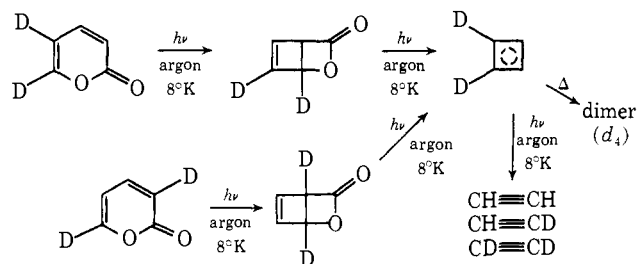
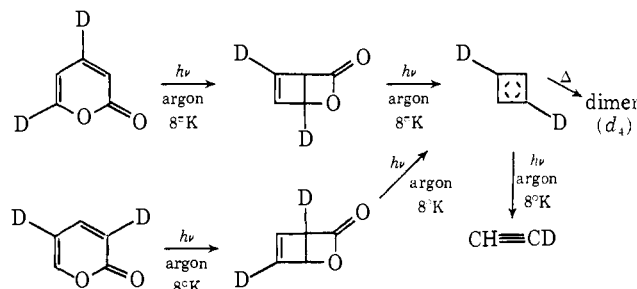


If a matrix containing monodeuteriocyclobutadiene and the acetylenes is warmed and pumped into a trap (77°K), the mass spectrum (14 eV) of the product shows parent ions for cyclobutadiene dimer containing two deuterium atoms⁴ (m/e 106), acetylene (m/e 26), and acetylene- d_1 (m/e 27).⁵



In similar fashion, irradiation of 2-pyrone-5,6- d_2 (86% d_2 , 14% d_1) and 2-pyrone-3,6- d_2 (81% d_2 , 19% d_1) gives cyclobutadiene-1,2- d_2 (1212, 1188, 770, 654, 583, 576 cm^{-1}). Irradiation of cyclobutadiene-1,2- d_2 gives acetylene (3260, 735 cm^{-1}), acetylene- d_1 (3330, 2580, 687 cm^{-1}), and acetylene- d_2 (2420 cm^{-1}). The mass spectrum of the product shows the cyclobutadiene- d_2 dimer (m/e 108), acetylene, acetylene- d_1 , and acetylene- d_2 .⁵



Cyclobutadiene-1,3- d_2 (1216, 1182, 781, 654, 633, 583, 576, 535 cm^{-1}) has been generated by irradiation of 2-pyrone-4,6- d_2 (85% d_2 , 14% d_1) and 2-pyrone-3,5- d_2 (64% d_2 , 33% d_1). Photochemical cleavage of cyclobutadiene-1,3- d_2 gives only acetylene- d_1 (3330, 2580, 687 cm^{-1}). The mass spectrum of the product confirms the presence of acetylene- d_1 and shows the parent ion of cyclobutadiene- d_2 dimer (m/e 108).

The formation of the same deuterated cyclobutadiene from different precursors in the three cases cited above leaves no room for doubt that the product formed from 2-pyrone is indeed cyclobutadiene.^{6,7} The photochemical cleavage of cyclobutadiene-1,2- d_2 to acetylene, acetylene- d_1 , and acetylene- d_2 also provides convincing evidence that the product is cyclobutadiene. The cleavage of cyclobutadiene-1,3- d_2 to only acetylene- d_1 shows clearly that tetrahedrane is not an intermediate in the photochemical conversion of cyclobutadiene to acetylene. A further interesting observation comes from these studies. The rate of photochemical cleavage of the cyclobutadienes is 1,3- d_2 > 1,2- d_2 > d_1 > d_0 . This could be due to an isotope effect on the rate constant

(4) The element composition of this ion ($\text{C}_8\text{H}_6\text{D}_2$) was established by exact mass determination.

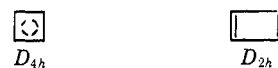
(5) The ratio of the deuterated to nondeuterated acetylene determined by mass spectrometry was that expected on the basis of the deuterium incorporation in the starting 2-pyrone in each case.

(6) C. Y. Lin and A. Krantz, *J. Chem. Soc., Chem. Commun.*, 1111 (1972).

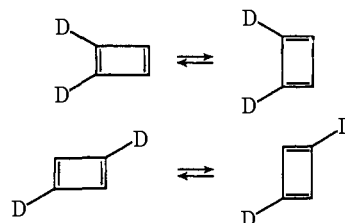
(7) O. L. Chapman, C. L. McIntosh, and J. Pacansky, *J. Amer. Chem. Soc.*, in press.

cleavage, but it is more likely due to an increase in the excited state lifetime in the deuterated cyclobutadienes.

The dideuteriocyclobutadienes give further insight into the details of the cyclobutadiene structure. The leading candidates for the structure have D_{4h} (square planar) and D_{2h} (rectangular planar) symmetries, respectively. If the structure of cyclobutadiene has D_{4h} sym-



metry, only one 1,2-dideuteriocyclobutadiene and one 1,3-dideuteriocyclobutadiene are possible. If the structure has D_{2h} symmetry, two 1,2-dideuteriocyclobutadienes and one 1,3-dideuteriocyclobutadiene are possible.



The infrared spectrum of 1,2-dideuteriocyclobutadiene is very similar to that of 1,3-dideuteriocyclobutadiene. No evidence for the presence of two 1,2-dideuteriocyclobutadienes is observed. This fits with our tentative conclusion based on the infrared spectrum that cyclobutadiene has D_{4h} symmetry.

Acknowledgment. This research was supported by Grant GP 28152X from the National Science Foundation and Grant AM 14624 from the National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service.

O. L. Chapman,* D. De La Cruz, R. Roth, J. Pacansky

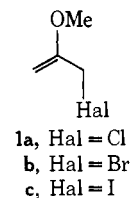
Department of Chemistry, Iowa State University
Ames, Iowa 50010

Received November 17, 1972

Cycloadditions and Reactivity of 2-Methoxyallyl Halides

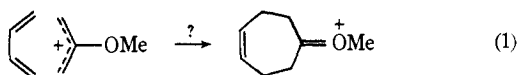
Sir:

The 2-methoxyallyl halides **1a-c** represent a novel class of organic compounds which have recently become accessible by two independent and efficient routes.¹ In studying the chemical properties of these compounds two questions seemed to us of special interest: (1) what is the reactivity of **1a-c** when compared with conven-

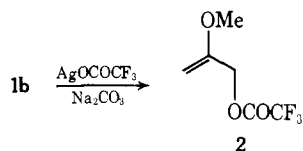


tional allyl halides and (2) can the 2-methoxyallyl cation be generated and captured with a conjugated diene according to eq 1?

(1) G. Greenwood and H. M. R. Hoffmann, *J. Org. Chem.*, **37**, 611 (1972); see also D. E. Horning, G. Kavadias, and J. M. Muchowski, *Can. J. Chem.*, **48**, 975 (1970).



From the outset it was clear that a quantitative estimate of the solvolytic reactivity of **1a-c** would be difficult. The electron-rich enolate grouping was expected to be vulnerable to protic solvents and, indeed, even in neutral methanol, which is not a good ionizing solvent anyway, the 2-methoxyallyl halides formed the corresponding ketal almost before one could scan their nmr spectra. However, it is already clear that under nonsolvolytic S_N1 like conditions, namely on treatment with silver trifluoroacetate in isopentane solvent, the bromide **1b** as well as the iodide **1c** react *surprisingly slowly*. For example, whereas 2-methylallyl bromide was known to form the trifluoroacetic ester² well below 0° under heterogeneous conditions, 2-methoxyallyl bromide (**1b**) reacted at room temperature only and gave the corresponding 2-methoxyallyl trifluoroacetate (**2**).³ Interestingly, S_N2 displacements in **1a** and **1b**



(NaI in acetone,¹ reaction with metal carbonyl anions such as Fe(CO)₄²⁻) were found to proceed also less readily than for the corresponding 2-methylallyl halides.

In view of these findings one could anticipate that cycloadditions of the hypothetical 2-methoxyallyl cation⁴ would be difficult. Indeed, under the conditions described previously² 2-methoxyallyl bromide was found to polymerize readily and in the presence of the silver salt, and the silver halide formed during the reaction tended to produce a solid, intractable mass together with the organic material. The following modifications were found essential to obtain positive results. (1) Solid Na₂CO₃ was added as a buffer to prevent harmful accumulation of trifluoroacetic acid. (2) The reaction flask was kept in the dark, silver halides being light sensitive. (3) Most important, the reaction mixture was stirred with an efficient vibromixer (100 cps).

The cycloaddition of the 2-methoxyallyl cation to furan may serve to exemplify our new procedure. 2-Methoxyallyl bromide (3.6 g, 24 mmol) in benzene (15 ml)⁵ was mixed with furan (20 ml, 276 mmol) and isopentane (60 ml), solid Na₂CO₃ (1 g) being suspended in solution. A mixture of silver trifluoroacetate (5 g, 23 mmol) and Na₂CO₃ (2 g) was added in small portions at

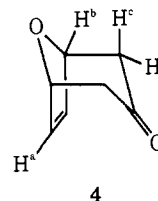
(2) H. M. R. Hoffmann, G. F. P. Kernaghan, and G. Greenwood, *J. Chem. Soc. B*, 2257 (1971).

(3) After **1b** (ca. 0.1 M) had been stirred in a suspension of silver trifluoroacetate in isopentane at 25° for 3.5 hr, 75% of the starting material disappeared with precipitation of AgBr and formation of a black polymeric solid as well as the desired ester **2** (30%). By adding solid Na₂CO₃ the reaction could be cleaned up giving **2** in ca. 60% yield: nmr δ 3.58 (s, 3 H), 4.67 (s, 2 H), 4.15 (d, 1 H), 4.24 ppm (d, 1 H) (*J*_{gem} = 2.5 Hz).

(4) Various attempts to generate a long-lived 2-methoxyallyl cation by standard procedures have failed, apparently because the precursor **1b** proved so sensitive that only complex mixtures resulted (G. A. Olah, unpublished experiments personally communicated).

(5) **1b** was prepared as described¹ and stored at 0° in solvent benzene, which also appears to be beneficial to the subsequent cycloaddition. The presence of isomeric 1-bromo-2-methoxypropene does not interfere in this reaction.

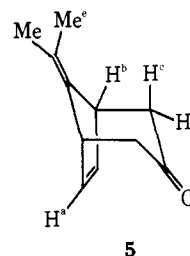
room temperature over a period of 10 hr,⁶ and the resulting suspension was stirred in the dark for a further 20 hr. The reaction mixture was worked up by careful addition of nitric acid (7%, 100 ml), evaporation of the bulk of the organic layer, and filtration of the black silver residue. The resulting yellow aqueous solution, which contained the desired product, was extracted with isopentane (3 × 30 ml), the organic layer was dried, and the solvent was evaporated, leaving a yellow oil which on sublimation at 25° (0.05 mm) gave 8-oxadicyclo[3.2.1]oct-6-en-3-one (**4**) (0.42 g, 15%) as a white crystal-



line solid: mp 38°; nmr δ (TMS, CCl₄) a 6.19 ppm, (s, 2 H), b 4.91 (d, 2 H, *J*_{bc} = 5 Hz), c (2 H, d of d centered on 2.61; *J*_{bc} = 5 Hz, *J*_{cd} = 17 Hz), d (2 H, d centered on 2.19, *J*_{cd} = 17 Hz, *J*_{bd} ~ 1.5 Hz; the bcd protons display a near perfect ABX pattern and each of the eight signals is broadened further by ca. 1 Hz); ir (CCl₄) 1720 cm⁻¹ (vs); mass spectrum at 70 eV (relative intensities) *m/e* 124 (16), 95 (8), 83 (4), 82 (60), 81 (100), 68 (14), 67 (14), 66 (4), 65 (4). When exposed to strong sunlight or at elevated temperature **4** decomposed to a brown oil. Hydrogenation (Adams catalyst, ethyl acetate solvent) followed by sublimation at 25° gave 8-oxabicyclo[3.2.1]octan-3-one: 60-MHz nmr (TMS, CCl₄) 1.6–3.0 (8 H, complex; however, the axial α-carbonyl protons are clearly discernible at 2.69, 2.64, 2.54, 2.49 ppm; *J*_{vie} = 5 Hz; *J*_{gem} = 16 Hz), 4.7 (2 H, br); ir (CCl₄) 1725 cm⁻¹ (vs); mass spectrum *m/e* 126 (100), 97 (10), 84 (44), 83 (32), 82 (12), 71 (32), 70 (12), 69 (56), 68 (24).

A similar procedure using freshly distilled cyclopentadiene (20 ml) in place of furan furnished bicyclo[3.2.1]oct-6-en-3-one⁷ (0.49 g, 17%): mp 100°; mass spectrum *m/e* 122 (58), 121 (6), 107 (10), 94 (8), 81 (6), 80 (70), 79 (100), 78 (8), 77 (18), 66 (6), 65 (6).

Finally, by starting with 6,6-dimethylfulvene (0.6 g, 37 mmol)⁸ as diene component we obtained 8-isopropylidenebicyclo[3.2.1]oct-6-en-3-one (**5**) (39 mg, 1%) as a



white solid; mp 22°; 60-MHz nmr (CCl₄, TMS) a 6.1 ppm (q, 2 H, apparent spacing of 1 and 2 Hz), b 3.4 (br, 2 H), c, d 2.30 (s, 2 H), 2.33 (s, 2 H), e 1.69 (s, 6 H); ir (CCl₄) 1710 cm⁻¹ (narrow doublet); mass spectrum

(6) Faster addition of the silver salt favors clagging of the materials and reduces the yield of product.

(7) This compound was obtained previously from norbornadiene *via* a lengthy ring expansion involving six steps; see N. A. LeBel and R. J. Maxwell, *J. Amer. Chem. Soc.*, **91**, 2307 (1969).

(8) Using a greater amount of fulvene does not appear to improve yields.

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 nonacarbonyliron, 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

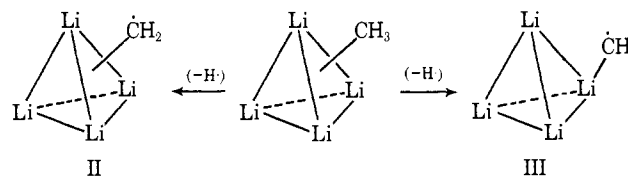
Radical	T_1^a , °C	$A_{\text{H or D}}$, G	A_{Li} , G	$\langle g \rangle$	Lw^b , G
$\cdot\text{CH}_2\text{Li}(\text{CH}_3\text{Li})_3$	-32	18.23	1.67	2.00293	0.56
$\cdot\text{CD}_2\text{Li}(\text{CD}_3\text{Li})_3$	-55	2.78	1.63	2.00293	0.27

^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 , $I = 3/2$).

Methylithium 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

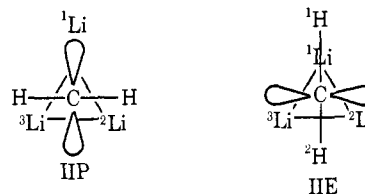
Table II. INDO Calculations for Hyperfine Splittings in Lithiomethyl Radicals^{a,b}

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 methylithium.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).