mixture obtained with t-butyl chloride ("mixture A") was slowly warmed to room temperature. During this process the red color of the solution turned green, suggesting the formation of LiDBB. After quenching with methanol and work-up norbornane (XII, 50%) and V (30%) were indicated by gaschromatography. Apparently, VI is oxidized to V. To exclude excess t-butyl chloride as oxidant, in another experiment (a very small amount of) LiDBB was added to "mixture A" until the green color of LiDBB persisted. Upon warming the same yields of XII and V as in the previous experiment were obtained. It is concluded that VI reduces p,p'-di-tert-butylbiphenyl (DBB) formed together with IV and still present in "mixture A". Most probably, the small amounts of V observed in all reaction mixtures obtained from IV and the butyl halides originate in the same way. Despite the increase of strain accompanying conversion of VI into V, the reducing power of VI exceeds that of LiDBB.¹⁰ In similar vein calculations indicate loss of Li₂ from monomeric I to be exothermic by 1.5 kcal/mol.¹¹ Our failure to generate VI from V is in line with this. Why, then, does ethylene react with lithium vapour to form I? Aggregation is regarded as an important reason. It is expected to be extensive^{2ab} and greatly stabilizing in the case of I, while sterically hindered VI should be much less influenced by this factor. Obviously, the tertiary nature of its carbanionic centers imbues VI with increased instability.

1,2-Bis(bromomagnesio)ethane is more stable than $I.^{12}$ In an attempt to prepare the bromomagnesioanalogue of VI, a solution of MgBr₂ in THF was added to "mixture A". After stirring at -95 °C for about 10 minutes, warming to 0 °C gave a greyish suspension of magnesium while, after protonation, approximately the same amounts of XII and V as before were found. This shows that VI reduces MgBr₂ faster than it undergoes transmetallation. Loss of (e⁺+Li⁺) by VI also supersedes carboxylation: bubbling CO₂ into "mixture A" at -95 °C followed by warming to room temperature gave V (41%) together with lithium norbornane-7-carboxylate (41%). With dimethyl sulfate (added at -95 °C to "mixture A", subsequently warmed to room temperature) protophilic reaction of VI predominated over reduction of DBB as indicated by the formation of 7,7'dinorbornyl (27%) and 7-methyl-7,7'-dinorbornyl (4%) besides V (7%) and 7-methylnorbornane (16%).¹³

In conclusion: (1) Oxidation of *gem*-dilithioalkanes by organic halides provides a new access to "simple" symmetrical *vic*-dilithioalkanes as exemplified by VI. (2) Easy loss in the presence of an oxidant of (e^++Li^+) constitutes a third source of instability of *vic*-dilithioalkanes, besides elimination of lithium hydride and protophilic attack on appropriate substrates.

References and notes

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