

163 (12), m/e 162 (100), 147 (40), 133 (10), 120 (38), 119 (44), 117 (10), 106 (12), 105 (72), 91 (34), 89 (12), 88 (12), 87 (16).

In conclusion, the reactivity pattern of an allyl system can be seen to have changed considerably by introducing the methoxy group at the central carbon.⁹ The diminished ionization tendency of **1a-c** is reminiscent of the meta deactivation of electrophilic aromatic substitution by a methoxy group. Owing to the electron-attracting inductive effect of oxygen, the Hammett substituent constant of methoxy is positive ($\sigma_{\text{meta}} = 0.12$, more strongly electron withdrawing than hydrogen), while σ_{para} is, of course, negative (-0.27).¹⁰ The new cycloadducts described herein, which are free from all methyl groups in the three-carbon bridge, would not have been accessible by any of the earlier methods.¹¹ In combining the 2-methoxyallyl cation with conjugated dienes, we have simplified the structure of the reactive oxyallyl moiety to its limit.

Acknowledgment. We thank the Science Research Council for support of our work.

(9) One unusual reaction of **1a**, namely formation of a vinylketene complex on treatment with nonacarbonyldiiron, has already been described; see A. E. Hill and H. M. R. Hoffmann, *J. Chem. Soc., Chem. Commun.*, 574 (1972).

(10) Cf. H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(11) N. J. Turro, S. S. Edelson, J. R. Williams, T. R. Darling, and W. B. Hammond, *J. Amer. Chem. Soc.*, **91**, 2283 (1969); H. M. R. Hoffmann, K. E. Clemens, and R. E. Smithers, *ibid.*, **94**, 3940 (1972); see also H. M. R. Hoffmann, T. A. Nour, and R. H. Smithers, *J. Chem. Soc., Chem. Commun.*, 963 (1972); R. Noyori, S. Makino, and H. Takaya, *J. Amer. Chem. Soc.*, **93**, 1272 (1971).

A. E. Hill, G. Greenwood, H. M. R. Hoffmann*
William Ramsay and Ralph Forster Laboratories
University College, London WC1H 0AJ, England

Received November 21, 1972

Alkyl Radicals in Lithium Clusters by Electron Spin Resonance

Sir:

We wish to report an unusual free radical **I** in which the odd electron is coupled to three lithium nuclei. **I** is generated from a solution of methyllithium in ether solution by hydrogen abstraction with *tert*-butoxy radicals generated photochemically from di-*tert*-butyl peroxide. The intense esr spectrum shown in Figure 1a disappears immediately on shuttering the light and its relatively high signal-to-noise level indicates a relatively stable but transient species. The triplet splitting (Table I) can be unambiguously assigned to the α -methylene

Table I. ESR Parameters for Lithiomethyl Radicals

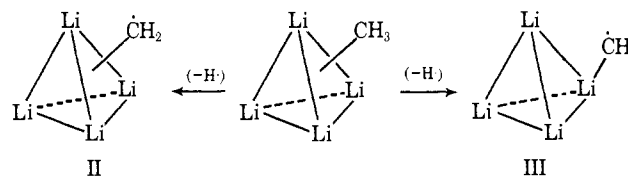
Radical	T_1^a , °C	$A_{\text{H or D}}$, G	A_{Li} , G	$\langle g \rangle$	Lw^b , G
$\cdot\text{CH}_2\text{Li}(\text{CH}_3\text{Li})_3$	-32	18.23	1.67	2.00293	0.56
$\cdot\text{CD}_2\text{Li}(\text{CD}_3\text{Li})_3$	-55	2.78	1.63	2.00293	0.27

^a No temperature dependences of the hfs or line widths were observed in the range 0 to -100° . ^b The larger line width of the protonated species is probably due to the larger H-H dipole-dipole interactions within the cluster.

protons, since deuterium substitution affords the spectrum in Figure 1b. The deuterated analog of **I** has the triplet splitting replaced by a 1:2:3:2:1 quintet,

the hfs of which has been reduced by a factor of 6.55 ($g_{\text{H}}/g_{\text{D}} = 6.514$). The simulated spectrum in Figure 1 shows that the additional decet splitting (with the correct theoretical intensity ratio) is due to three equivalent lithium nuclei (^7Li , $I = 3/2$).

Methyllithium consists of a tetrahedral array of lithium atoms in which methyl groups are located in each of the four triangular faces.¹⁻³ Hyperfine splitting by three equivalent lithium nuclei in the spectrum limits **I** to two basic tetrameric structures **II** and **III**. The



terminal model **III** would be consistent with the data only if the hfs of the lithium directly bonded to the radical center were small. However, the INDO calculations⁴ given in Table II for the monomeric species

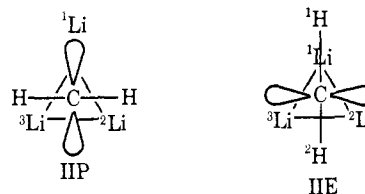
Table II. INDO Calculations for Hyperfine Splittings in Lithiomethyl Radicals^{a,b}

Position	Model ^d			
	IIE	IIP	$\text{LiCH}_2\cdot$	$\text{CH}_3\cdot$
H(1)	-16.82	-16.33	-17.00	-22.96
H(2)	-15.88	-16.33	-17.00	-22.96
C	31.10	31.10	42.61	45.98
Li(1)	-0.69	-0.34	-4.34	-22.96 (H)
Li(2)	-0.42	-0.59		
Li(3)	-0.42	-0.59		
Li(4)	-0.69	-0.69		
$\rho_{\text{C}}^{\text{SCF}}$	5.826 ^c	5.826 ^c	6.245 ^c	6.054 ^c

^a Geometric parameters obtained from ref 3. ^b Atomic splitting of lithium taken from G. W. Canters, C. Corvaja, and E. de Boer, *J. Chem. Phys.*, **54**, 3026 (1971). Hyperfine splitting in gauss. ^c Total spin density on carbon in au. ^d Calculations based on the assumption of planar radical sites.

predict a rather large splitting for a lithium nucleus located in this position.

The face-bridged structure **II** can exist in two conformations shown below in projection. Table II



gives the INDO results for the hfs and the total SCF electron density⁵ on the methylene carbon for each conformation. The calculations are in reasonable

(1) L. M. Seitz and T. L. Brown, *J. Amer. Chem. Soc.*, **88**, 2174 (1966).

(2) P. West and R. Waack, *ibid.*, **89**, 4395 (1967).

(3) (a) E. Weiss and E. A. C. Lucken, *J. Organometal. Chem.*, **2**, 197 (1964); (b) E. Weiss and G. Hencken, *ibid.*, **21**, 265 (1970).

(4) Obtained from the Quantum Chemistry Program Exchange; QCPE No. 141 has been converted for CDC 6600.

(5) Interestingly, these calculations indicate that the three-lithium cluster withdraws electrons from the carbon center relative to the monomeric species and methyl radical itself. Similar results were obtained for tetrameric methyllithium.⁶

(6) (a) G. R. Peyton and W. H. Glaze, *Theor. Chim. Acta*, **13**, 259 (1969); (b) A. H. Cowley and W. D. White, *J. Amer. Chem. Soc.*, **91**, 34 (1969); (c) M. F. Guest, I. H. Hillier, and V. R. Saunders, *J. Organometal. Chem.*, **44**, 59 (1972).

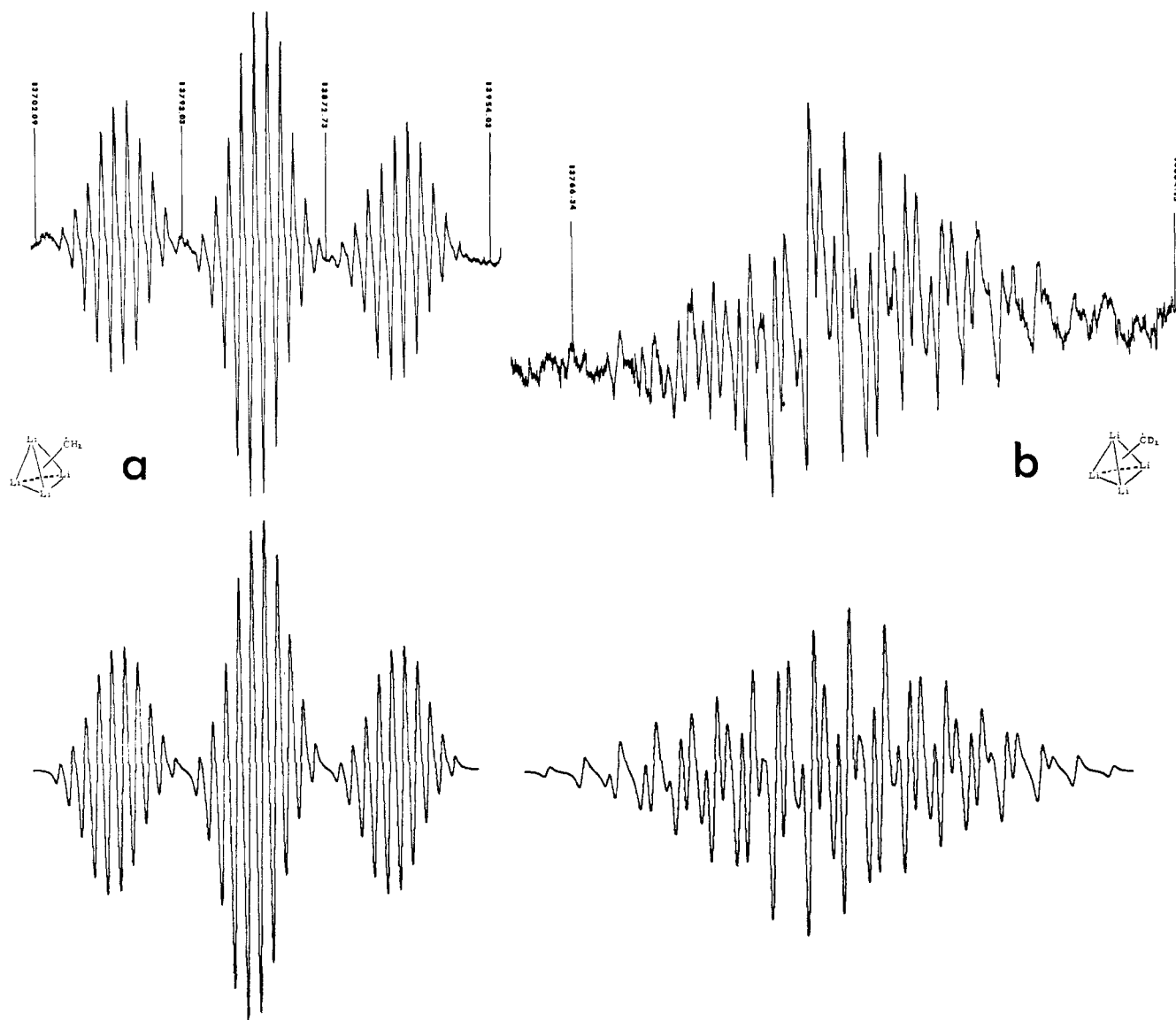


Figure 1. ESR spectra of (a) lithiummethyl and (b) lithioduteriomethyl radicals in diethyl ether solution at -50° . Simulated spectra using parameters in Table I are directly below. Proton nmr field markers are in kHz.

agreement⁷ with the data in Table I with one exception, *viz.*, the sizable hfs due to the fourth lithium. However, ^7Li and ^{13}C nmr studies of tetrameric methyl-lithium indicate a near-zero bond order between lithium nuclei and have led to the "local environment" hypothesis,^{1,8-10} in which each methyl group (lithium atom) interacts with only three lithium atoms (methyl groups). If so, the spin density will not be efficiently transferred by direct spin polarization to the fourth lithium (as given by the INDO model) but rather by a less effective indirect process involving only C-Li bonds.¹¹

(7) As yet there is only limited agreement between the experimental and calculated (by INDO) hfs for nuclei other than hydrogen; see J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

(8) L. D. McKeever, R. Waack, M. A. Doran, and E. B. Baker, *J. Amer. Chem. Soc.*, **90**, 3244 (1968); **91**, 1057 (1969).

(9) T. L. Brown, L. M. Seitz, and B. Y. Kimura, *ibid.*, **90**, 3245 (1968).

(10) A recent normal mode analysis supports a similar conclusion: W. M. Scovell, B. Y. Kimura, and T. G. Spiro, *J. Coord. Chem.*, **1**, 107 (1971).

(11) (a) Alternatively, trimeric or hexameric species are possible but unlikely. (b) The spectrum of I appears immediately upon ir-

The observation of three equivalent lithium splittings and the absence of either a temperature-dependent proton hfs or selective line broadening in the spectrum of I cannot be explained by one fixed conformation (*cf.* Table II).¹² Rather, a rapid rotation ($>10^7 \text{ sec}^{-1}$) of the methylene group about a sixfold barrier is indicated.

Insight into the bonding in alkyllithium clusters has not been fully provided as yet by nmr studies or theoretical calculations.^{6,13,14} We hope that these esr observations will afford a new probe for the additional understanding of these electron-deficient systems.

Acknowledgment.

We wish to thank the National radiation and does not change perceptibly on further irradiation indicating that exchange by *tert*-butoxy groups is not important in the cluster under these conditions.

(12) Further, there is no indication from the esr data of intermolecular exchange of the radical site in these clusters; *cf.*, K. C. Williams and T. L. Brown, *J. Amer. Chem. Soc.*, **88**, 4134 (1966), for exchange in the methyl lithium tetramer.

(13) L. D. McKeever in "Ions and Ion-Pairs in Organic Reactions," Vol. I, M. Szwarc, Ed., Wiley-Interscience, New York, N. Y., 1972, pp 263 ff.

(14) ^{13}C studies are in progress.

Science Foundation for financial support, Dr. David Edge for the initial observation, and Drs. G. E. Hartwell and W. N. Lipscomb for helpful discussions. F. B. wishes to thank CNR (Rome) for a fellowship and a travel grant.

Kuang S. Chen, Franco Bertini, Jay K. Kochi*

Department of Chemistry, Indiana University
Bloomington, Indiana 47401

Received November 7, 1972

9-Oxabicyclo[3.3.1]non-1-ene^{1,2}

Sir:

Over the past few years we and others have demonstrated that bridgehead alkenes in moderately sized ring systems are stable enough to permit their synthesis and purification at ordinary temperatures.³ To date all isolable bridgehead alkenes have had the bridgehead double bond endocyclic in a ring of at least eight members.^{3a} In smaller ring systems there is ample evidence for the existence of compounds with bridgehead unsaturation,⁴ but none of these very highly strained compounds has yet been isolated in pure form. The torsional constraints on the double bonds in these compounds lead to interesting effects on their chemical behavior and reactivity.^{3,4}

We have initiated a research program for the study of the chemical properties of some bridgehead alkenes substituted with heteroatoms within the bicyclic framework.⁵ In ordinary unstrained systems the heteroatoms of enamines, enol ethers, and vinyl halides exert a very considerable influence on the chemical properties of the carbon double bond through the operation of inductive and resonance effects in the alkenes themselves and in the intermediates and products of their reactions. By constraining the heteroatom-substituted alkene in a bridged bicyclic framework, it should be possible to inhibit the resonance of the heteroatom with the double bond while leaving the inductive effect essentially unchanged.⁶

(1) Paper VI in the Bredt's Rule series. For previous papers in the series see ref 3 and 4.

(2) This work was supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society, and by a grant from Eli Lilly and Co.

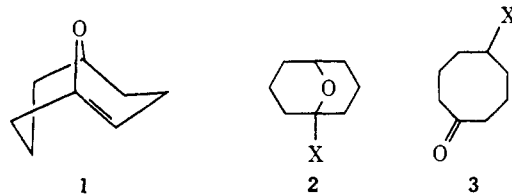
(3) (a) J. R. Wiseman and W. A. Pletcher, *J. Amer. Chem. Soc.*, **92**, 956 (1970); (b) J. A. Marshall and H. Faubl, *ibid.*, **92**, 948 (1970); (c) J. R. Wiseman, H.-F. Chan, and C. J. Ahola, *ibid.*, **91**, 2812 (1969); (d) W. Carruthers and M. I. Qureshi, *Chem. Commun.*, 832 (1969); (e) N. M. Weinshenker and F. D. Greene, *J. Amer. Chem. Soc.*, **90**, 506 (1968); (f) G. L. Buchanan and G. Jamieson, *Tetrahedron*, **28**, 1123 (1972); (g) G. L. Buchanan and G. Jamieson, *ibid.*, 1129 (1972).

(4) (a) J. R. Wiseman and J. A. Chong, *J. Amer. Chem. Soc.*, **91**, 7775 (1969); (b) J. A. Chong and J. R. Wiseman, *ibid.*, **94**, 8627 (1972); (c) S. F. Campbell, R. Stephens, and J. C. Tatlow, *Tetrahedron*, **21**, 2997 (1965); (d) R. Keese and E. P. Krebs, *Angew. Chem., Int. Ed. Engl.*, **10**, 262 (1971); (e) R. Keese and E. P. Krebs, *ibid.*, **11**, 518 (1972); (f) P. Warner, R. LaRose, C.-M. Lee, and J. C. Clardy, *J. Amer. Chem. Soc.*, **94**, 7607 (1972); (g) J. E. Gano and L. Eizenberg, *ibid.*, in press.

(5) For examples of compounds with bridgehead unsaturation involving a heteroatom see (a) J. O. Reed and W. Lwowski, *J. Org. Chem.*, **36**, 2864 (1971); (b) M. Toda and Y. Hirata, *Chem. Commun.*, 1597 (1970); (c) H. Newman and T. L. Fields, *Tetrahedron*, **28**, 4051 (1972); (d) P. G. Gassman, R. L. Cryberg, and K. Shudo, *J. Amer. Chem. Soc.*, **94**, 7600 (1972); (e) R. D. Fisher, T. D. Bogard, and P. Kovacic, *ibid.*, **94**, 7599 (1972); (f) C. A. Grob and A. Sieber, *Helv. Chim. Acta*, 2531 (1967).

(6) For examples of steric inhibition of resonance see (a) M. S. Newman, Ed., "Steric Effects in Organic Chemistry," Wiley, New York, N. Y., 1956; (b) H. Pracejus, M. Kehlen, H. Kehlen, and H. Matscheiner, *Tetrahedron*, **21**, 2257 (1965); (c) G. Wittig and G. Steinhoff, *Justus Liebig's Ann. Chem.*, **676**, 21 (1964); (d) K. C. Dewhirst and D.

We now report on the synthesis and chemical behavior of 9-oxabicyclo[3.3.1]non-1-ene (**1**). Hydroboration oxidation of 1,5-cyclooctadiene^{7,8} produced *cis*-1,5-cyclooctanediol which was oxidized with Jones' reagent to 1-hydroxy-9-oxabicyclo[3.3.1]nonane (**2a**)⁹ in 49% overall yield.



- a, X = HO
b, X = CH₃CO₂
c, X = CH₃SO₃
d, X = *p*-CH₃C₆H₄SO₃
- e, X = CH₃CH₂O
f, X = Cl
g, X = H

The hemiketal **2a** is more stable than the hydroxy ketone **3a** as the infrared spectrum shows no carbonyl band. Nevertheless, most attempts to derivatize the hydroxyl group of **2a** gave derivatives of **3a** due to the greater reactivity of the secondary alcohol. Thus, reaction of **2a** with *p*-toluenesulfonyl chloride in pyridine gave **3d** exclusively,¹⁰ and reaction with acetic anhydride in pyridine gave a mixture of acetates **2b** and **3b**.⁹ Successful derivatization was achieved by the use of methanesulfonyl chloride and triethylamine¹¹ which gave mesylate **2c** as a stable white crystalline solid in 84% yield.¹² Treatment of mesylate **2c** with potassium *tert*-butoxide in *tert*-butyl alcohol at 80° caused a smooth elimination of methanesulfonic acid with production of the bridgehead olefin **1** in 32% yield after purification by distillation on a spinning band column.

The spectra of **1** indicate the absence of conjugation of the bridging oxygen with the double bond. The infrared spectrum shows a *weak* split band at 1640 cm⁻¹ in contrast to the very intense bands usually observed for vinyl ethers,¹³⁻¹⁶ and the nmr spectrum shows the vinyl proton at δ 5.74 (t, *J* = 6 Hz), shifted by 1.4 ppm from the "expected" position.^{14,15} In the ultraviolet, **1** absorbs at 190 nm (ε 6200).

Hydrolysis of **1** in 50% aqueous acetone containing 1

J. Cram, *J. Amer. Chem. Soc.*, **80**, 3115 (1958); (e) B. Ree and J. C. Martin, *ibid.*, **92**, 1660 (1970); (f) V. Buss, R. Gleiter, and P. v. R. Schleyer, *ibid.*, **93**, 3927 (1971).

(7) R. K. Sharma, B. A. Shoulders, and P. D. Gardner, *Chem. Ind. (London)*, 2087 (1962).

(8) E. F. Knights and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 5280 (1968).

(9) C. Ganter and J. F. Moser, *Helv. Chim. Acta*, **52**, 725 (1969). The ratio of acetates **2b** and **3b** is determined kinetically. *p*-Toluenesulfonic acid in acetic acid catalyzes the quantitative conversion of **2b** to **3b**.

(10) J. K. Crandall, R. D. Huntington, and G. L. Brunner, *J. Org. Chem.*, **37**, 2911 (1972).

(11) J. F. King and T. Durst, *J. Amer. Chem. Soc.*, **86**, 287 (1964); W. E. Truce, R. W. Campbell, and J. R. Norell, *ibid.*, **86**, 288 (1964); G. Stork and I. J. Borowitz, *ibid.*, **84**, 313 (1962).

(12) Mesylate **2c** is a stable compound, but does isomerize on long storage at room temperature to **3c**. The isomerization apparently is catalyzed by traces of methanesulfonic acid. On heating to 75°, **2c** decomposes to 4-cyclooctenone and methanesulfonic acid.

(13) (a) Y. Mikawa, *Bull. Chem. Soc. Jap.*, **29**, 110 (1956); (b) G. D. Meakins, *J. Chem. Soc.*, 4170 (1953).

(14) J. Feeney, A. Ledwith, and L. H. Sutcliffe, *J. Chem. Soc.*, 2021 (1962).

(15) Spectra for 2-methyl-5,6-dihydropyran;¹⁶ ir (CCl₄) 1680 (s) cm⁻¹; (CCl₄) vinyl H, δ 4.34; uv (pentane) 190 nm (ε 5700).

(16) (a) W. H. Perkin, Jr., *J. Chem. Soc.*, **51**, 702 (1887); (b) J. G. Montagne, *Ann. Chim., (Paris)*, 314 (1954); (c) I. S. Trubnikov and Yu. A. Tentin, *Zh. Obshch. Khim.*, **32**, 3590 (1962).