The Reductive σ Bond Cleavage of Barbaralane and 2,6-Diphenylbarbaralane

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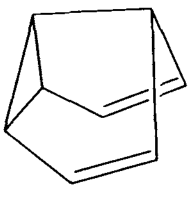
Barbaralane (2) and 2,6-diphenylbarbaralane (8) are synthesized in a straightforward way. The reductive cleavage of the strained hydrocarbons is achieved with alkali metals. The structure of the metallation products, in particular the bonding in the resulting allyl moieties, is elucidated by ^{1}H- and ^{13}C-NMR spectroscopy. The chemical behavior (oxidation, protonation, alkylation) sheds light on the modes of stabilization of the alkali metal derivatives.

Die reduktive σ-Bindungsspaltung von Barbaralan und 2,6-Diphenylbarbaralan

Barbaralan (2) und 2,6-Diphenylbarbaralan (8) werden auf rationelle Weise synthetisiert und die gespannten Kohlenwasserstoffe durch Reaktion mit Alkalimetallen reduktiven Bindungsspaltungen unterworfen. Die Struktur der Metallierungsprodukte, insbesondere die Bindungssituation in den entstehenden Allyleinheiten, wird durch ^{1}H- und ^{13}C-NMR-Spektroskopie aufgeklärt. Das chemische Verhalten (Oxidation, Protonierung, Alkylierung) erlaubt Rückschlüsse auf die Stabilisierung der Alkalimetallderivate.

The rate of the degenerate Cope rearrangement of the divinylcyclopropane species **1**–**4** depends sensitively upon the degree of strain[1–4]. Semibullvalene (**1**) with the lowest activation barrier constitutes the borderline case of the series, and there have been many attempts directed toward the synthesis of semibullvalene derivatives with a "bishomoconjugated" ground state[5–10].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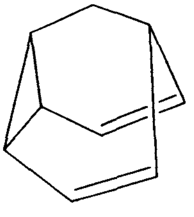
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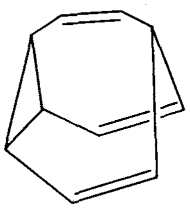
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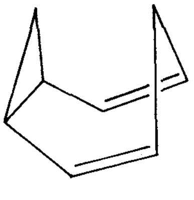
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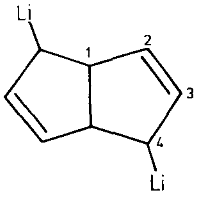

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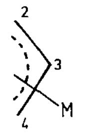
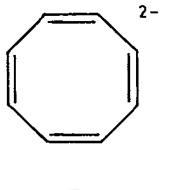


6 a: M = Li
c: M = K



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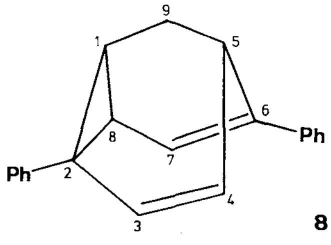


8

An additional aspect in the chemistry of **1**–**4** is provided by the recent finding of Goldstein et al.[11–13] that semibullvalene can be reductively cleaved. Thus reaction of **1** with lithium yields the allyllithium species **5** which undergoes various dynamic processes including a dimer aggregation. In a naive view the ease of the reductive σ bond cleavage in **1** can be explained by the relief of strain and by the efficient stabilization of the two excess charges in the resulting allyllithium subunits.

The characteristic differences in the chemical and dynamic behavior of semibullvalene (**1**), on the one hand, and its less strained analogue barbaralane (**2**)[2a,d], on the other hand, prompted us to investigate the metallation of **2**. Herein we describe the reduction of **2** with lithium, sodium, potassium, and caesium. The structures of the metallation products and, in particular, the formation of allyl moieties are elucidated by ^{1}H- and ^{13}C-NMR spectroscopy at different temperatures as well as by various quenching and reoxidation experiments. Compound **5** and the parent allyl metal systems **6** serve as suitable models whereby the relative importance of covalent and ionic structures is a crucial aspect.

A chemically relevant question concerns the thermal stability and basicity of a species with two nearby allyl anion subunits. Depending on the nature of the metal, reduction of semibullvalene gives rise to the alkali metal salt of the cyclooctatetraene dianion **7** implying cleavage of both the C-2–C-8 and the C-1–C-5 σ bonds[12,13]. Inclusion of barbaralane in such studies appears promising since its framework neither allows the latter valence isomerization nor a metal hydride elimination.

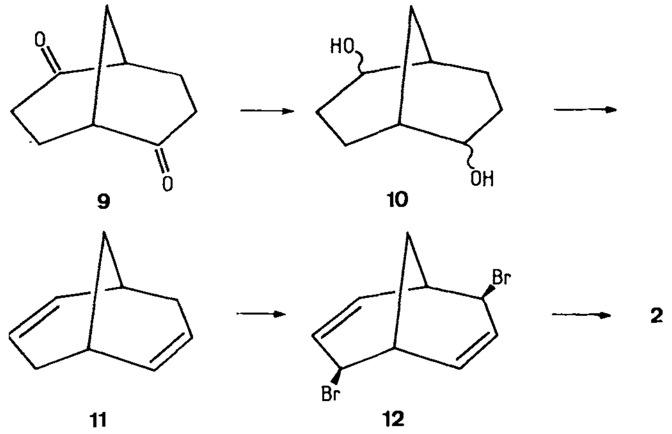
Since allyllithium, a subunit in the metallated semibullvalene **5**, is known to suffer from a marked structural change upon phenyl-substitution at the terminal carbon[14,15], we selected 2,6-diphenylbarbaralane (**8**) as another substrate for metallation.

When we started this work 2,6-diphenylbarbaralane was still elusive, and the known literature procedures for the preparation of barbaralane suffered from various drawbacks[2a,b,c,16,17]. Therefore, an efficient synthesis of both title compounds has been worked out and is described here.

1. Results

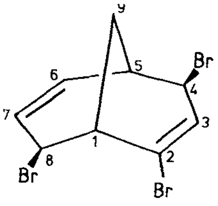
The synthesis of barbaralane followed the sequence given in Scheme 1. The starting compound, diketone[18] **9**, was easily accessible according to Meerweins's procedure[19]. Reduction of **9** with $LiAlH_4$ afforded the diol **10**[20-22]. While different methods were suggested for the preparation of the diene **11**, we found that the Cugaev elimination provides an easy access to **11**[23-26]. Pyrolysis of the xanthogenate gave a light yellow liquid which was easily purified by flash chromatography (pentane/silica gel)[27] and distillation. The bromination of **11** with *N*-bromosuccinimide (NBS, 2 eq.) afforded compound **12** which according to its ^1H- and ^{13}C-NMR spectra (see Exp. Part) exists as a single diastereomer, most probably with an *exo* configuration of the substituents[28]. A compound with more than two bromo substituents in allylic positions should constitute a suitable starting compound for brominated barbaralanes. When the amount of NBS was increased to 6 equivalents, a tribromide **13** was obtained which according to its NMR spectra possesses one bromine substituent in a vinyl position.

Scheme 1



The reductive debromination of **12** to yield barbaralane (**2**) was readily accomplished with a reactive Zn/Cu couple[29]. Unlike the literature procedure the metal was not dried prior to use, but was washed with dry ether and transferred into the reaction flask together with the solvent. This prevents deactivation by oxygen and moisture. When acetone was used as solvent the reaction gave rise to the formation of side products[17]. A clean reaction occurred in ether. After aqueous workup the solvent had to be removed over a packed column in order to prevent loss of the highly volatile product **2**.

The yet unknown 2,6-diphenylbarbaralane (**8**) was prepared using experience accumulated in the synthesis of the parent compound. The sequence started with the preparation of the diol **14** via addition of phenyllithium to the diketone **9**, most probably with an *exo* configuration of the phenyl groups. The corresponding diene **15** was easily obtained by elimination of water in acetic acid/sulfuric acid (19:1). The further route to **8** via the dibromide **16** was analogous to the barbaralane case. In the course of our studies the same synthesis of **8** was described by Quast and co-workers[30]. The only difference concerned the preparation of **14**. Instead of dissolving **9** in ether/tetrahydrofuran (THF) and adding it to the solution of phenyllithium we prepared a suspension of **9** in a small amount of ether and added phenyllithium/ether via a syringe. Our procedure provided **14** in 75% yield.



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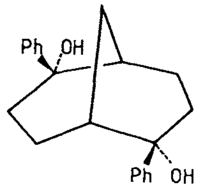

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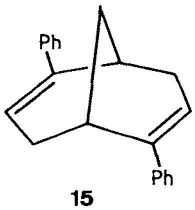

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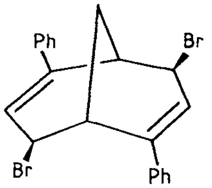

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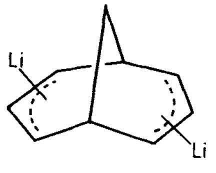

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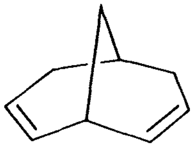

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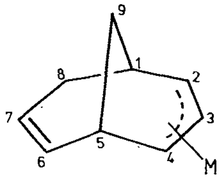
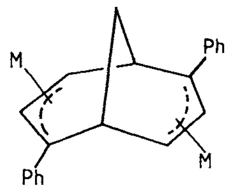


19 b: M = Na
c: M = K
d: M = Cs



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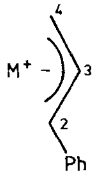
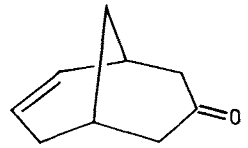


21 a: M = Li
c: M = K

22



The lithiation of **2** was performed at −78 °C under NMR spectroscopic control in a sealed NMR tube. Dry, degassed $[D_8]THF$ was used as solvent, lithium wire was freshly pressed into the evacuated tube prior to sealing in order to give a highly active lithium surface. Upon the first contact between the solution and the lithium wire red spots appeared on the metal, and the color of the solution turned to orange-red. While the ^1H-NMR signals of the starting compound gradually decreased in intensity, the four signals of a single product grew out of the noise. The spectra of the product, obtained after 3 days of metal contact, are shown in Figure 1.

The number of signals points toward a compound with C_{2v} symmetry, and the relative intensities and splitting patterns allow for a ready signal assignment. As expected from the simple ^1H-NMR spectrum, the ^{13}C-NMR spectrum shows four signals which are assigned from their relative intensities and from an "off-resonance" ^{1}H-decoupled spectrum. Particularly characteristic in the spectra are the resonances of C-2, C-4, C-6, C-8 (2-H, 4-H, 6-H, 8-H) at high field (δ_C 81.9, δ_H 3.14), and those of C-3, C-7 (3-H, 7-H) at low field (δ_C 134.4, δ_H 6.20). The above findings leave no doubt that the metallation has proceeded with reductive cleavage of the C-2–C-8-cyclopropane bond. Formula **17** is ment to indicate the existence of a dilithium bicyclo[3.3.1]nonadienediide, but for the moment has no structural implication. The structural elucidation of **17** will be described in the following section.

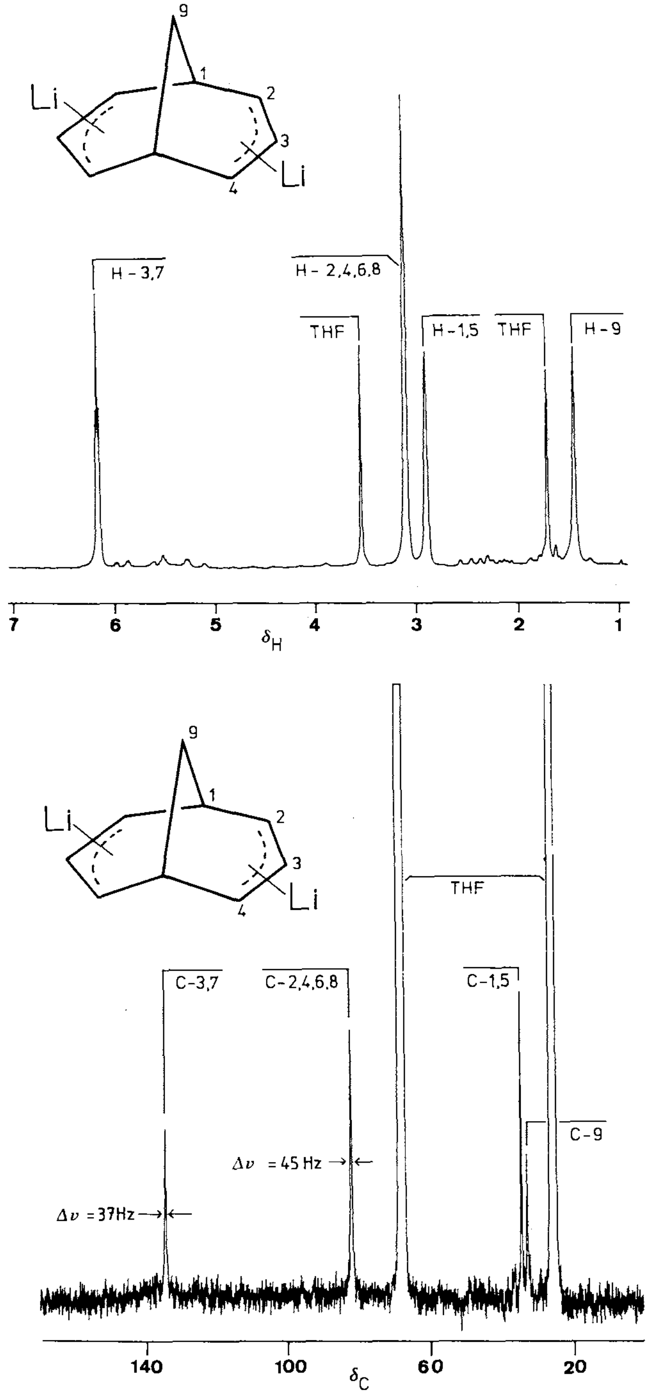


Figure 1. ^{1}H- and ^{13}C-NMR spectra of **17**

Support for the formation of a dilithio species **17** comes from chemical evidence. Upon addition of degassed methanol, the color of the solution disappeared instantaneously. The ^{1}H-NMR spectrum recorded after the quenching pointed toward a small amount of the starting material **2** and a dihydro derivative of **17** as main product. From the ^{1}H-NMR spectrum the isomers **11** and **18**[26,31] cannot be differentiated; however, GC analysis and the ^{13}C-NMR spectra leave no doubt that both dihydro products were formed in a 3:1 ratio. Most probably, **2** was produced via reoxidation by air which was present in the reaction mixture. Indeed, when dry oxygen was bubbled through the solution of the metallation product the starting material was obtained as main product.

While a C_{2v} symmetry of **17** was inferred from the NMR spectra taken at −40°C, further cooling revealed dynamic line-broadening effects. At −90°C the line widths of the signals of C-1 (C-5) and C-9 are not affected, however, those of C-2 (C-4, C-6, C-8) and C-3 (C-7) increase to 42 and 37.5 Hz, respectively. With [D_8]THF as solvent the slow-exchange domain of the dynamic processes could not be obtained. Therefore we performed the lithium reduction of **2** in dimethyl ether (DME) and in mixtures of DME and THF. Reaction in pure DME proceeded similarly to that in THF, however, an orange precipitate was observed already at an early stage. Obviously, the solubility of the metallation product is extremely low, and all attempts to detect its ^{13}C resonances in DME solution at low temperatures failed.

The reaction of **2** with sodium, potassium, and caesium was performed in a similar fashion to that described for lithium. Potassium and caesium were purified by repeated sublimations in vacuo and, finally, deposited in the upper part of the NMR tube as a highly active mirror. Thereby caesium was obtained via thermal decomposition of the azide. A typical experiment was as follows. Brief contact between the THF solution of **2** and potassium caused the color of the solution to turn to deep red. In the course of the reduction the ^{1}H-NMR signals of **2** disappeared while those of a single new compound, **19c**, could be detected.

The ^{1}H-NMR spectrum of **19c** is much more complicated than that recorded in the lithium case and requires a more detailed analysis. In particular, the observation of nine signals with equal intensity indicates a species with only C_1 symmetry. Most characteristic are the occurrence of three signals (1 H each) in the olefinic region and the complex ^{1}H resonances in the aliphatic part of the spectrum which point toward an allyl subunit *and* a C=C double bond. The low-field resonance at δ 6.00 (dd) can be assigned to the central hydrogen (3-H) of the allyl moiety. The splitting patterns of the signals of 2-H and 4-H [δ 3.10 and 2.47, respectively (dd)], can be explained by the coupling with 3-H and the hydrogen atoms at the bridgehead positions. Further assignments followed from H,H decoupling experiments. Irradiation with the frequency of the highfield THF signal simplified the doublet at δ 2.20 and the multiplet at δ 5.55 to a broad singlet and a doublet, respectively. Obviously, the signal of one hydrogen of the methylene group at position 8 is hidden by the solvent signal; consequently, the resonance at δ 5.55 and 5.28 is to be ascribed to 7-H and 6-H, respectively. The absorption of one hydrogen of the methylene bridging group at C-9 appears as a shoulder of the solvent signal, the resonance of the other hydrogen is identified via a decoupling experiment as δ 1.33. The broad signals at δ 2.40 and δ 2.99 are due to the hydrogens 1-H and 5-H, respectively, at the bridgehead positions.

Support for the suggested structure of **19c** came from the ^{13}C-NMR spectrum. It exhibits nine resonance lines and allows the identification of an allyl unit [δ 132.9 (C-3), 76.8 (C-2), 57.9 (C-4)] and a C=C-double bond [131.6 (C-7), 121.7 (C-6)].

As deduced from a gas chromatographic comparison with authentic samples of **11** and **18**[31], the protonation of **19c** with methanol gave rise to a mixture of the isomeric dienes. In a related fashion methylation of **19c** with dimethyl sulfate afforded a product which from its mass spectrum was identified as a *mono*methyl derivative. The failure to observe a dimethyl adduct upon quenching excludes the formation of a "dianion" which might have escaped NMR spectroscopic detection due to precipitation.

The reaction of **2** with sodium and caesium proceeded similarly to that with potassium and gave rise to **19b** and **19d**, respectively, whose structures were deduced from the NMR spectra. The ^{1}H-NMR spectrum of **19c** is shown in Figure 2.

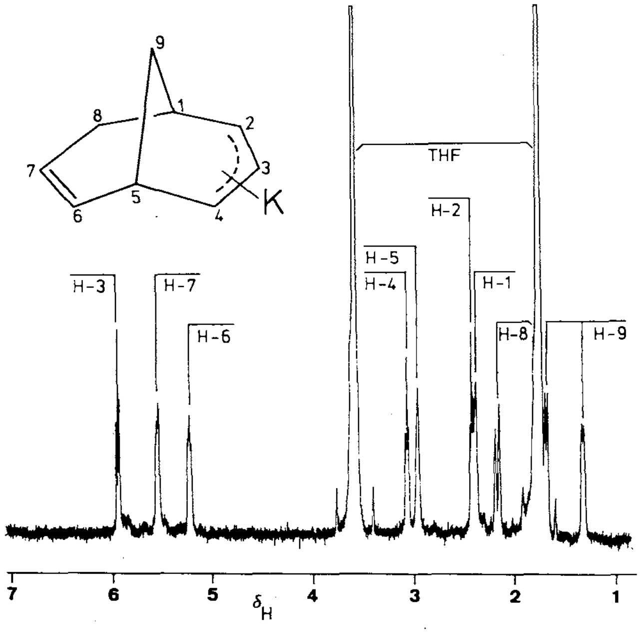


Figure 2. ^{1}H-NMR spectrum of **19c**

In a simple view the formation of the monoanion **19** can be explained by a protonation of the "dianion". Therefore two experimental findings must be noted: (i) a "dianion" was not detected throughout the metallation process, and (ii) the formation of **19b** and **c** is expected to imply the incorporation of deuterium since the reduction has been performed in deuterated THF. A decision as to the source of the electrophile is not possible from the ^{1}H-NMR spectra since the signals of the methylene group at C-8 are partly covered by the solvent signal (see above). However, the ^{13}C-NMR spectra leave no doubt that both the deuterated and protonated monoanions have been formed. In order to exclude water as a potential proton source the following experiment was performed. The starting compound was deposited at the bottom of an NMR tube, and a potassium mirror was prepared by sublimation. [D$_8$]THF was kept over dipotassium stilbenediide in a side arm and transferred between the reaction chamber and the storage vessel by repeated distillation in vacuo. After the final distillation the NMR tube, containing a frozen [D$_8$]THF-solution of **2** and the potassium mirror, was sealed. Even after such a scrupulous drying procedure the formation of protonated monoanion could not be prevented.

2,6-Diphenylbarbaralane (**8**) was treated with lithium according to the above procedure. The ^{13}C-NMR spectrum of the resulting product **20a** and the ^{1}H-NMR spectrum of **20c** are presented in Figure 3. The shifts of the signals of **20a** (see Table) with respect to those of the starting compound and the obvious C_2 symmetry point out that, again, a reductive cleavage of the C-2—C-8 σ bond has occurred. The ^{1}H signal assignments, in particular those of the phenyl protons, were achieved by H,H decoupling experiments. The resonance line of 3-H (7-H) is shifted downfield with respect to those of **8**. The strongest shielding effects are observed for 4-H (8-H) (δ 4.55) and the *para*-hydrogen of the phenyl group (δ = 5.26). Another significant result is the nonequivalence of the two *ortho*- and *meta*-protons, respectively, which is observed even at room temperature. From the ^{1}H-NMR spectrum of **20a** (see Table) it is expected that the corresponding ^{13}C-NMR spectrum exhibits 11 resonance lines. Ten signals are actually observed from which the one at δ 112.1 represents two collapsing lines. The signal assignments follow from the multiplicities in the "off-resonance" ^{1}H decoupled spectra.

Reaction of **8** with potassium provided the dimetallated species **20c** which from its NMR spectroscopic data showed a close structural analogy with the dilithio species **20a**. This finding constitutes a significant difference between **2** and **8**.

Upon reoxidation of **20a** with oxygen or iodine the recyclized barbaralane species could not be detected, instead, polymerization occurred. However, the existence of a dilithium 2,6-diphenylbicyclo[3.3.1]nonadienediide was chemically proven via protonation. Injection of a THF solution of **20a** into an excess of degassed methanol caused immediate decolorization. After addition of pentane, filtration over silica gel, and evaporation of the solvent a crude product was obtained in nearly quantitative yield. An analysis by ^{1}H-NMR and mass spectrometry revealed that, apart from 10% of **8**, a complex mixture of isomeric dihydro products had been formed. Attempts of separating the dihydro derivatives were inhibited by their strong tendency to polymerize.

In another experiment we investigated 3-bromo-1-cyclohexene as an electrophile. If dialkylation of **20a** occurred at C-4 and C-8, a potential starting material for the synthesis of 2,4,6,8-tetraphenylbarbaralane might be obtained. Alkylation of **20a** with 3-bromo-1-cyclohexene under inverse quenching conditions gave a product mixture which, according to mass spectrometry, indeed contained dialkyl adducts. While the complex ^{1}H-NMR spectrum exhibited the correct intensity ratio of aromatic, olefinic, and aliphatic signals, the ^{13}C-NMR spectrum pointed toward the presence of several isomers. A GC analysis indicated four different compounds with similar retention times. Obviously, the dilithio species **20a** is not dialkylated in a regioselective manner.

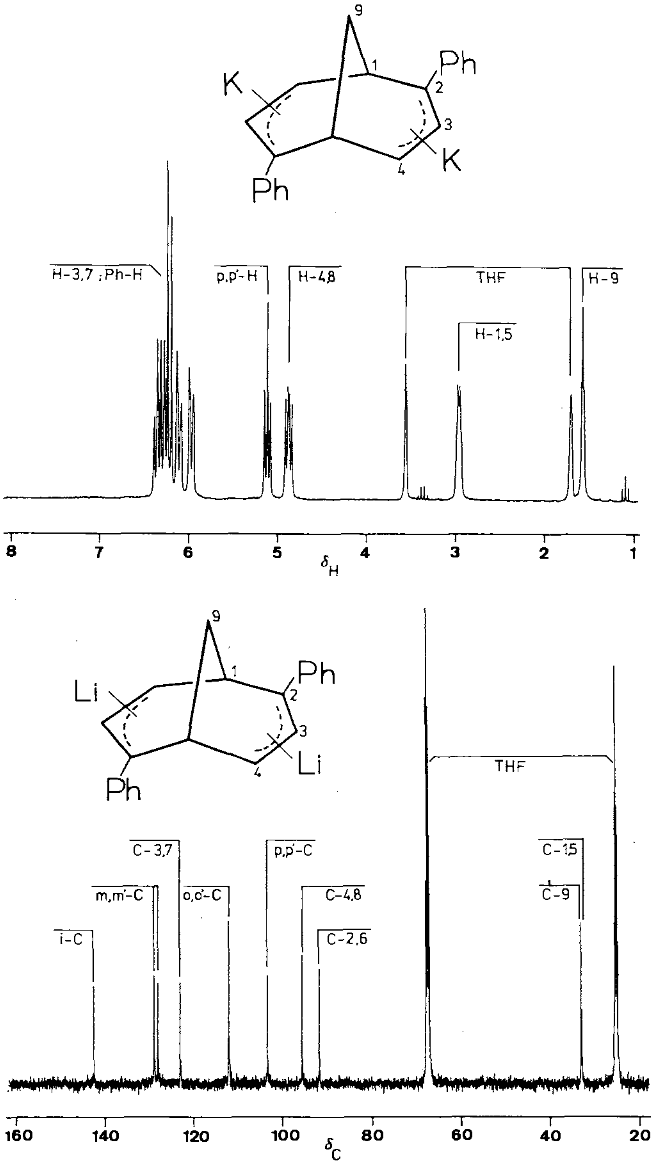


Figure 3. ^{1}H-NMR spectrum of **20c** and ^{13}C-NMR spectrum of **20a**

2. Discussion

The present approach required a convenient synthesis of the starting compounds **2** and **8**. A method recently reported for the preparation of **2** implied allylic bromination of ketone **22** with NBS as a crucial step[16]. However, the yields depend sensitively upon the purity of the NBS used. Our synthesis of **2** followed a sequence (see Scheme 1) which has already proven of great value in the preparation of various semibullvalene[7] and barbaralane[28,30] derivatives. Thereby the troublesome conversion of the diol **10** into the diene[20,23] **11** was simply achieved via a Cugaev elimination. The synthesis of **8** is described in the foregoing section.

If barbaralene is treated with lithium a two-electron transfer occurs which induces a cleavage of the C-2−C-8 σ bond without affecting the remaining framework. The formation of the dilithio compound **17** can be inferred from chemical evidence: reoxidation with oxygen refurnishes the strained barbaralane molecule, and protonation gives rise to a mixture of the dienes **11** and **18**. Not unexpectedly from these findings, lithiation of 2,6-diphenylbarbaralane (**8**) affords a dilithio derivative **20a** incorporating two 1-phenylallyllithium moieties. The reaction of **20a** with electrophiles proceeds in a similar fashion to that of **17**. Alkylation of **20a** with 3-bromo-1-cyclohexene provides dialkyl adducts in a nonregioselective manner. Related findings come from Tanaka et al.[32] who studied the alkylation of phenylallyl metal systems with *tert*-butyl halides and found that the electrophile enters both at position 1 and 3 of the allyl moiety.

It is concluded that lithiation of barbaralane (**2**) proceeds in the same fashion as that of semibullvalene (**1**) (see structural discussion below). A comparison of **1** and **2** as well as of **5** and **17** is particularly promising since the reductive ring opening of **1** affords a cyclooctatetraenediide when potassium is used instead of lithium[13]. A similar reaction is impossible in **2** where the C-1−C-5 bond is replaced by the methylene bridge. However, a disodium, dipotassium, or dicaesium analogue of **17** is not observed. The exclusive formation of the monoanion **19** upon reaction of **2** with Na, K, or Cs can be rationalized by the assumption that the corresponding "dianion", having a weaker interaction with the counterions than in the case of **17**, is too basic and suffers from rapid protonation. Although this argument does not necessarily prove the intermediacy of a "dianion" in the formation of **19**, it is clear, on the other hand, that the "dianionic" bicyclodienyl frame with two allyl subunits can only persist if it is stabilized by a strong interaction with the lithium counterions. It is in accord with these arguments that the dilithio species **5** is protonated by the solvent when the eigensolvation of the lithium ions is improved by the addition of crown ether[13]. Furthermore, when the allyl anion moieties are stabilized by substitution and the excess charge is thus delocalized over a larger π system, as is the case in the diphenyl analogue **20**, then the "dianion" can survive in ethereal solution even as dipotassium derivative.

Another question concerning the formation of **19** is the role of the proton source since both the hydro- and the deuterio derivative **19** are formed in deuterated THF. Related findings have been reported[13,33]. In spite of our careful drying procedure traces of water cannot be excluded. In principle, the starting hydrocarbon or side products formed in the course of the metallation could also act as proton (or hydrogen) source so that the occurrence of the hydro derivative **19** is not yet fully understood.

Table. ^{1}H- and ^{13}C-NMR chemical shifts of metallated barbaralane species and of structurally related allyl systems

	1	2	3	4	5	6	7	8	9
δ_H (6a)[37]		1.78	6.38	1.78					
δ_C (6a)[34]		51.1	147.2	51.1					
δ_H (6c)[37]		1.94	6.28	1.94					
δ_C (6c)[34]		52.9	144.1	52.9					
δ_H (5)[11]	3.78	2.56	6.40	2.56					
δ_C (5)[11]	61.5	73.7	146.5	79.7					
δ_H (23)[38]		2.26	6.23	2.26					
δ_C (23)[38]	67.9	80.0	142.6	80.0					
δ_H (17)[a]	2.94	3.14	6.20	3.14	2.94	3.14	6.20	3.14	1.49
δ_C (17)[b]	34.4	81.9	134.4	81.9	34.4	81.9	134.4	81.9	32.7
δ_H (19b)[c]	2.36	2.44	6.16	3.07	3.00	5.31	5.56	2.10/1.7	1.7/1.29
δ_C (19b)[d]	31.1	74.5[h]	131.1	56.2[h]	35.4	120.7	129.7	40.1	31.9
δ_H (19c)[e]	2.40	2.47	6.00	3.10	2.99	5.28	5.55	2.20/1.7	1.7/1.33
δ_C (19c)[f]	31.3	76.8[h]	132.9	57.3[h]	35.8	121.7	131.3	40.4	32.4
δ_H (19d)[g]	2.36	2.54	5.66	3.14	2.93	5.16	5.50	2.16/1.8	1.64/1.31

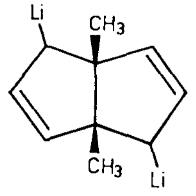
a) [D$_8$]-THF, 400 MHz, -40 °C; b) [D$_8$]-THF, 100 MHz, -40 °C; c) [D$_8$]-THF, 400 MHz, -20 °C; d) [D$_8$]-THF, 100 MHz, -20 °C; e) [D$_8$]-THF, 400 MHz, 25 °C; f) [D$_8$]-THF, 100 MHz, 25 °C; g) [D$_8$]-THF, 400 MHz, -40 °C; h) assignment uncertain.

	1	2	3	4	9	ipso	o	o'	m	m'	p
δ_C (20a)[h']	33.2	91.8	122.9	95.6	32.9	142.2	112.1	112.1	128.8	127.9	103.5
δ_H (20a)[i]	3.06	-	6.46	4.55	1.60	-	6.20	6.05	6.20	6.36	5.26
δ_C (20c)[j]	33.6	93.7	124.2	101.2	33.8	140.3	110.7	110.1	129.8	128.9	101.1
δ_H (20c)[k]	2.98	-	6.2-6.4	4.82	1.58	-	6.15	6.00	6.2-6.4	6.2-6.4	5.13
δ_C (21a)[46]	-	78.4	137.5	66.1	-	148.7	117.1	117.1	128.5	128.5	109.8
δ_C (21c)[15]	-	79.8	136.2	72.6	-	148.0	118.3	111.8	129.2	129.2	107.1
δ_C (25c)[15]	-	81.1	127.7	93.2	-	141.1	109.5	110.1	129.2	130.3	100.9

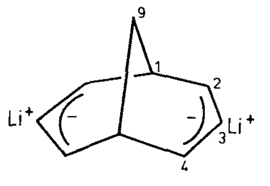
h') [D$_8$]-THF, 100 MHz, -30 °C; i) [D$_8$]-THF, 300 MHz, -50 °C; j) [D$_8$]-THF, 100 MHz, 25 °C; k) [D$_8$]-THF, 200 MHz, 25 °C

Turning to a structural description of **17**, **19**, and **20** it can be learned from the NMR spectroscopic data (see Table) that there is a close analogy of the bicyclic dilithio systems derived from barbaralane and semibullvalene. In each of the species **5**[11] and **17** and the parent allyllithium system **6a**[34–37] the terminal (central) carbons resonate at rather high (low) field. It might be assumed that the two allyl moieties in **17** approach each other due to the bending of the molecule which is created by the methylene bridge. This might induce a redistribution of the charge within the allyl units. However, there is no firm experimental evidence for this assumption since the differences in the ^{13}C-NMR chemical shifts of **5** and **17** can satisfactorily be rationalized on the basis of substituent effects. Thus the shielding of C-3 in **17** can be due to the interaction with C-9 (γ-position) of the bridge. Support for this interpretation comes from the inclusion of **23**[38], the 1,5-dimethyl analogue of **5**, in which C-3 also resonates at somewhat higher field than in **5**.

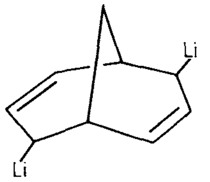
The ^{1}H- and ^{13}C-NMR spectra of **17** at −40°C reveal a C_{2v} symmetry which is compatible with the ionic structure **17A** or a rapid equilibrium of structures with lower symmetry. A distortion might be brought about by a nonsymmetric ion pairing in an essentially ionic structure or by the formation of η^1 instead of η^3 structures in the separate allyllithium units. The parent allyl system has been described by a distorted η^3 structure or a covalent Li-bridged structure[34]. It has also been claimed that the covalent η^1 structures occurring in sterically hindered allyl anions are in equilibrium with essentially ionic structures[39,40]. That, indeed, **17** undergoes a dynamic process follows from the line broadening effects which occur in the ^{13}C-NMR spectra at temperatures below −40°C. This clearly excludes an ionic bonding situation (**17A**). Furthermore, the obvious nonpersistence of truly ionic "bisallyl dianions" in ethereal solvents (see the formation of **19**) rules out contributions of **17A** to an equilibrium. The effective C_{2v} symmetry at higher temperatures can be brought about by dynamic equilibria of structures **17B** and **17B'** with C_2 symmetry and/or of structures **17C** and **17C'** with C_s symmetry. Thereby, **17C**/**17C'** seems less likely for steric and electrostatic reasons. The line widths of C-2 and C-3 at −90°C are significantly broadened, while the signals of C-1 and C-9 do not suffer from a dynamic line broadening. These findings are neither compatible with **17B**/**17B'** nor with **17C**/**17C'**, since the



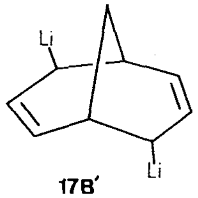
23



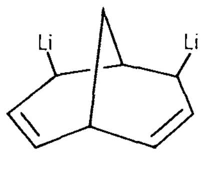
17A



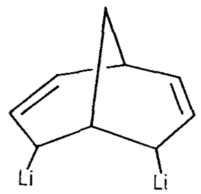
17B



17B′

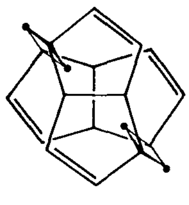


17C

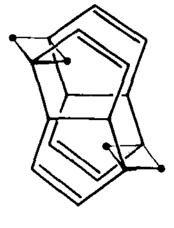


17C′

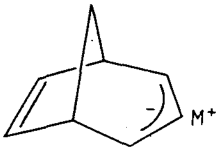
former process should not affect the magnetic sites of C-3 (C-7) and the latter should strongly influence the surrounding of C-1 and C-5. Unfortunately, because of the extremely low solubility of **17** in dimethyl ether or mixtures of dimethyl ether and tetrahydrofuran at temperatures below −100°C, it is not possible to proceed to the slow-exchange domain of the dynamic processes. Related measurements for the analogous semibullvalene species **5** have shown that axially symmetric structures **5B** form diastereomeric dimers of type $(\mathbf{5B})_2$ and $(\mathbf{5B})_2'$. As a consequence, interconversion is expected of the enantiomeric species **5B** and **5B′** as well as of the diastereomeric dimers. Dimer formation is also feasible in **17**, since the methylene bridges do not disturb an approach of two molecules from the *endo* side, and, indeed, a dynamic behavior analogous to that of **5** is the only obvious way of explaining the observed line broadening effects of **17**.



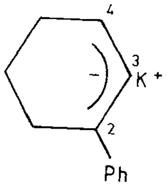
$(\mathbf{5B})_2$



$(\mathbf{5B})_2'$



24



25

The ^{13}C-NMR data of the sodium and potassium species **19b** and **19c** (see Table and Figure 2) point toward a close structural analogy. When comparing the allyl units of **19b** and **19c** with those of **17** it is found that the average signal of δ(C-2) and δ(C-4) in **19b** and **c** is upfield with respect to δ(C-2, C-4) of **17** by 15.0 and 16.5 ppm, respectively. The resonance line of the central carbon of the allyl units remains essentially unaffected.The difference in the ^{13}C-NMR chemical shifts of **17** and **19c** contrasts with the similarity of the data observed for the lithium and potassium derivatives of the parent allyl system, i.e. for **6a** and **6c**. Furthermore, the ^{13}C-NMR spectra of **19b** and **c** do not exhibit line broadening effects at low temperatures. Obviously, the larger radii of the Na and K counterions favor an η^3 allyl structure in **19b** and **c** which finding differs from the occurrence of a η^1 structure in the allyl unit of **17**.

The continuing interest in the potential bishomoconjugation of **24**[41–45] and its derivatives raises the question whether in **19** there is some charge delocalization from the allyl to the ethylene π system. While in **24** a pronounced shielding of the olefinic carbon (δ 90) is observed a similar effect cannot be detected for **19c** [δ 121.7 (C-6), 131.6 (C-7)].

Upon reduction with alkali metals 2,6-diphenylbarbaralane (**8**) undergoes a cyclopropane ring opening to yield bisallyl systems. The most important experimental findings are (i) the existence of "dianions", **20a** and **20c**, with lithium *and* potassium as counterparts, (ii) the similarity of the ^{1}H- and ^{13}C-NMR spectra of **20a** and **20c** as well as (iii) the failure to observe dynamic line broadening effects in the ^{13}C-NMR spectrum of **20a** even at −90°C. The charge transfer to the phenyl ring can, clearly, be seen by the ^{1}H- or ^{13}C-NMR chemical shifts of the *para*-phenyl position in **20a** and **20c**, which closely correspond to those of the model systems[14,15,46] and **25**[15]. According to the well-established correlation between ^{13}C-NMR chemical shifts and local π charge densities[47–50] the carbons C-2 (C-6), C-4 (C-8) and phenyl C-*para* of **20a** and **20c** adopt the greatest portion of the excess charge. These results suggest a strongly increased tendency toward ionic structures. Increasing charge delocalization from the allyl units into the attached phenyl ring stabilizes the bisallyl system and weakens the cation/anion interaction.

It might be expected from electrostatic arguments that the intramolecular interaction of two allyl anion moieties in **20** causes a stronger charge delocalization into the phenyl rings. Comparison with the model compound **21** might, indeed, reveal a charge redistribution in **20**. However, reference to **25**, which is structurally closer to **20**, does not support this possibility. On the other hand, when comparing the shifts of the *para*-phenyl carbons in **20a** and **20c** it appears that the charge delocalization is larger for the potassium system **20c**.

The conjugative interaction of the allyl and phenyl moieties increases the partial π bond character of the C-2–C-*ipso* bond. This follows from the fact that the rotation of the phenyl ring about this bond is slow within the NMR time scale. Even at +40°C the magnetic sites of the *ortho*- and *meta*-carbons, respectively, in **20c** are nonequivalent, and their signals do not show any line broadening. A comparison with the dynamic behavior of the parent 1-phenylallyl system (**21**)[14] seems to indicate a higher rotational barrier in **20a** and **20c**, but in view of the differences in stereochemistry and ion pairing a comparison in terms of the C-2–C-*ipso* π bond order has no sound basis.

3. Conclusion

The similar behavior of semibullvalene (**1**) and barbaralane (**2**) toward lithiation and the structural analogy of the lithiation products **5** and **17** are in sharp contrast to the ring opening reactions induced by higher alkali metals. The occurrence of valence isomerizations and of protonations upon reaction of potassium with **1** and **2**, respectively, strongly suggests the inclusion of such semibullvalene and barbaralane derivatives in which the bisallyl structures are stabilized and, thus, escape the above side reactions. Indeed, the reduction of 2,6-diphenylbarbaralane (**8**) with both lithium and potassium affords structurally analogous products of the bisallyl type. It is along this line that we are now studying ion formation from suitably substituted semibullvalenes.

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Experimental

^{1}H and ^{13}C NMR: Bruker AM 200 (200, 50 MHz), WM 300 (300, 75 MHz), AM 400 (400, 100 MHz). – MS: Varian MAT CH 7 A with data system AMD Intectra DP 10. – Melting points are not corrected.

The diketone **9**[18] and diol **10**[20] were prepared according to literature procedures. The synthesis of **8** was described independently, see ref.[30].

Bicyclo[3.3.1]nona-2,6-diene (**11**): A solution of diol **10** (11.23 g, 72.2 mmol) in 650 ml of dry THF was added dropwise to a suspension of sodium hydride (9.06 g, 210 mmol) in 250 ml THF. The mixture was then refluxed for 2 h whereupon the color turned pink. After cooling of the reaction vessel in an ice bath and addition of carbon disulfide (11.26 ml, 184 mmol) the reaction mixture was refluxed for another 2 h. The resulting orange-brown mixture was allowed to cool, methyl iodide (11.26 ml, 183 mmol) was added followed by another 2 h reflux period. After cooling to room temp. the mixture was hydrolyzed with 6 ml of water. The solvent was evaporated under reduced pressure and the residue dissolved in 300 ml of chloroform. The solution was washed with water and brine, dried with sodium sulfate, and evaporated. The methyl xanthogenate remained as a yellow powder. The pyrolysis of the ester was performed in a distillation apparatus which was heated by a metal bath. In the course of the reaction the temperature of the bath was increased to 250°C. The condensed yellow liquid was subjected to a flash chromatography (silica gel, 40 cm × 4 cm, pentane). Elution was stopped before yellow fractions were obtained. Pentane was removed by distillation over a packed column. Final distillation of the residue (108°C, 200 mbar) gave 4.07 g of diene **11** (46%) as a colorless liquid. The spectral data are identical with those given in the literature[25a].

4,8-Dibromobicyclo[3.3.1]nona-2,6-diene (**12**): A mixture of diene **11** (1.00 g, 8.33 mmol), *N*-bromosuccinimide (3.00 g, 16.67 mmol), 50 ml of dry tetrachloromethane, and a small amount of AIBN was heated to reflux under argon for 1 h. The suspension was allowed to cool to room temp., succinimide was removed by filtration and the solvent evaporated under reduced pressure. Recrystallization of the remaining colorless solid from methanol gave 1.6 g (70%) of the pure dibromide **12**, m.p. 117°C. – ^{1}H NMR (CDCl$_3$): δ = 5.84 (m, 2-, 3-, 6-, 7-H); 4.44 (m, 4-, 8-H); 2.93 (m, 1-, 5-H); 2.20 (t, 9-H). – ^{13}C NMR (CDCl$_3$): δ = 129.5; 127.9 (C-2, 6 and C-3, 7); 47.1 (C-4, 8); 36.7 (C-1, 5); 18.9 (C-9). – MS (70 eV): *m/z* (%) = 278 (4, $M^{+\bullet}$); 199, 197 (79, 81, $M^{+\bullet}$ – Br); 171, 169 (2, 3, bromotropylium ion); 117 (100, $M^{+\bullet}$ – HBr – Br); 91 (67, tropylium ion).

$C_9H_{10}Br_2$ (278.0)	Calcd.	C 38.88	H 3.63	Br 57.49
	Found	C 38.93	H 3.69	Br 57.61

2,4,8-Tribromobicyclo[3.3.1]nona-2,6-diene (**13**): The diene **11** (1.0 g, 8.33 mmol) was brominated with *N*-bromosuccinimide (8.88 g, 50 mmol) according to the above procedure. The resulting semicrystalline material which contained three components according to TLC was subjected to flash chromatography (silica gel, 50 cm × 3 cm, petroleum ether). The second fraction was the tribromide **13** which was purified by recrystallization from ether (270 mg, 9%), m.p. 78°C (transparent prisms). – ^{1}H NMR (CDCl$_3$): δ = 6.12 (d, 3-H); 5.87 (m, 7-H); 5.75 (m, 6-H); 4.64 (m, 8-H); 4.36 (m, 4-H); 3.10 (broad, 1-H); 2.85 (broad, 5-H); 2.30 (m, 9-H); signal assignment by H,H decoupling experiments. – ^{13}C NMR (CDCl$_3$): δ = 128.6, 128.5, 128.4 (C-3, 6, 7); 126.1 (C-2); 47.4, 46.5, 44.8 (C-1, 4, 8); 35.6 (C-5); 20.8 (C-9). Assignments uncertain. – MS (70 eV): *m/z* (%) = 358 (6, $M^{+\bullet}$); 277 (64, $M^{+\bullet}$ – Br); 197, 195 (19, 18, $M^{+\bullet}$ – HBr – Br); 171, 169 (8, 8, bromotropylium ion); 91 (34, tropylium ion).

$C_9H_9Br_3$ (356.9)	Calcd.	C 30.29	H 2.54	Br 67.17
	Found	C 30.25	H 2.60	Br 67.20

Tricyclo[3.3.1.0^{2,8}]nona-3,6-diene (Barbaralane) (**2**): Zn powder (25 g) was stirred three times with 40 ml of hydrochloric acid (3%) and four times with water for 1 min, respectively. Each time the supernatent liquid was decanted. 40 ml of an aqueous solution of copper(II) sulfate (3%) was added which gave rise to the instantaneous formation of the black Zn/Cu couple. The liquid was exchanged by 40 ml of fresh $CuSO_4/H_2O$, and the metal was washed with dry acetone. The latter solvent was then substituted by ether (saturated with argon). Finally, the Zn/Cu couple was rinsed with ether into a three-necked round-bottomed (250 ml) flask under argon. The flask was equipped for magnetic stirring and reflux condenser. The dibromide **12** (2.8 g, 10.1 mmol) was added in solid form. After the exothermic reaction had ceased the mixture was heated to reflux for 1 h. The disappearance of the starting compound and the formation of the debromination product was monitored by TLC (iodine chamber). In addition to the product only oligomeric components with low R_f values were observed. After cooling, addition of 100 ml of pentane, and filtration over celite, the solution was washed with water and dried with sodium sulfate. Upon removal of the solvent by distillation over a packed column some loss of the compound could not be avoided. The remaining residue was distilled in a microapparatus (95°C, 20 mbar) to give 440 mg (37%) of **2** as a colorless solid of m.p. 42°C. The spectral data of **2** are identical with those reported[2].

Dilithium Bicyclo[3.3.1]nona-2,6-dienediide (**17**): Compound **2** (15 mg) was deposited at the bottom of a 5-mm-NMR tube. The tube was attached to a special lithium press and evacuated. Dry [D$_8$]THF (0.5 ml) was distilled in from a storage vessel under vacuum and degassed by repeated freeze-and-pump-cycles. Several pieces (1 cm) of lithium wire were pressed into the evacuated tube and kept in the upper part by a constriction in the glass. The tube was sealed and the solution set into contact with lithium at −78°C. The lithiation gave rise to red spots on the metal surface, and the color of the solution turned to orange. ^{1}H-NMR spectroscopic control of the reaction gave a superposition of the spectra of **2** and **17**, after 3 d of metal contact **17** was detected as single product (NMR data of **17**: see Table).

Sodium Bicyclo[3.3.1]nona-2,6-dienide (**19b**): The reduction of **2** with sodium was performed according to the above technique. The formation of **19b** was complete after 1 d (NMR data see Table).

Potassium Bicyclo[3.3.1]nona-2,6-dienide (**19c**): The NMR tube used for the reaction of **2** with potassium was equipped with a side arm in which the metal could be sublimed under vacuum. Upon the final sublimation the metal was deposited as a highly active mirror in the upper part of the NMR tube. The side arm was sealed off. Contact of the $[D_8]$THF solution of **2** with the metal at −20°C rapidly produced a red color. The formation of **19c** was complete after 2 h as detected from the NMR spectra. In order to avoid even traces of water in the reaction mixture the following technique was applied. The side arm carried a storage vessel with $[D_8]$THF over dipotassium stilbenediide. The solvent was repeatedly transferred between the storage device and the NMR tube (containing **2**) by distillation in vacuo. Finally, the NMR tube with the frozen $[D_8]$THF solution of **2** was sealed. The reaction reproduced the formation of **19c**.

Caesium Bicyclo[3.3.1]nona-2,6-dienide (**19d**): Preparation according to **19c**. Caesium azide was inserted into the side arm and thermally decomposed under vacuum. After several sublimations the caesium metal was deposited as a golden mirror. The quantitative formation of **19d** (with very low solubility) required several days of metal contact.

Dilithium and Dipotassium 2,6-Diphenylbicyclo[3.3.1]nona-2,6-dienediide (**20a** and **20c**): Upon cooling with liquid nitrogen the yellow color of the starting compound **8** reversibly disappeared. The metallation reactions were performed as described for **2**. The NMR spectroscopic data of **20a** and **20c** are reported in the Table.

Quenching Procedures: The chemical structures of the NMR spectroscopically detected organometal systems were proven by quenching reactions. The sealed NMR tube was broken under argon and an excess of the degassed protonation (methanol) or methylation (dimethyl sulfate) agent was injected through a syringe. The color of the solution disappeared instantaneously.

Preparative Alkylation of **20a** *with 3-Bromo-1-cyclohexene:* The metallation and quenching on a larger scale were performed in sealed glass ampoules which contained two separate compartments connected by a small constriction in the glass. **8** (0.90 g, 3.33 mmol) was deposited in one compartment, 80 ml of dry THF were distilled in and degassed. After insertion of lithium wire the evacuated ampoule was sealed and the metallation was started. The solution was kept in metal contact for 7 d. The deep red solution of **20a** was transferred to the second compartment of the ampoule and thus separated from the metal. The ampoule was broken at a side arm and connected to a Schlenk-ware flask which contained a solution of an excess of 3-bromo-1-cyclohexene in THF. When the solution of **20a** was added dropwise to the alkylating agent, its color disappeared immediately. After the addition of ether and filtration (silica gel) an aqueous workup was performed. Upon removal of the solvent the yellow residue was proven via TLC and GC analysis to contain at least four different products which could not be separated on a preparative scale.

2,6-Diphenylbicyclo[3.3.1]nonane-2,6-diol (**14**): 6.08 g (40 mmol) of diketone **9** was covered with 100 ml of ether. The vigorously stirred mixture was cooled to −10°C, 200 ml of an ethereal solution of phenyllithium (1.2 M) was added over a period of 30 min. After another 30 min **9** had completely dissolved. The solution was allowed to warm to 0°C and was then stirred for another 2 h. Upon careful addition of 5 ml of water a white precipitate appeared. After addition of 200 ml of aqueous ammonium chloride (10%) the solution was extracted with ether. The combined organic layers were washed with aqueous ammonium chloride and water. After drying with sodium sulfate, the solvent was removed under vacuum, the semicrystalline, foamy residue was recrystallized from a mixture of ether and petroleum ether to yield 9.19 g (75%) of **14**, m.p. 139°C (white needles). For spectroscopic data see ref.[30].

$C_{21}H_{24}O_2$ (308.4)	Calcd.	C 81.78	H 7.84
	Found	C 81.82	H 7.82

CAS Registry Numbers

2: 14693-11-9 / **8**: 106913-96-6 / **9**: 16473-11-3 / **10**: 16473-12-4 / **10** [bis(methyl xanthogenate)]: 108816-31-5 / **11**: 13534-07-1 / **12**: 198816-29-1 / **13**: 108816-30-4 / **14**: 106913-98-8 / **17**: 108834-47-5 / **19b**: 108816-33-7 / **19c**: 108816-35-9 / **19d**: 108816-37-1 / **20a**: 108834-43-1 / **20c**: 108834-45-3

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