the flask at 15 mmHg pressure and then by lowering the pressure to 0.05 mmHg and heating the flask in an oil bath at 60–70 °C. The crude product weighed 4.02 g (74%) and showed only a trace of acetophenone when examined by 300-mHz NMR. The NMR spectrum was identical with the previously reported spectrum of unlabeled **13**-^{18}*O*. This crude product was converted without purification to the trifluoroacetate.

Preparation of Trifluoroaceate 1-^{18}*O*. The procedure was analogous to that described for the preparation of unlabeled **1**.[1] A solution of 4.018 g of **13**-^{18}*O* in 35 mL of freshly distilled pyridine (from P_2O_5) was cooled at 0 °C as 4.80 g of trifluoroacetic anhydride was added dropwise. The mixture was stirred at room temperature for 4 h and then taken up into 50 mL of ether and 50 mL of Skelly F. The mixture was washed with three portions of cold water, cold 10% HCl, and saturated NaCl solution and dried over $MgSO_4$. The solvents were removed by using a rotary evaporator, and the residue was distilled to give 4.978 g (92%) of **1**-^{18}*O*, bp 94–97 °C (0.05 mm). Mass spectral analysis by examination of the peaks at *m/e* 373 (M + 1 peak for **1**-^{18}*O*) and *m/e* 370 (parent peak for **1**-^{16}*O*) indicated 96% ^{18}O incorporation in the product trifluoroacetate.

Preparation of Trifluoroacetate 1-^{17}*O*. Acetophenone-^{17}*O* was prepared by hydrolysis of acetophenone dimethyl acetal with $H_2{}^{17}O$ (Merck Shape & Dome Isotopes, 23% ^{17}O) using a procedure analogous to that described above. The ^{17}O NMR of acetophenone-^{17}*O* showed a signal at δ 539. Conversions to **13**-^{17}*O* (^{17}O NMR δ 40.3) and **1**-^{17}*O* (^{17}O NMR δ 170.7) were also analogous to the procedures described above.

Acetolysis of Trifluoroacetate 1-^{17}*O*. The procedure was analogous to that described for the acetolysis of unlabeled **1**.[1] A solution of 1.956 g of **1**-^{17}*O* (23% ^{17}O) in 60 mL of 0.1 M NaOAc in acetic acid containing 1% acetic anhydride was heated for 11 h at 100 °C. A standard aqueous workup followed as previously described. The thiol **3** was removed by extraction with K_2CO_3 solution. After solvent removal by using a rotary evaporator, the ^{17}O NMR spectrum of the crude residue (which contained **2**-^{17}*O* and small amounts of **4** and **5**) was recorded (Figure 1). The spectrum shown corresponds to 44 000 scans with an aquisition time of 0.295 s/scan. The spectrum shows signals at δ 85 (doublet, J = 145 Hz, P=^{17}O) and 524 (C=^{17}O) in a 399:100 ratio (±3%) respectively. The spectrum is identical with that of a sample of pure **2**-^{17}*O* isolated by preparative gas chromatography.

Reaction of 2-^{17}*O* with Ammonia. The crude solvolysis product obtained above (660 mg) was placed in a 25-mL flask, and 10 mL of liquid ammonia (distilled from sodium) was condensed into the flask under nitrogen by using a cold finger condenser. After 90 min at −33 °C, the ammonia was allowed to evaporate and a short-path distillation head was attached. The flask was evacuated at 20-mmHg pressure, and the receiver flask was then cooled to −78 °C. The pressure was then lowered to 0.05 mmHg, and the flask was heated to about 70 °C. The solid amide **14** was sublimed and condensed in the short-path condenser. The solid **14** (75 mg; 37%) was collected and washed with a small amount of Skelly F. The product is relatively insoluble in $CDCl_3$. Recrystallization from $CDCl_3$ gave a sample which had a infrared spectrum identical with that of an authentic sample of unlabeled **14**. Figure 2 shows the ^{17}O NMR spectrum of 50 mg of this mixture of **14**-^{17}*O* and **14**-^{16}*O* in 3.5 mL of diethyl ether. The spectrum shown corresponds to 15 000 scans with an aquisition time of 0.2147 s/scan. **14**-^{17}*O* shows a signal at δ 324, while the ether solvent appears at δ 14.3.

Acetolysis of Trifluoroacetate 1-^{18}*O*. The procedure was analogous to that described for the acetolysis of unlabeled **1**. Reaction of 270 mg of **1**-^{18}*O* (96% ^{1}·O) in 14 mL of HOAc at 100 °C for 9 h gave. after a standard aqueous workup, 194 mg of a mixture of **2**-^{18}*O*, **4**, and **5**. (The thiol **3** was removed by an aqueous K_2CO_3 extraction.) This mixture was analyzed by ^{31}P NMR. The phosphoryl region of this spectrum is shown in Figure 3. The relative areas of the P=^{16}O signal at δ 20.95 and the P=^{18}O signal at δ 20.89 were determined by computer simulation of the partially overlapped spectrum obtained when the spectrum is recorded with a line broadening of 1 Hz (Figure 3b).

Acetolysis of Trifluoroacetate 1-^{18}*O* with Added Unlabeled Thiol 3. A mixture of 80 mg of **1**-^{18}*O* and 29 mg of **3** (prepared from solvolysis of unlabeled **1** in formic acid)[1] was heated in 3 mL of 0.075 M sodium acetate in acetic acid containing 1% acetic anhydride at 100 °C for 25 min (25% reaction). The mixture was analyzed directly in the acetic acid solvent by ^{31}P NMR which showed a P=^{16}O signal at δ 21.44 and a P=^{18}O signal at δ 21.40 in a 20:80 ratio. After 60 min (50% reaction) the P=^{16}O to P=^{18}O ratio was identical.

Acetolysis of Trifluoroacetate 1. Product Study as a Function of Time. A solution of 120 mg of unlabeled **1** in 3 mL of 0.075 M sodium acetate in acetic acid containing 1% acetic anhydride was heated at 100 °C in a NMR tube. At certain time intervals, the tube was analyzed by ^{31}P NMR for **2** (which appears at δ 26.34) and **3** (which appears at δ 21.44) by integration of the appropriate signals. Results are presented graphically in Figure 4.

Acetolysis of Trifluoroacetate 1-^{18}*O* for 1 Half-Life. Analysis of Recovered Unreacted 1-^{18}*O*. A solution of 600 mg of **1**-^{18}*O* in 22 mL of HOAc was heated at 100 °C for 60 min (1 half-life), and a standard aqueous workup followed. The residue, after solvent removal, was chromatographed on 17 g of silica gel and eluted with 10% ether in Skelly F. The unreacted **1**-^{18}*O* and olefin **4** (11.6:1 ratio) eluted immediately with no trace of **2** or **3**. This mixture (296 mg) was placed in a 10 mL flask, and 4 mL of anhydrous ammonia was condensed under nitrogen. After 90 min at −33 °C, the ammonia was allowed to evaporate and the trifluoroacetamide **14** was isolated as previously described above. The crude **14** (65 mg; 53%) was washed with Skelly F and recrystallized from $CDCl_3$. Mass spectral analysis showed 95% of **14**-^{16}*O* and 5% of **14**-^{18}*O*.

Acknowledgment is made to the National Science Foundation and to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also thank Prof. A. Serianni and D. Schifferl for their many useful suggestions.

Registry No. **1**-^{18}O, 103712-06-7; **1**-^{17}O, 103712-09-0; **2**(C=^{17}O), 103712-10-3; **2**(P=^{17}O), 103712-11-4; **3**, 99668-46-9; **4**, 99668-44-7; **5**, 99668-45-8; **11**, 4316-35-2; **12**-^{17}O, 103712-07-8; **12**-^{18}O, 73007-56-4; **13**-^{17}O, 103712-08-9; **13**-^{18}O, 103712-05-6; **14**-^{16}O, 354-38-1; **14**-^{17}O, 103712-12-5; **14**-^{18}O, 103712-13-6; ^{17}O, 13968-48-4; ^{18}O, 14797-71-8; $HP(S)(OEt)_2$, 991-01-9.

Novel Benzyllithium Structures

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Abstract: Novel benzyllithium systems, e.g., **2**, **4**, and **5**, have been prepared and characterized via chemical and NMR spectroscopic evidence. The important experimental aspects of this work are the method of carbanion preparation via reductive cleavage of σ-bonds and the multinuclear NMR (^{1}H, ^{13}C, ^{7}Li, ^{6}Li) approach. It appears that carbanion and dianion structures are deeply affected by the intramolecular interaction between a carbanion moiety and a remote π-system as well as by the interaction of two carbanion subunits.

The structures of lithiated hydrocarbons are the subjects of extensive experimental and theoretical studies.[2] An important question is concerned with the hybridization of the carbanion center and, thus, the degree of covalent or ionic bonding.[2-7] The

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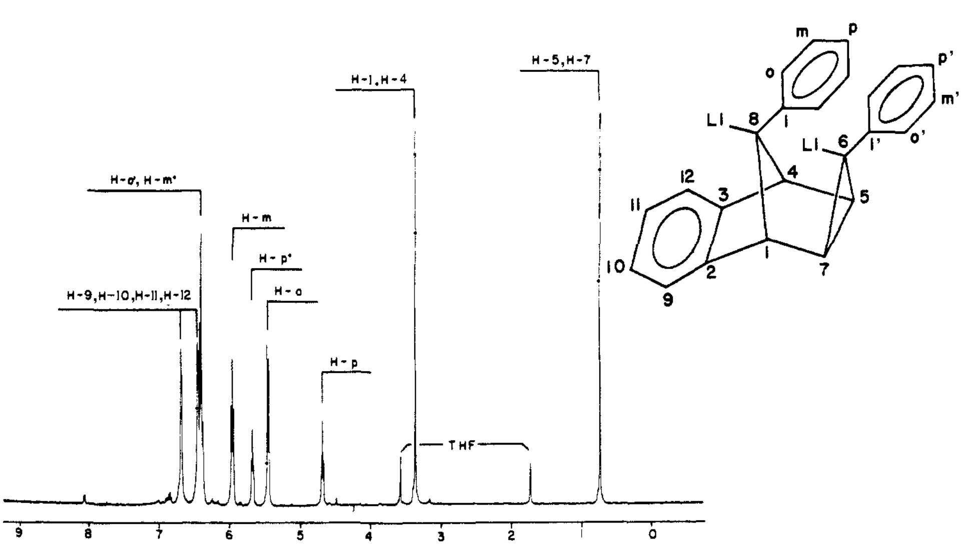
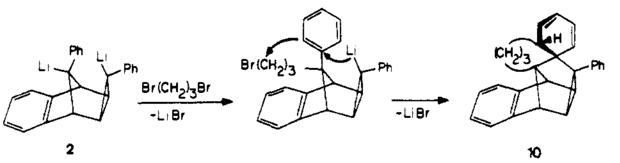


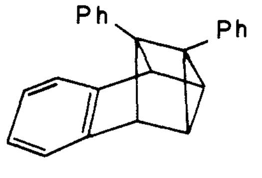
Figure 1. ^{1}H NMR spectrum of **2** (400 MHz, −80 °C, THF-d_8).

Scheme I

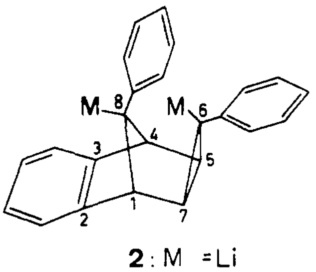


potential tetravalent character of lithium attracts the attention toward additional structural features such as the intermolecular aggregation of carbanions,[2,7–13] the intramolecular interaction between a carbanionic unit and a remote π-system,[14,15] and the intramolecular interaction, in particular via Li bridging, between two separate carbanion moieties of dianions.[4,16–18]

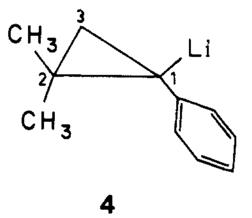
In coping with such subtle carbanion properties the novel dianion **2** appeared as the most suitable subject. Compound **2** is



1



2 : M = Li
3 : M = Na



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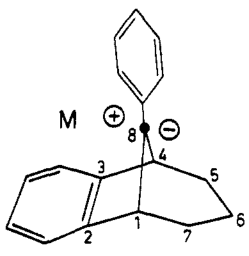

5 : M = Li
6 : M = Na
7 : M = K

formed quite unexpectedly upon lithium reduction of **1**[19] and incorporates, as will be shown below, two completely different benzyllithium moieties. In order to elucidate the unprecedented structure of **2**[20] we had to include the cyclopropyllithium species **4** and the benzobicyclooctenyllithium system **5** as hitherto unknown model compounds.[21,22]

We describe the preparation of the lithiated hydrocarbons **2**, **4**, and **5** and their structural characterization via ^{1}H, ^{13}C, ^{6}Li, and ^{7}Li NMR spectroscopy as well as the stereochemistry of their reactions with electrophiles.

Results

Upon reaction with lithium in tetrahydrofuran the polycycle **1** transforms into a brown dilithio derivative **2** (see below) of

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Table I. ^{13}C and ^{1}H NMR (in Parentheses) Chemical Shifts of the Title Carbanions **2**, **3**, **4**, **5**, and **7**

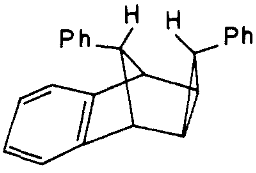
	2[a]	**3**[b]	**4**[c]		**5**[d]		**7**[d]	
C-1,4	51.4 (3.35)	49.2 (3.21)	C-1	46.5	C-1,4	46.8	C-1,4	45.2
C-2,3	157.5	156.5	C-2	19.2	C-2,3	152.3	C-2,3	150.7
C-5,7	36.2 (0.72)	35.6 (0.74)	C-3	[c](0.17; 0.53)	C-5,7	26.0	C-5,7	29.5
C-6	59.0	*b*	CH_3	32.1 (0.80 and 1.04)	C-6	21.5	C-6	21.4
C-8	100.0	106.1	CH_3'	*c*	C-8	74.5	C-8	92.0
C-10,11	117.2 (6.43)	117.0 (6.46)			C-9,12	121.2	C-9,12	120.7
C-9,12	121.6 (6.65)	121.6 (6.65)			C-10,11	124.5	C-10,11	124.6
C-*i*	145.3	135.5	C-*i*	163.9	C-*i*	148.3[e]	C-*i*	134.9
C-*o*	108.9 (5.41)	103.5 (5.04)	C-*o*	123.0 (6.35)	C-*o*	113.8	C-*o*	106.1
C-*m*	128.1 (5.93)	130.3 (5.79)	C-*o*	124.1 (6.46)	C-*m*	129.1	C-*m*	130.4
C-*p*	96.9 (4.63)	90.0 (4.12)	C-*m*	126.7 (6.57)	C-*p*	100.9	C-*p*	90.8
C-*i*′	164.1	162.8	C-*m*	127.9 (6.57)				
C-*o*′	121.3 (6.38)	120.3 (6.24)	C-*p*	112.2 (6.00)				
C-*m*′	127.3 (6.38)	127.6 (6.31)						
C-*p*′	108.6 (5.66)	106.6 (5.47)						

[a] THF-d_8, -30 °C, 75 (400) MHz; the assignment of C-9,12/C-*o*′ (H-9,12/H-10,11) is tentative. [b] THF-d_8, -50 °C, 100 (400) MHz; the assignment of C-9,12/C-*o*′ (H-9,12/H-10,11) is tentative. The signal of C-6 has not been detected. [c] THF-d_8, -100 °C, 75 (300) MHz; the high-field signal of THF is covering sample resonances. [d] THF-d_8, -40 °C, 75 MHz; the assignment of C-9,12/C-10,11 is tentative. [e] The assignment is tentative.

unknown structure. Reoxidation of the dianion with oxygen yields back the starting compound **1**. Accordingly, the lithiation does not seriously change the molecular framework. The disodium analogue of **2**, namely species **3**, can also be prepared.

The dilithiohydrocarbon **2** can be characterized by a well-resolved ^{1}H NMR spectrum (see Figure 1). The ^{1}H signal assignments follow from the splitting pattern (e.g., AA′BB′ spin system of H-9–H-12) and from extensive decoupling experiments (see Experimental Section). The latter allow one to identify the ortho, meta, and para protons of two separate phenyl groups. It appears from the number of ^{1}H NMR resonances that the dilithio product must maintain a plane of symmetry through C-6, C-8, and the middle of the C-5–C-7 bond. Both the aliphatic and aromatic resonances experience a significant upfield shift with respect to those of the starting material.

More significant for a structural elucidation is the reaction of **2** with electrophiles. Protonation of **2** with alcohol affords mixtures of the diastereomeric dihydro systems **8** and **9**. The ^{1}H and ^{13}C NMR chemical shifts of **8** and **9** do not allow for a reliable structural assignment;[23,24] the structures given in the formulas follow from NOE measurements (irradiation of H-8; see Experimental Section).



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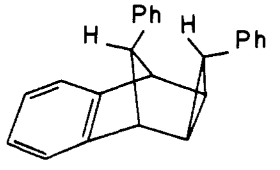

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The relative amount of **8** and **9** depends sensitively upon the nature of the proton source. With *tert*-butyl alcohol as quenching agent the ratio of **8** and **9** is 5:1; with methanol, 1:1.

As expected from the formation of the dihydro derivatives, the alkylation of the dianion **2** with 1,3-dibromopropane leads to the incorporation of a propylene moiety. The structure of the alkylation product **10** (see Scheme I and Figure 2) is proven by an X-ray analysis.[25] The alkylation reaction, while supporting the dianion character of **2**, proceeds as a complex multicenter process (see Discussion).

The quenching reactions indicate that the lithiation of **1** implies the reductive cleavage of the C-6–C-8 σ-bond. The ^{13}C NMR spectrum (see Figure 3) is in accord with this interpretation. The signal assignments of proton-bearing carbons are obtained from selective $^{13}C\{^{1}H\}$ decoupling experiments which allow one to identify the resonances of the benzene unit at C-2, C-3 as well as of two phenyl rings. The signals of two (quaternary) carbanion carbons are found at δ 59 and 100. Their assignment is based on a comparison with the ^{13}C NMR spectra of the reference compounds **4** as well as **5** and will be discussed in the following section.

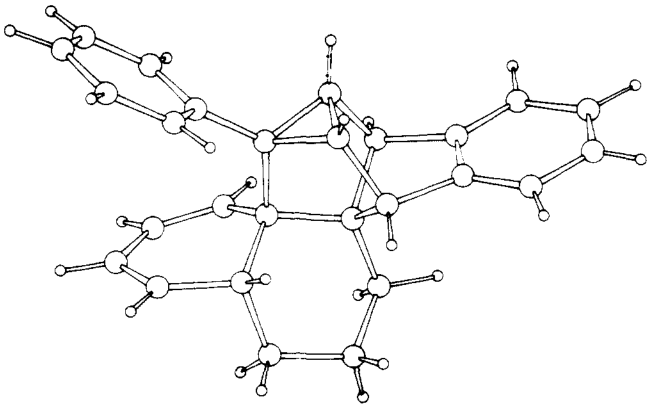

Figure 2. Crystal structure of **10**.

Table II. ^{1}H NMR Chemical Shifts (THF-d_8) of Phenyl Protons in the Benzyl Moieties of **2**, **3**, **4**, **5**, **6**, and **7**

	2[a]	**3**[b]	**4**[c]	**5**[d]	**6**[e]	**7**[d]
o-H	5.41	5.04	6.35	5.89	5.58	5.32
o-H			6.46			
m-H	5.93	5.79	6.57	6.40	6.26	6.10
m-H			6.57			
p-H	4.63	4.12	6.00	5.20	4.73	4.42
o′-H[f]	6.38	6.24				
m′-H	6.38	6.31				
p′-H	5.66	5.47				

[a] -30 °C, 400 MHz. [b] -50 °C, 400 MHz. [c] -100 °C, 300 MHz. [d] -40 °C, 300 MHz. [e] -10 °C, 400 MHz. [f] This sign (′) denotes the phenylcyclopropyl moiety in **2** and **3**.

As expected from the existence of two separate carbanion units, **2** gives rise to two different ^{7}Li signals at δ 0.61 ($\Delta\nu$ = 25 Hz, -70 °C) and -1.09 ($\Delta\nu$ = 36 Hz, -70 °C) (δ measured with respect to 1 M LiCl in D_2O). The ^{13}C NMR signal at δ 59 is significantly broadened ($\Delta\nu$ = 35 Hz, -30 °C). More significant for the C–Li bonding is the relevant one-bond coupling constant whose measurement, however, requires the use of ^{6}Li.[3,26-29] When **1** is

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(25) Crystals of **10** are triclinic, a = 6.963 (2) Å, b = 8.894 (2) Å, c = 15.802 (4) Å, α = 97.29 (2)°, β = 102.61 (2)°, ν = 91.38 (2)°, Z = 2, space group $P\bar{1}$. The structure was solved by direct methods and was refined by full-matrix least-squares procedures to R = 0.052 and R_W = 0.043 for 1847 independent reflections with $I > 3\sigma(I)$ collected with Mo Kα radiation on an Enraf-Nonius CAD4 diffractometer. Crystallographic details are given in the supplementary material.

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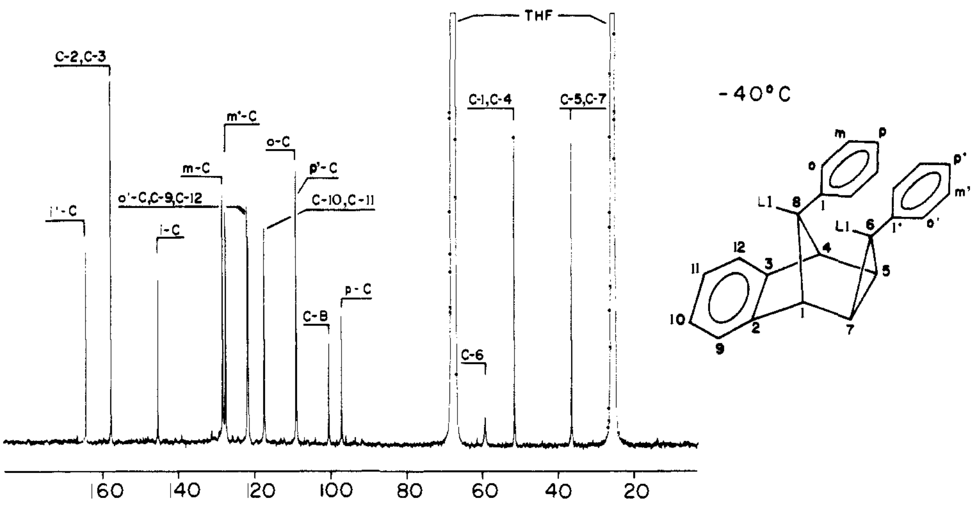
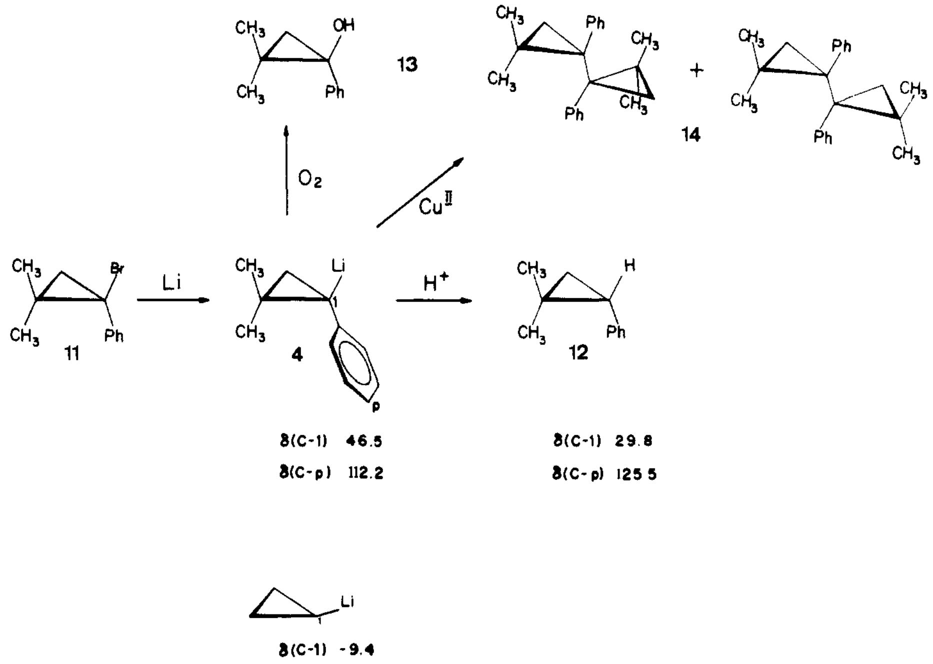


Figure 3. ^{13}C NMR spectrum of **2** (75 MHz, -40 °C, THF-d_8).

Scheme II



reduced with ^{6}Li (95%) and the ^{13}C NMR spectrum is recorded, one carbanion carbon gives rise to a sharp resonance at δ 100, while the other appears as a triplet centered at δ 59 (^1J(C–Li) = 6.9 Hz; -78 °C).

The appearance of the ^{1}H NMR spectrum of the disodium compound **3** is very similar to that of **2**, and signal assignments (see Tables I and II) are achieved in a quite analogous fashion.

While the constitution of the novel dianions **2** and **3**, i.e., the existence of two benzylmetal moieties at C-6 and C-8, can readily be inferred from the above chemical and spectroscopic information, a deeper insight into the prevailing bonding situation requires the inclusion of structurally related reference compounds.

We have therefore prepared and NMR spectroscopically characterized the yet unknown organolithium species **4**[21] and **5**. The 1-lithio-1-phenyl-2,2-dimethylcyclopropane (**4**) is accessible upon reaction of the corresponding bromide **11** with lithium metal in THF at low temperatures. The sodium and potassium analogues of **4** cannot be prepared via reduction of the bromo precursor. The NMR spectroscopic data of **4** and the related hydrocarbon **12** are given in the tables and in Chart II.

The chemical structure proof of **4** rests upon several quenching experiments (Scheme II). Protonation of **4** gives **12**, reaction of **4** with oxygen, after workup with ammonium chloride/water, provides the alcohol **13**, and oxidative coupling of **4** with copper(II) triflate provides an almost 1:1 mixture of the *meso* and *d*/*l* forms of the dimer **14**.

The other model compounds, **5**, **6**, and **7**, are accessible from ketone **15**.[30] Its reaction with phenyllithium, after aqueous workup, diastereoselectively produces the alcohol **16** whose configuration is established from an X-ray analysis. The methylation of **16** to the ether **17** can be achieved by reaction of **16** with sodium hydride, cation exchange with tetra-*n*-butylammonium bromide, and alkylation of the "naked" anion with dimethyl sulfate.[31]

The ether **17** can be cleaved with alkali metals in THF at low temperatures to yield the corresponding organometal systems **5**, **6**, and **7**. The NMR spectroscopic characterization (see Figure 4 and Tables I and II) is performed as described for the title compound **2**. The protonation of **5** with methanol gives only the hydro product **18**. The configuration at C-8 of **18** is established

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(27) Bywater, S.; Lachance, P.; Worsfold, D. J. *J. Phys. Chem.* **1975**, *79*, 2148.

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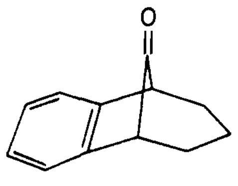

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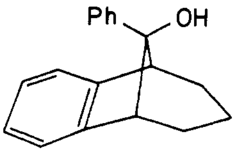

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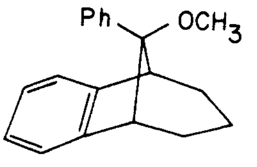

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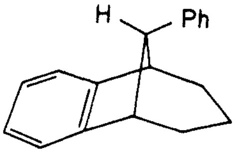


18

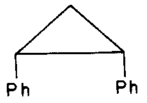
from the deshielding of H-8 due to the benzene moiety at C-2 and C-3 and the lack of a significant shielding of the ortho protons of the phenyl ring (see Experimental Section).

Discussion

The protonation of the dianion **2** to yield the dihydro systems **8** and **9** points out that the lithiation of **1** proceeds via the reductive cleavage of the C-6–C-8 σ-bond and does not affect the remaining framework. Thereby, the diphenylethane moiety transforms into two separate benzyllithium moieties. The reductive cleavage of diarylethane species such as **19** is well documented.[32,33] Also important for the reduction of **1** is the relief of strain within the polycycle. The ring opening of 1,2-diphenylcyclopropane (**20**)[34,35] and of the semibullvalenes **21**[36,37] and **22**[38] upon treatment with lithium to yield the dianions **23**, **24**, and **25**, respectively, can, therefore, be regarded as a related process: a strained σ-bond is cleaved and the resulting charge is effectively stabilized. Reoxidation of the dianion **2** with oxygen yields back the starting hydrocarbon, and similar findings hold for the examples **20**/**23** and **22**/**25**.

$Ar-CH_2-CH_2-Ar$

19



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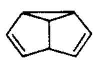

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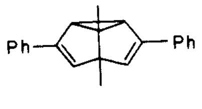

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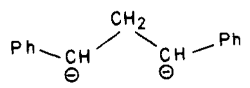

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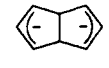

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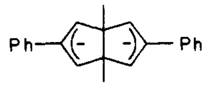

25

$Ph-CH_2Li$

26

One might anticipate from these results that the reaction of **2** with 1,*n*-dihaloalkanes should allow the insertion of an alkanediyl chain between the carbanion units. An insertion product is not obtained; instead one isolates **10**, a stable crystalline compound, whose structure is convincingly proven by an X-ray analysis (see Figure 2).[25] While experimental evidence on the mechanism of this reaction is not available, the following route can be postulated: the electrophile first alkylates the carbanion center C-8 (see Scheme I); in a subsequent step the carbanion unit at C-6 attacks the ipso position of the phenyl ring at C-8. The negative charge is, thereby, transferred to the remaining π-unit of the phenyl ring at C-8. The latter is then alkylated in the ortho position by the neighboring bromopropyl group.

The reoxidation, protonation, and alkylation experiments prove the constitution of the dianion **2** and indicate the existence of two benzyllithium moieties.

Before describing, via spectroscopic evidence, the prevailing bonding situation, it is helpful to realize the following characteristic properties of **2**: (i) **2** persists in THF solution even at room temperature. The interaction between the "dianionic" hydrocarbon framework and the metals is not significantly affected by a change of the solvent; i.e., the ^{1}H and ^{13}C NMR chemical shifts suffer from only minor changes when either HMPA or benzene is added to the THF solution. (ii) **2** exists in one single configuration with nonequivalent Li nuclei. These conclusions can readily be inferred from the number of ^{1}H, ^{13}C, and ^{7}Li NMR signals. (iii) It has been shown by the work of Seebach[3] that the use of ^{6}Li in the NMR description of carbanions allows the easy detection of C–Li couplings. The multiplicity of the ^{13}C NMR signal of the carbanion center reveals the number of "covalently" bonded lithium nuclei.[3,26-29] Thus, the detection of a triplet resonance for C-6 in the ^{13}C spectrum of **2** (produced upon treatment of **1** with ^{6}Li) indicates that C-6 is bonded to a single lithium. The observation of a C-6-Li coupling and the failure to detect a C-8–Li coupling are also indicative for the electronic structure of **2** (see Tables I and II).

In the ^{1}H and ^{13}C NMR spectra of **2** the signals of one phenyl ring (see Figure 3 and Tables I and II) are at much higher field than those of the other phenyl ring; i.e., they suffer from a pronounced charge-induced shielding. The effective delocalization of the carbanion charge into the attached phenyl ring requires a sp^2 hybridization of the carbanion center, so that it must give rise to the carbon resonance at δ 100. Consequently, the second benzyllithium system with less charge delocalization to the phenyl ring must give rise to the high-field absorption of the carbanion centre at δ 59.

The above-mentioned ^{13}C–^{6}Li coupling with only one carbanion carbon (C-6) is in accord with this finding. It has been pointed out by several authors that ionic organolithium systems fail to exhibit C–Li coupling even at very low temperatures.[3,26-29] Likewise, when **2** is prepared with normal lithium metal the ^{13}C NMR signal of C-6 is significantly broadened ($\Delta\nu_{1/2}$ = 35 Hz, −30 °C). This must be ascribed to the interaction of C-6 and the quadrupolar ^{7}Li nucleus within a partially covalent bond.[39] When the chemical shifts of the *p*-phenyl carbons in **2** are contrasted with the corresponding value of benzyllithium (**26**) itself (δ

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[33] Grovenstein, E., Jr.; Bhatti, A. M.; Quest, D. E.; Sengupta, D.; VanDerveer, D. *J. Am. Chem. Soc.* **1983**, *105*, 6290.

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[36] Goldstein, M. J.; Wenzel, T. T.; Whittaker, G.; Yates, S. F. *J. Am. Chem. Soc.* **1982**, *104*, 2669.

[37] Goldstein, M. J.; Wenzel, T. T. *J. Chem. Soc., Chem. Commun.* **1984**, 1654. Goldstein, M. J.; Wenzel, T. T. *J. Chem. Soc., Chem. Commun.* **1984**, 1655.

[38] Schnieders, C.; Altenbäch, H. J.; Müllen, K. *Angew. Chem.* **1982**, *94*, 638; *Angew. Chem., Int. Ed. Engl.* **1982**, 21, 637.

[39] We don't touch upon the principle question of the covalent or ionic character of a C-Li bond, see ref. 2 and 3. These terms are meant to indicate the differences of the C-Li bonding between **2**, **4**, and **5**.

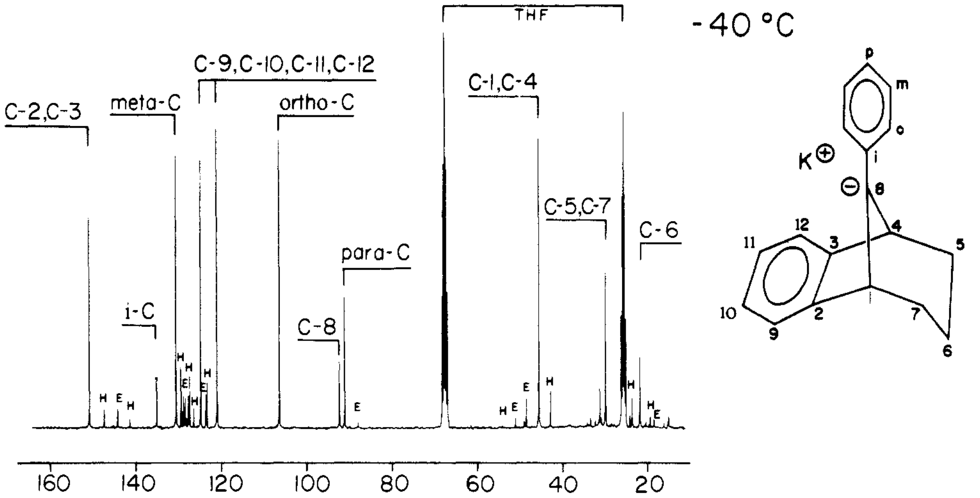


Figure 4. ^{13}C NMR spectrum of **7** (75 MHz, −40 °C, THF-d_8). Signals of the starting compound **17** and the hydro derivative **18** are marked by "E" and "H", respectively.

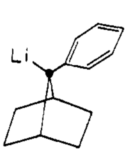
104.2),[40] the charge delocalization in the latter species, **26**, appears to be more pronounced than in the benzyllithium moieties at C-6 (δ 108.6) and less pronounced at C-8 (δ 96.9).

The most important finding from a comparison of the dilithium and disodium hydrocarbons (see the ^{1}H NMR chemical shifts from Table II) is their close structural analogy. However, the charge delocalization within the benzyl units is more effective in **3** than in **2**.

If the benzylic carbon C-6 of **2** is still within a cyclopropane ring, then it is expected to resist a sp^2 hybridization. The inclusion of a 1-lithio-1-phenylcyclopropane is revealing. Toward that end we have prepared 1-lithio-1-phenyl-2,2-dimethylcyclopropane (**4**) from the corresponding bromide **11** via reaction with lithium metal. Here again, this method of metalation is superior to the use of strong base[41] since—due to the lack of additional resonances from reagents or cosolvents—it allows the firm detection of each organometal signal. The presence of two geminal methyl substituents in **4** is advantageous for the configurational description of the carbanion. As outlined in the preceding section the chemical structure proof of **4** is based on various quenching experiments. The bonding in **4** is deduced from the following: (i) The ^{1}H and ^{13}C NMR spectra at low temperatures point toward the nonequivalence of the *gem*-methyl groups and, thus, to the fixation of the metal on one side of the ring plane. (ii) The signals of the phenyl groups (^{1}H, ^{13}C) in **4** are shifted upfield with respect to those of **12**, indicating some transfer of the carbanion charge into the phenyl π-system. (iii) The signal of the carbanion carbon C-1 is broadened ($\Delta\nu_{1/2}$ = 85 Hz, −100 °C) and appears in the aliphatic domain of the spectrum (δ 46), but somewhat downfield ($\Delta\delta$ = +17) from that of the hydrocarbon **12** (see Scheme II). This finding is in marked contrast with the upfield shift of the resonance of C-1 ($\Delta\delta$ = −6) observed upon lithiation of the parent cyclopropane.[21,40] (iv) The free enthalpy of activation (calculated for 4 °C) for the isodynamic configurational inversion of **4** is 56 kJ/mol[21] and thus markedly lower than in the configurationally stable (estimated 150 kJ/mol) cyclopropyllithium.[42,43]

Certainly, a quantitative analysis of the dynamic behavior is difficult since one has to take into account the existence of aggregates and of temperature-dependent ion-pair equilibria. Nevertheless, it appears reasonable to describe the transition state of the inversion as being more ionic than the ground state.

As concerns the title system **2** it is clear from the inspection of the model compound **4** that **2** incorporates an intact lithiophenylcyclopropane moiety (C-6) although the charge delocalization to the phenyl ring is somewhat larger in **2**. Another subunit present in the dianion **2** is the 7-lithio-7-phenylnorbornane **27**.



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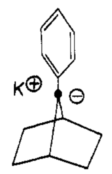

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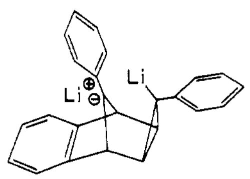

2A

The latter species has been investigated NMR spectroscopically by Grutzner and Peoples.[44] The authors found a ^{13}C NMR chemical shift of C-7 at δ 64 and concluded that the compound possesses a highly covalent character. In contrast, the corresponding potassium compound **28** gave rise to the resonance of C-7 at δ 88. This finding and the observed symmetry of the molecule (the C-2/C-3 and C-5/C-6 units are equivalent) were interpreted by the ionic structure **28**. The striking contrast between **27** (C-7 δ 64; C-*p*-phenyl δ 107) and **2** is obvious when one realizes that in the latter species the related carbons resonate at δ 100 and 97, respectively. The above arguments seem to indicate a stronger ionic character of the lithium phenylnorbornyl moiety in **2** than in **27** (see the borderline structure **2A**). Two structural features can be invoked when the bonding within the phenyllithionorbornane moiety in **2** is rationalized: the interaction of the two carbanion units, in particular a lithium bridging between C-6 and C-8, and the potential interaction of the phenyllithium moiety with the remote benzene ring. In dealing with the latter effect one realizes that the structure elucidation of **2** demands the inclusion of the yet unknown benzobicyclooctene derivative **5** as an appropriate reference compound.

The organolithio species **5** became available since, in a separate project,[30] we had recently prepared the ketone **15** and reacted it with phenyllithium. There is no doubt from the crystal structure of the resulting alcohol that the phenyl substituent introduced is syn to the benzene unit according to formula **16**.[30] The corresponding methyl ether **17** constitutes a suitable precursor for the preparation of the required carbanions. In fact the reductive cleavage of the C-7–oxygen bond in **17** could be achieved by reaction with lithium, sodium, or potassium to yield the resulting carbanions **5**, **6**, and **7**. Relying, again, on the ^{13}C NMR resonances of C-8 and C-*p*-phenyl as criteria of the carbanion structure, one would conclude that the lithium compound **5** is less ionic than, e.g., the potassium analogue **7** (see Chart I).[45] This

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(40) Van Dongen, J. P. C. M.; Van Dijkman, H. W. D.; De Bie, M. J. H. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 29.
(41) Schlosser, M.; Schneider, P. *Helv. Chim. Acta* **1980**, *63*, 2404.
(42) Wagner, H.-U.; Boche, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 1339.
(43) Dewar, M. J. S.; Shanshal, M. *J. Am. Chem. Soc.* **1969**, *91*, 3654.
(44) Peoples, P. R.; Grutzner, J. B. *J. Am. Chem. Soc.* **1980**, *102*, 4709.
(45) The significant spectroscopic differences between **5** and **7** cannot be rationalized by an eventual oligomer formation in the former; see ref 7).

Chart I

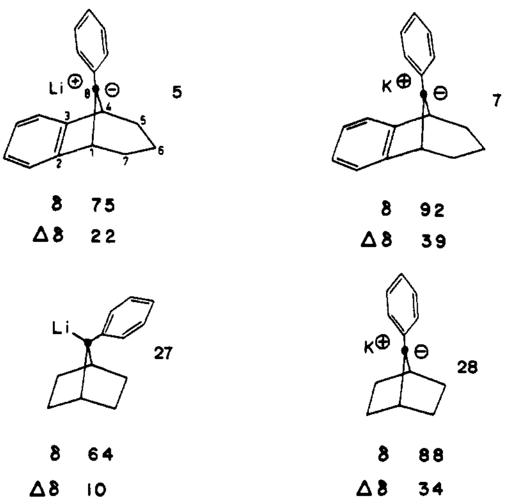
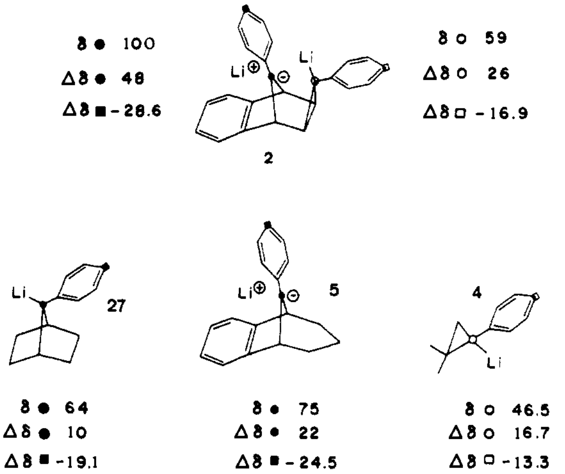


Chart II



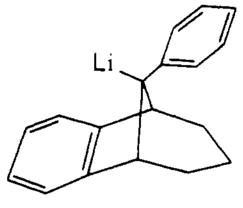
is in agreement with the finding made by Grutzner and Peoples for the structurally related species **27** and **28**[44] (see formulas **5**, **7**, **27**, and **28**). According to the data in Chart I, the tendency toward sp^2-hybridization of the carbanion carbon and toward a π-charge delocalization into the phenyl ring is much greater in **5** than in the related species **27**. It is tempting to ascribe this outcome to the interaction of the organometal unit of **5** with the attached benzene π-system at C-2 and C-3, although the different geometries of the molecules cannot be ignored.

Inspection of the ^{1}H NMR chemical shifts of the phenyl protons in **5**, **6**, and **7** (see Table II) supports the conclusions drawn from the ^{13}C NMR data: the π-charge-induced signal shift is more pronounced in the ionic structure **7**. As expected the sodium compound **6** is intermediate between **5** and **7** and, therefore, does not require special attention.

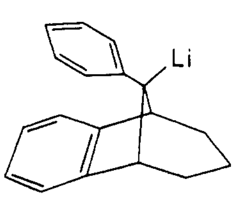
One can now combine the information from the study of the model compounds **4**, **5**, and **27** and proceed to a structural description of the title system **2** (see Chart II). The fact that the charge delocalization within the benzyllithium unit at center C-8 of **2** is by far more pronounced than that in **5** and **27** can be ascribed to the influence of the remote benzene ring *plus* the coordinative interaction of the carbanion unit with the lithium metal of the neighboring cyclopropyllithium moiety.

It has been pointed out above that the dilithium and the disodium hydrocarbons **2** and **3** are structurally analogous. Clearly, a discussion of **3** is less straightforward since the cyclopropylsodium reference compound analogous to **4** is not available. Nevertheless, the stability of **3**, with a cyclopropyl moiety similar to that in **2**, seems to support the assumption of a cooperative effect of an intramolecular carbanion/carbanion and carbanion/benzene interaction.

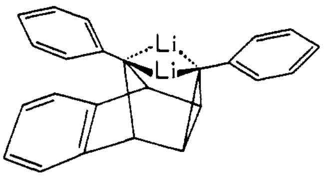
While the ^{13}C and ^{1}H NMR spectroscopic description of **2**, **5**, and **6** in solution provides a consistent view of the carbanion structures, the locations of the metals with respect to the hydrocarbon frame and thus the actual configurations at the carbanion centers are less clear. It is, in fact, adequate to elucidate the "fixed" positions of the lithium nuclei within **2** since the observation of two separate ^{7}Li resonances indicates that, within the NMR time scale, there is no intra- or intermolecular exchange of the (nonequivalent) metals at low temperatures. The organolithio compound **5**, when being described by a covalent structure, may exist in two diastereomeric forms **5A** and **5B**; the question whether or not the metal is above the plane of the benzenoid π-system is still valid when the ionic structure **5** is accepted. It is most important in this context that, according to the ^{13}C and ^{1}H NMR spectra, **5** exists as one single configuration on the NMR time scale. The ether **17**, which is used as a starting compound for the reductive formation of **5**, possesses the configuration given in the formula. The protonation of the carbanion **5** only provides the diastereomeric hydro derivative **18**. It is reasonable to ascribe the necessary inversion of configuration to the metalation reaction which must be described as selectively producing structure **5** or **5A**.



5A



5B



2B

The above experiments leave no doubt that the lithium nuclei of **2** are nonequivalent and that the carbon C-6 is coupled (due to some covalent interaction) with only one lithium. Both features are not compatible with structure **2B**.

Conclusions

We have demonstrated that the dilithiohydrocarbon **2** when present in ethereal solutions adopts an unprecedented structure with two significantly different carbanionic subunits. Essential for an understanding of the bonding situation are the intramolecular interaction of a carbanionic unit with the second carbanion and the influence of a remote π-system. It thus appears that "unusual" organolithium structures can be elucidated not only by an X-ray analysis of the crystals but also by an NMR spectroscopic description of the solutions. Essential for the success of the present study are (i) the multinuclear NMR approach, (ii) the method of preparation of the organometalic species, namely via reductive σ-bond cleavage, and (iii) the careful inclusion of suitable reference compounds.

Experimental Section

Reductive Cleavage. For the reductive σ-bond cleavage the substrates were placed at the bottom of a NMR tube or a reaction flask with two separate compartments. Dry solvents were distilled in from a storage vessel under vacuum. After the solution was degassed by repeated freeze and thaw cycles the alkali metals were inserted and deposited at the top of the tube or flask. Finally the cells were sealed.

A specially constructed press allows one to bring in the lithium under vacuum; potassium is sublimed from a side arm. The solvents were dried over sodium/potassium alloy.

Reductive Cleavage of 2,3-Benzo-6,8-diphenyltetracyclo[3.2.1.0^{5,7}.0^{6,8}]octene (1). **1** was prepared according to literature procedures.[19] By use of the above technique, the 2,3-benzo-6,8-diphenyltetracyclo[3.2.1.0^{5,7}.0^{6,8}]octene (**1**) (20 mg, 0.065 mmol) was placed in a NMR tube and brought in contact with lithium in THF-d_8 at −78 °C. The reaction was complete after 2 or 3 days of contact, the actual reaction time depending on the activity of the metal surface. The NMR chemical shifts of the resulting dilithio compound **2** are given in Table I; quenching experiments with **2** (performed in the reaction flasks) are described below.

H,H-Decoupling Experiments (100 MHz). Irradiation with the frequency of the triplet at 5.93 ppm led to singlets at 5.41 and 4.63 ppm; irradiation at the multiplet (6.3–6.5 ppm) gave a singlet at 5.66 ppm.

^{13}C{^{1}H} Decoupling experiments (75 MHz) showed the following:

irradiation of the H signal at	singlet signal in the ^{13}C NMR spectrum
6.67, m, 2 H	117.2
5.93, tr, 2 H	128.1
5.66, m, 1 H	108.6
5.41, d, 2 H	108.9
4.63, tr, 1 H	96.9
3.35, s, 2 H	51.4
0.72, s, 2 H	36.2
6.3–6.5	127.3; 121.3; 121.6

The spectra of **2** did not show a significant temperature dependence. Between −60 and 24 °C the ^{1}H NMR chemical shifts remained unchanged within the experimental error.

The addition of benzene-d_6 (THF-d_8/C_6D_6 7:1) caused a downfield shift of the ^{1}H NMR resonances: δ (−20 °C) 0.92 (H-5,7), 3.53 (H-1,4), 4.87 (*p*-H), 5.62 (*o*-H), 5.85 (*p'*-H), 6.13 (*m*-H), ca 6.6 (*m'*-H, *o'*-H), 6.6–6.8 (H-9,10,11,12).

The addition of HMPT-d_{18} (THF/HMPT 3:1) induced slow decomposition of **2**, but did not cause a significant shift of the ^{1}H NMR signals (−20 °C): δ 0.79 (H-5,7), 3.33 (H-1,4), 4.68 (*p*-H), 5.46 (*o*-H), 5.57 (*p'*-H), 5.90 (*m*-H) ca 6.3–6.6 (*m'*-H, *o'*-H, H-9,10,11,12).

Reoxidation of 2. **1** (57 mg, 0.19 mmol) in dry THF was sealed in a glass tube and lithiated with activated lithium. After 3 days the ampule was opened, and dry oxygen was bubbled in. After aqueous workup and evaporation of the solvent, the raw material was chromatographed (alumina, neutral, activity II–III, hexane). The first fraction gave 27 mg of compound **1** (47 % yield).

Protonation of 2. To a solution of **2** in THF-d_8 at −78 °C under argon atmosphere a proton source like methanol, *tert*-butyl alcohol, or aqueous THF was added. The brown-red color of the anion solution disappeared rapidly and turned to light yellow. The mixture was extracted with water/pentane. According to thin-layer chromatography, the crude product obtained after evaporation of the solvent contained two main components with similar R_f values. After chromatography on silica gel (hexane/ethyl acetate 20:1) and crystallization, one product **8** was obtained pure (mp 145–147 °C). Other fractions contained mixtures of **8** and **9** from which pure **9** could not be isolated.

In a typical experiment 380 mg (1.2 mmol) of 2,3-benzo-6,8-diphenyltetracyclo[3.2.1.0^{5,7}.0^{6,8}]octene (**1**) were reduced with an excess of lithium in THF and quenched at −78 °C with *tert*-butyl alcohol. A GPC analysis of the product mixture (pure dihydro product **8** as internal standard) showed a yield of 232 mg (60%) of the dihydro product 2,3-benzo-6-*anti*-phenyl-8-*syn*-phenyltricyclo[3.2.1.0^{5,7}]octene (**8**). The 2,3-benzo-6-*anti*-phenyl-8-*anti*-phenyltricyclo[3.2.1.0^{5,7}]octene (**9**) was produced in about 40–50 mg (10–14% yield, estimated by integration of the ^{1}H NMR signals).

Reaction of **2** with aqueous THF or methanol at −78 °C afforded a nearly 1:1 mixture of the two isomers (**8** and **9**).

2,3-Benzo-6-*anti*-phenyl-8-*anti*-phenyl-*exo*-tricyclo[3.2.1.0^{5,7}]octene (9). ^{1}H NMR (60 MHz, CDCl$_3$): δ 4.02 (broad, 2 H, H-1,4), 2.95 (broad, 1 H, H-8), 1.30 (dd, 2 H, H-5,7), 2.65 (t, 1 H, H-6), 6.43–6.63 (m, 2 H, aromatic H), 6.83–7.30 (m, 12 H, aromatic H).

2,3-Benzo-6-*anti*-phenyl-8-*syn*-phenyl-*exo*-tricyclo[3.2.1.0^{5,7}]-octene (8). ^{13}C NMR (75 MHz, CDCl$_3$): δ 48.0 (C-1,4), 51.8 (C-8), 33.7 (C-5,7), 33.2 (C-6), 148.0 (C-2,3); 141.5 (s), 139.3 (s), 128.3, 127.7, 125.8, 125.4, 122.0 (aromatic C). ^{1}H NMR (60 MHz, CDCl$_3$): δ 3.68 (broad, 2 H, H-1,4), 3.35 (broad, 1 H, H-8), 1.45 (d, 2 H, H-5,7), 3.23 (t, 1 H, H-6), 6.85–7.19 (m, 14 H, aromatic H).

In the case of **9** no nuclear Overhauser enhancement of the signal of H-6 could be detected upon irradiation of H-8. In contrast, the signal intensity of H-6 in compound **8** increased by 4.5 ± 1% upon irradiation of H-8.

Reaction of 2 with 1,3-Dibromopropane. To a solution of **2** (prepared from 290 mg, 0.95 mmol) of 2,3-benzo-6,8-diphenyltetracyclo[3.2.1.0^{5,7}.0^{6,8}]octene (**1**) in THF-d_8 at −78 °C was added an excess of 1,3-dibromopropane under an argon atmosphere. The resulting faint yellow solution was extracted with water/pentane. After filtration on silica gel (thus removing oligomeric products) and crystallization from 2-propanol one obtained 90 mg of colorless crystals (mp 138 °C) of 2,3-benzo-15-phenylhexacyclo[12.3.0.0^{4,16}.0^{5,14}.0^{9,14}.0^{15,17}]heptadeca-2,10,12-triene (**10**) (27% yield; the mother liquor of the crystallization contained an additional amount of **10** which was not isolated). Absolute mass: 348.1883; calcd for $C_{27}H_{24}$ 348.1878. ^{13}C NMR (20 MHz, CDCl$_3$): δ 146.4, 145.6, 139.0, 132.3, 130.9, 126.8, 126.2, 126.0, 125.6, 125.4, 125.3, 123.1, 121.5, 70.1, 54.0, 51.2, 50.5, 50.4, 35.4, 30.4, 29.8, 28.0, 21.7, 21.1.

Protonation of 4. 1-Bromo-1-phenyl-2,2-dimethylcyclopropane (**11**) (250 mg, 1.1 mmol) was lithiated in a sealed glass tube according to the above technique. Opening of the ampule under an argon atmosphere followed by the injection of aqueous THF lead to an instantaneous decolorization of the brown solution. The light yellow solution in hexane was washed with water, and the organic layer was separated and filtered over alumina (neutral, activity II–III). Evaporation of the solvent yielded 150 mg of pure **12** (92% yield). ^{1}H NMR (CDCl$_3$, 60 MHz): δ 0.85 (s, 3 H), 0.77–0.89 (m, 2 H), 1.29 (s, 3 H), 1.94 (m, 1 H); 7.20 (broad, 5 H). ^{13}C NMR (CDCl$_3$, 20 MHz): δ 18.3 (tr), 18.9 (s), 20.3 (q), 27.4 (q), 29.8 (d), 125.5 (d), 127.3 (d), 128.4 (d), 140.2 (s).

Oxidation of 4 with Oxygen. 1-Bromo-1-phenyl-2,2-dimethylcyclopropane (**11**) (288 mg, 1.3 mmol) was lithiated as described above. The ampule was opened and dry oxygen (dried over KOH) was bubbled through the solution at −78 °C. Addition of an aqueous ammonium chloride solution (5%) followed by extraction with hexane, drying of the separated organic layer, and evaporation afforded a crude product (123 mg) which contained the alcohol **13** and the protonation product **12**. From the ^{1}H NMR intensities the yield of **13** could be determined as 43%. Upon attempted chromatographic purification the alcohol **13** underwent decomposition. ^{1}H NMR (CDCl$_3$, 60 MHz): δ 0.79 (s, 3 H), 1.42 (s, 3 H), 2.35 (broad, 1 H), 7.30 (m, 5 H). (The signals of the protons attached to C-2 are covered by signals of **12**.)

Oxidative Coupling of 4. 1-Bromo-1-phenyl-2,2-dimethylcyclopropane (**11**) (155 mg; 0.69 mmol) was lithiated as described above. To the cooled solution (−78 °C) was given an excess of solid copper(II) bis(trifluormethanesulfonate) in small portions under an argon atmosphere. After about 30 s of shaking, the color of the solution disappeared. The solution was allowed to stand at room temperature for 45 min and was finally transferred to a separation funnel filled with hexane/water. After evaporation of the organic layer there remained 100 mg of raw material which contained the *meso* and *d*/*l* dimers **14** and the protonation product **12**. From the relative intensities of the ^{1}H NMR signals of the raw material the yield of the dimers was determined to be 32%. Chromatography on alumina (neutral, activity II–III) with hexane gave 35 mg (17%) of the dimer **14**. Absolute mass: 290.2027; calcd for $C_{22}H_{26}$ 290.2035. ^{1}H NMR (THF-d_8 −50 °C, 300 MHz, *meso* and *d*/*l* form of **14**): δ 0.60 (d, 1 H), 0.70 (s, 3 H), 1.13 (d, 1 H), 1.57 (s, 3 H), 6.8–7.5 (m), and 0.57 (s, 3 H), 0.80 (d, 1 H), 1.01 (d, 1 H), 1.49 (s, 3 H), 6.8–7.5 (m).

Preparation of 2,3-Benzo-8-*anti*-hydroxy-8-phenylbicyclo[3.2.1]octene (16). To a stirred solution of 200 mg of 2,3-benzo-8-oxobicyclo[3.2.1]-octene (**15**) (1.16 mmol) in dry diethyl ether was added 1 mL of phenyllithium solution (3 M in diethyl ether; 3.0 mmol) at −78 °C.

After the cooling bath had been removed, the solution was stirred for another 30 min. The solution was carefully neutralized with water and worked up in the usual manner (extraction with water/pentane). After chromatography on alumina (activity II–III, pentane/ethyl acetate 10:1) and crystallization, the pure product was obtained in 235 mg (mp 70 °C, 81% yield): ^{13}C NMR (20 MHz, CDCl$_3$): δ 49.2 (C-1,4), 143.6 (C-2,3), 24.5 (C-5,7), 16.7 (C-6), 82.0 (C-8), 146.6 (ipso phenyl C), 122.5, 126.5, 126.7, 127.7 (aromatic C). ^{1}H NMR (90 MHz, CDCl$_3$): δ 7.4–7.1 (9 H, m), 3.32 (2 H, m), 2.46–2.09 (2 H, m), 1.99 (1 H, s) 1.79–1.20 (3 H, m) 1.02–0.51 (1 H, m).

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.33; H, 7.27.

Preparation of 2,3-Benzo-8-*anti*-methoxy-8-phenylbicyclo[3.2.1]octene (17). To a stirred solution of 580 mg (2.3 mmol) of 2,3-benzo-8-hydroxy-8-phenylbicyclo[3.2.1]octene (**16**) in dry tetrahydrofuran was added 180 mg of NaH (80% NaH in paraffin, 6.0 mmol) in portions under nitrogen atmosphere (20 °C). After stirring for 1 h 65 mg (0.1 equiv) of tetrabutylammonium bromide was added (under a nitrogen atmosphere). After an additional 3 h of stirring at room temperature, dimethyl sulfate (0.5 ml, ca. 7 mmol) was injected through a serum cap, and the solution was stirred for 16 h. The reaction mixture was added to Florisil and evaporated. The resulting powder was transferred to a Florisil chromatography column (15 × 2 cm). Chromatography with petroleum ether–ethyl acetate (10:1) lead to a product/educt mixture.

After a second chromatography (silica gel 60, 20 × 2 cm, petroleum ether–ethyl acetate (10:1)) the pure ether **17** (500 mg, 1.9 mmol, 80% yield) was obtained as a colorless oil. The yields depend critically upon the purity of the educts. ^{13}C NMR (75 MHz, $CDCl_3$): δ 47.7 (C-1,4), 24.4 (C-5,7), 17.4 (C-6), 87.4 (C-8), 143.6 and 143.4 (C ipso); 128.0, 127.7, 126.9, 126.6, 122.8 (aromatic C). Absolute mass: 264.1511, calcd for $C_{19}H_{20}O$ 264.1514.

Protonation of 5. A THF-d_8 solution of 30 mg of 2,3-benzo-8-*anti*-methoxy-8-phenylbicyclo[3.2.1]octene (**17**) (0.11 mmol) was placed in contact with activated lithium within a sealed NMR tube. The reaction was monitored NMR spectroscopically. The signals of the methyl ether **15** disappeared while new signals (particularly the signals of a benzyllithium structure) grew out of the noise (data are given in Table II). When the reaction was complete, the NMR tube was broken under an argon atmosphere (−78 °C) and quenched with water. The hydro derivative 2,3-benzo-8-*anti*-phenylbicyclo[3.2.1]octene (**18**) remained as a colorless oil after filtration on silica gel and evaporation of the solvent (80% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.75 (1 H, m), 1.05 (1 H, m), 1.24 (2 H, br), 1.81 (2 H, m), 3.53 (3 H, br), 7.16 (5 H, m), 7.33 (4 H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.1 (C-1,4), 146.7 (C-2,3), 22.6 (C-5,7), 18.2 (C-6), 52.8 (C-8), 140.8, 128.5, 126.5, 125.5, 122.4 (aromatic C).

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Supplementary Material Available: Ortep drawing of **10** and tables of fractional atomic coordinates, thermal parameters, bond lengths, and bond angles for **10** (5 pages). Ordering information is given on any current masthead page.

Nucleophilic Aromatic Substitution Reactions with Carbanions and Nitranions in Dimethyl Sulfoxide Solution

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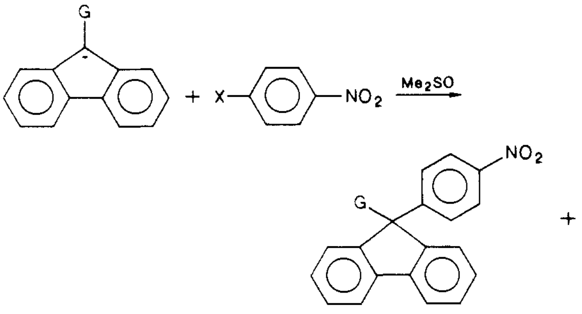
Abstract: Rate constants for S_NAr reactions between families of substituted fluorenide carbanions and phenothiazinide nitranions and p-$NO_2C_6H_4X$ (X = F, Cl, Br, I, and PhO) have been measured in Me_2SO solution and compared with literature data for S_NAr reactions of families of oxanion and thianion nucleophiles. The Brønsted β_{Nu} values for S_NAr reactions are in the range 0.5–0.7, distinctly larger than those for S_N2 reactions (0.2–0.5) but not so large as to indicate an electron-transfer mechanism ($\beta_{Nu} \simeq 1$). Although the size of β_{Nu} is believed to be associated with the extent of charge transfer and bonding in the transition state, no charge-transfer (CT) bands were observed in the carbanion reactions. For anions at the same basicity the order of donor-atom effects was observed to be $S^- \gg C^- > O^- > N^-$. This order is the same as that usually observed in S_N2 reactions, but the spread in reactivity is of the order of 10^9 compared to 10^5. The larger spread is believed to be associated with a larger steric effect. For S_NAr reactions, increasing steric effects in G of 9-GFl$^-$ (Fl$^-$ = fluorenide) ions along the series 9-MeFl$^-$ < 9-(PhS)Fl$^-$ > 9-(C_6H_5)Fl$^-$ < 9-(o-MeC_6H_4)Fl$^-$ caused a rate retardation of 10^5 compared to $10^{2.4}$ for S_N2 reactions. No evidence for a buildup of a carbanion intermediate, $Nu(X)C_6H_4NO_2^-$, was observed in instances where the basicities of Nu$^-$ and X$^-$ are nearly equal.

In studies in Me_2SO solution of S_N2 reactions at saturated carbon with families of carbanions, nitranions, oxanions, and thianions, we have found that when solvation, steric, and donor-atom effects are held constant, the rates of the reactions depend on only two factors: (1) the relative basicity of the anion as measured by the acidity of its conjugate acid, pK_{HA}, and (2) the sensitivity of the anion to changes in basicity, as measured by the Brønsted β of its family.[1] This has allowed us to determine donor-atom effects at the same basicity, which for S_N2 reactions generally follow the order $S^- \gg C^- > O^- > N^-$.[2] The β_{Nu} values in these studies range from 0.2 to 0.5. We now report the results of an investigation of substitution reactions at aromatic carbon, primarily with p-nitrohalobenzenes, designed to see if these observations are applicable for nucleophilic attack at sp^2 carbon as well as sp^3 carbon.

Results

Families of 9-substituted fluorenide carbanions, 9-GFl$^-$ (G = Me, Ar, or ArS, Fl$^-$ = fluorenide), and substituted phenothiazinide nitranions, GPz$^-$ (G = H, 2-Cl, and 3,7-Br$_2$, Pz$^-$ = phenothiazinide), were reacted with p-nitrohalobenzenes, p-$NO_2C_6H_4X$ (X = F, Cl, Br, and I), in Me_2SO solution to form substitution products in over 90% yields (eq 1 and 2). Rate constants for these and analogous reactions are summarized in Table I.



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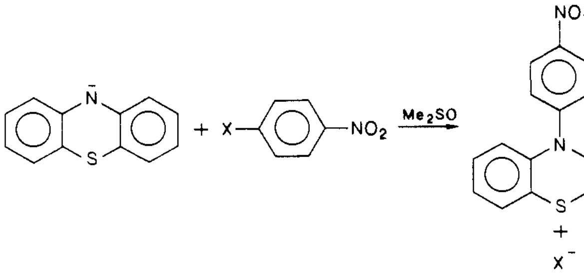

(2)

Discussion

Mechanism. There is strong eveidence to indicate that most S_NAr substitutions of this kind occur by addition–elimination

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