

Although formed at 0 °C, HO allylic cuprates are best utilized at low temperatures with most sp³-based electrophiles. Our data in Table I are highly suggestive of the variety of substrates that participate in these mild and efficient couplings.¹⁰ Moreover, the following noteworthy features deserve special comment: (1) diprenylcuprates, which react with epoxides by way of α -attack (entries 2 and 4), reverse this trend with halides where attachment at the γ -carbon prevails (entry 6); (2) crotylcuprates likewise react preferentially with halides at the γ -locus (entries 7 and 9); (3) cyclic epoxides (e.g., entry 3), highly prone toward Li⁺-induced rearrangement to cyclic ketones,¹¹ undergo clean displacement with minimal Lewis acid related side-product formation; (4) the presence of heteroatoms, in particular sulfur (entry 6) and nitrogen (entry 7), which can oftentimes perturb cuprates by their copper and lithium ion sequestering properties, respectively, do not alter these reactivity patterns; (5) use of lower order, Gilman-like cuprates tend not to effect these displacements (see entry 7).

Perhaps most significant, in strong testimony to the intense reactivity of these allylic cuprates, is their ability to displace primary, unactivated chlorides. Normally, even with the most reactive of Gilman cuprates (i.e., those containing sp³ carbon-copper bonds), chlorides are unacceptably slow at 0 °C¹² and are rarely used at room temperature¹³ due to competing cuprate decomposition. Even higher order dialkylcuprates normally require several hours at 0 °C to consume starting material.¹² By comparison, allylic cuprates effect this transformation at -78 °C in minutes (Scheme 1).¹⁴

In summary, a new method for forming relatively thermally stable allylic cuprates has been discovered. These reagents appear to be among the most reactive cuprates presently known toward substitution processes. The preparation relies on ligand-exchange events¹⁶ between alkyl cuprates and allylic stannanes, which completely eliminates the need for prior generation of allyllithium intermediates.

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Registry No. 1, 91328-60-8; 2, 126036-05-3; 3, 126035-99-2; (*E*)-Me₂C=CH(CH₂)₂CH=C(Me)CH₂OH, 32663-38-0; (*Z*)-Me₂C=CH(CH₂)₂CH=C(Me)CH₂OH, 58649-77-7; PhO(CH₂)₄CH=CH₂, 74972-56-8; PhCH₂O(CH₂)₄C(Me)=CH₂, 126036-01-9; PhO(CH₂)₃Br, 588-63-6; PhCH₂O(CH₂)₃Cl, 26420-79-1; (Me₂C=CHCH₂)₂Cu(CN)Li₂, 122700-73-6; (*E*)-Me(CH=CHCH₂)₂Cu(CN)Li₂, 124020-72-0; (*Z*)-(MeCH=CHCH₂)₂Cu(CN)Li₂, 126036-06-4; (H₂C=C(Me)-CH₂)₂Cu(CN)Li₂, 122700-72-5; H₂C=CHCH₂SnBu₃, 24850-33-7; Me₂Cu(CN)Li₂, 80473-70-7; MeCH=CHCH₂Li, 16327-44-9; methyl 4,6-O-benzylidene-2-deoxy-2-(2-propenyl)- α -D-allohexopyranoside, 126108-10-9; 2,6-dimethyl-1-phenyl-5-hepten-2-ol, 18091-00-4; *trans*-

2-(2-methyl-1-propen-3-yl)-cyclohexan-1-ol, 101859-19-2; 6-(benzyloxy)-6-(1,3-dithian-2-yl)-3,3-dimethyl-1-hexene, 126035-97-0; 7-(benzyloxy)-7-(1,3-dithian-2-yl)-2-methyl-2-heptene, 126035-98-1; (*Z*)-7-(2-phenylimidazol-1-yl)-2-heptene, 126036-00-8; 4-(2,3-dimethoxyphenyl)-3-methyl-1-butene, 126036-02-0; (*Z*)-5-(2,3-dimethoxyphenyl)-2-pentene, 126036-03-1; 2-methoxy-6-phenyl-1a,2,3a,4-tetrahydrooxireno[4,5]pyrano[3,2-*d*][1,3]dioxin, 66537-92-6; 2-methyl-2-benzyloxirane, 36099-42-0; 7-oxabicyclo[4.1.0]heptane, 286-20-4; 2-ethenyl-2-methyloxirane, 1838-94-4; 3-(benzyloxy)-3-(1,3-dithian-2-yl)-1-bromopropane, 126036-04-2; 2,3-dimethoxy-1-(chloromethyl)-benzene, 3893-01-4; 2-(4-chlorobutyl)-2-methyl-1,3-dioxolane, 57558-50-6; 2-methyl-2-(1-hepten-7-yl)-1,3-dioxolane, 76731-09-4.

Supplementary Material Available: A detailed, typical procedure and data (chromatographic, spectral, analytical) for all new compounds (3 pages). Ordering information is given on any current masthead page.

Structure of the 2-Butyl Cation. H-Bridged or Methyl Bridged?

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The nature of the 2-butyl cation has been the subject of many experimental and theoretical investigations and affords a continuing challenge for the structural chemist. This is the smallest secondary carbocation that can be stabilized by either C-C or C-H hyperconjugation.

The 2-butyl cation was first observed in superacid solution at -110 °C.¹ The ¹H NMR spectrum at -140 °C revealed only two peaks due to the very rapid 2,3-hydride shifts. The barrier must lie below 2.4 kcal/mol.² This rearrangement could not be frozen out even on the ¹³C NMR time scale in the solid state at -190 °C.³ Since the rate of such chemical exchange processes is often reduced in the solid state, this hydride-shift barrier in solution might be considerably less than 2.4 kcal/mol.³ The fully ¹H coupled ¹³C NMR spectrum shows a coupling pattern that agrees with a rapidly exchanging cation, where each central carbon is coupled simultaneously (on the NMR time scale) to the three central hydrogens.⁴ By analyzing the isotope effects and their temperature dependence on both the ¹H and ¹³C NMR spectra, Saunders and Walker concluded that the best fit was obtained with a model assuming two structures to be present.⁵ It was

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(10) Displacements also occur in far simpler non-heteroatom-containing systems as well; e.g., *n*-heptyl bromide reacts with diallylcyanocuprate (-115 → -78 °C, 1 h) to afford decene in 90% (VPC) yield. Substitution reactions at sp² centers have also been studied in detail: Lipshutz, B. H.; Elworthy, T. R. *J. Org. Chem.*, in press.

(11) In the specific case of cyclohexene oxide, ca. 30% of the product mix consists of cyclohexanone; cf.: Lipshutz, B. H.; Kozlowski, J. A.; Parker, D. A.; Nguyen, S. L.; McCarthy, K. E. *J. Organomet. Chem.* **1985**, *285*, 437. See also: Bertz, S. H.; Dabbagh, G. *J. Org. Chem.* **1984**, *49*, 1119. Johnson, C. R.; Herr, R. W.; Wieland, D. M. *Ibid.* **1973**, *38*, 4263. Bertz, S. H.; Dabbagh, G. *J. Am. Chem. Soc.* **1982**, *104*, 5824. Acker, R.-D. *Tetrahedron Lett.* **1977**, 3407.

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(14) For comparison purposes, imidazole chloride **2** (see Table I, entry 7) was treated with crotyllithium (-78 °C, 20 min) to afford a 50% yield of **3** (no educt remained), while treatment of **2** with crotyl Grignard (-78 → 0 °C) returned 66% of the educt with none of **3** being formed.

(15) Only starting material was recovered (70.4%); base-line material was also formed.

(16) For a related transmetalation/conjugate addition study on vinylstannanes, see: Behling, J. R.; Babiak, K. A.; Ng, J. S.; Campbell, A. L.; Moretti, R.; Koerner, M.; Lipshutz, B. H. *J. Am. Chem. Soc.* **1988**, *110*, 2641.

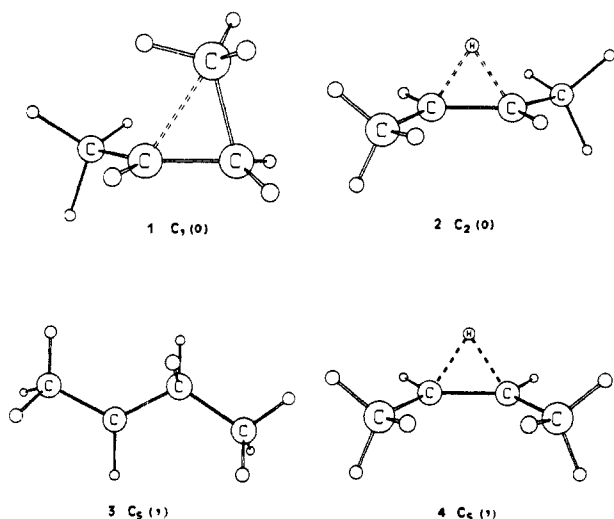


Figure 1. MP2(fu)/6-31G* optimized 2-butyl cation structures. The number of imaginary frequencies is given in parentheses (at HF/6-31G* for 1, 3, and 4; at MP2(fu)/6-31G* for 2. The last was calculated analytically with the CADPAC program; ref 22).

concluded that the H-bridged structure was more stable by about 0.4 kcal/mol. Solvolytic studies of 2-butyl derivatives were interpreted in favor of the H-bridged cation intermediate.⁶

The most recent experiments have led to different conclusions. Johnson and Clark prepared the 2-butyl cation by deposition of 2-butene on a superacid surface in the source of an ESCA spectrometer.⁷ The observed spectrum did *not* have two peaks with a 1:1 intensity ratio, as required for the H-bridged cation. The best fit was given by a three-peak model with intensities 1:1:2. Johnson and Clark concluded that the 2-butyl cation "is substantially methyl bridged".⁷ However, the quality of the ESCA spectrum was low and the possibility of contamination with neutral material or the presence of a second C₄H₉⁺ isomer was not excluded. Indeed, the separation of the main peaks corresponds to that calculated for the H-bridged form. In addition, there is the possibility that the species observed on the surface may be different from that in the bulk.

Prior theoretical investigations on the 2-butyl cation employed lower levels of theory and are also inconclusive.⁸⁻¹⁰ Electron correlation with extended basis sets is needed to treat systems that have nonclassical structures. Very flat potential energy surfaces often are involved.¹¹⁻¹⁴ Geometry optimizations at correlated levels are essential. While we provide support for the methyl bridging of Johnson and Clark,³ our evidence favors a symmetric H-bridged structure for the 2-butyl cation, at least under equilibrium conditions.

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Table I. Relative Energies (Kilocalories/Mole) of 2-Butyl Cation Isomers

level	1	2	3	4
HF/3-21G//HF/3-21G	0.00	12.03	2.48	13.12
HF/6-31G*//HF/6-31G*	0.00	4.15	1.04	5.31
MP2(fu)/6-31G*//MP2(fu)/6-31G*	0.00	2.47	5.29	3.37
MP2(fc)/6-31G**//MP2(fu)/6-31G*	0.00	1.43	5.44	2.33
MP3/6-31G**//MP2(fu)/6-3uG*	0.00	0.12	2.96	1.04
MP4(sdtq)/6-31G**//MP2(fu)/6-31G*	0.00	0.74	3.75	1.63
MP2(fu)/6-31G*//MP2(fu)/6-31G**	0.00	1.52		
MP2(fc)/6-311G**//MP2(fu)/6-31G**	0.00	1.78		
MP3/6-311G**//MP2(fu)/6-31G**	0.00	0.29		
MP4(sdtq)/6-311G**//MP2(fu)/6-31G**	0.00	0.78		
ZPE ^a	79.57	78.34	78.53	78.42
final + ZPE ^b	0.00	-0.31	2.82	0.61

^a Zero-point energy (kcal/mol) calculated at HF/6-31G*//HF/6-31G*.

^b The highest level relative energy corrected by ZPE scaled by 0.89 (see ref 18).

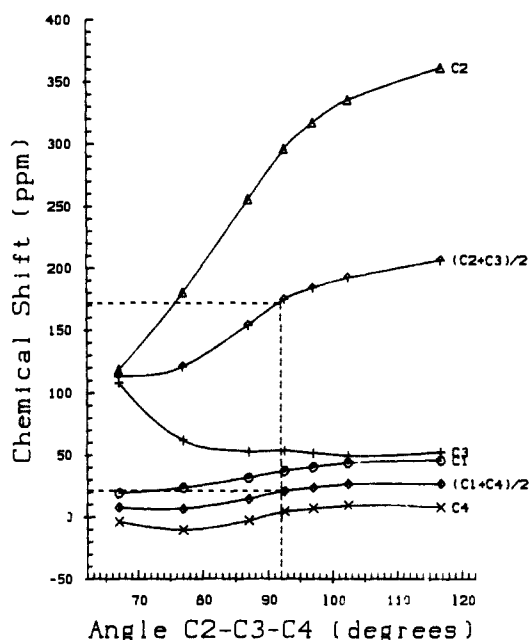


Figure 2. IGLO ¹³C NMR chemical shifts of **1** as a function of the C₂⁺-C₃-C₄ angle. This angle was fixed, but all other parameters were fully optimized at HF/6-31G*. The dotted lines give averaged experimental chemical shifts from ref 4.

We have calculated¹⁵ the structures of the methyl-bridged (1, C₁) and open (3, C₃) forms of the 2-butyl cation as well as the trans (2, C₂) and cis (4, C₄) H-bridged structures at many standard theoretical levels¹⁶ (Figure 1). As both 3 and 4 are higher energy transition structures, we concentrate on the other isomers.¹⁷ It is well established that polarization functions on hydrogens (e.g., 6-31G**) are needed when H-bridged structures are involved.^{13,16} Hence, the MP2(fc)/6-31G**//MP2(fu)/6-31G* relative energies in Table I are at the lowest acceptable level. At and above this level, the 1-2 energy difference varies within a narrow range, 0.12-1.43 kcal/mol. This indicates that further basis set extension and electron correlation treatments are not likely to change the situation. However, the zero-point energies favor 2 over 1, and

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(16) For a discussion of the standard basis sets and procedure, see: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

(17) We will discuss these geometries in detail in a full paper to be submitted.

Table II. IGLO ^{13}C NMR Chemical Shifts (vs CH_4) for 2-Butyl Cation Isomers

descriptn	IGLO basis//geometry level	angle ^a $\text{C}_2^+-\text{C}_3-\text{C}_4$	$\delta(^{13}\text{C})$						
			C_1	C_2	C_3	C_4	$(\text{C}_1\text{C}_4)_{\text{av}}^b$	$(\text{C}_2\text{C}_3)_{\text{av}}^c$	
open chain (3) (classical)	DZ//6-31G*	116.7	45.5	360.8	52.3	7.8	26.7	206.6	
	DZ//6-31G*	102.4	43.5	335	49.1	9.3	26.4	192.1	
methyl bridged (1)	II//6-31G* ^d		39.2	338	48.1	5.2	22.2	193.1	
	DZ//3-21G	101.4	41.3	328.3	51.7	15.1	28.2	190.0	
	DZ//MP2/6-31G*	77.4	24.0	178.3	57.0	-13.7	5.2	117.7	
	II//MP2/6-31G* ^d		20.5	173	52.7	-14.0	3.3	115.4	
	II//MP2/6-31G* ^d		20.4	177	52.9	-13.4	3.5	115.0	
	DZ//MP2/6-31G**	76.9	23.0	174.2	55.1	-15.9	3.6	114.7	
	H-bridged (2)	DZ//6-31G*		19.1	160				
		II//6-31G* ^d		15.0	156				
DZ//MP2/6-31G*			19.8	161.2					
DZ//MP2/6-31G**			19.1	161.2					
II//MP2/6-31G* ^d			15.8	157					
II//MP2/6-31G* ^d			15.4	156					
expt (vs TMS) ^e							21.0	171.6	

^a Angles in degrees. ^b Average values for C_1 and C_4 . ^c Average values for C_2 and C_3 . ^d IGLO calculations with basis II and II' by U. Fleischer. ^e Averaged values; ref 4. The ^{13}C absolute chemical shifts of CH_4 and TMS calculated with the DZ basis set differ by only 0.2 ppm.

the former becomes slightly (0.3 kcal/mol) more stable when this correction is included.

Does the MP2(fu) optimization overemphasize the degree of methyl bridging in **1**? We investigated this possibility by optimizing structures with varying degrees of bridging (the $\text{C}_2^+-\text{C}_3-\text{C}_4$ angle was fixed, and all other parameters were allowed to optimize fully at HF/6-31G*). Subsequent MP4(sdtq)/6-31G* single-point calculations show that no structure is more stable than **1** (angle $\text{C}_2^+-\text{C}_3-\text{C}_4 = 77^\circ$).

Can differential solvation invert the relative stability of **1** and **2**? Although accumulating evidence shows that solvation has only a minor influence on relative stabilities of isomeric carbocations,¹⁸ we investigated this possibility with the self-consistent reaction field (SCRf) method.¹⁹ Calculations on the two minima, **1** and **2**, reveal a preferential stabilization of the *H-bridged* structure **2**. While specific solvation effects are not treated in this model, there is no basis on which to expect that these would change the relative stability.

We believe that this information is sufficient to establish the H-bridged **2** as the most stable 2-butyl cation structure. Nevertheless, additional evidence reinforces this conclusion. In an extensive investigation of carbocation structures, we have shown that chemical shifts calculated by the IGLO method²⁰ can be used to decide between isomers that have similar energies but different structures.^{12,14b,20,21} Table II summarizes the IGLO chemical shifts calculated for **1**-**3**. These do not depend on the size of the IGLO basis set (DZ, II, II'). All geometries for **2** give acceptable agreement of IGLO chemical shifts vs experiment. This is not true for **1** and **3**. The classical structure (**3**) can be excluded from consideration on this basis. The chemical shifts for **1** depend strongly on the $\text{C}_4-\text{C}_3-\text{C}_2^+$ angle (Figure 2). All the fully optimized geometries of **1** (HF/3-21G, HF/6-31G*, MP2(fu)/6-31G*, and MP2(fu)/6-31G**) lead to IGLO chemical shifts that differ by over 50 ppm from experiment. Agreement with experiment can only be achieved by artificially fixing the $\text{C}_4-\text{C}_3-\text{C}_2^+$ angle to 92.5° (Figure 2). However, this geometry is 0.6 kcal/mol higher in energy than the corresponding 77° structure (at MP4sdtq/6-31G**//HF/6-31G*).

Our evidence favors the C_2 H-bridged structure (**2**) for the 2-butyl cation, although the methyl-bridged alternative (**1**) is only

slightly (ca. 0.3 kcal/mol, possibly increased by small solvation differences) less stable. This conclusion agrees excellently with Saunders's findings.⁵ In view of the small energy differences between the 2-butyl cation isomers, it might be possible that surface effects dominate the situation under the conditions of the Johnson-Clark measurements.⁷

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Registry No. 1, 16548-59-7; 2, 126191-46-6.

Supplementary Material Available: Table of the absolute energies of 2-butyl cation isomers (1 page). Ordering information is given on any current masthead page.

Differentiation of Two Stages during Establishment of Strong Metal-Support Interaction in Rh/TiO₂ Catalysts

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It is known that treatment under H_2 at 773 K of catalysts consisting of group VIII metals supported on TiO_2 gives rise to strong metal-support interaction (SMSI behavior),^{1,2} which inhibits hydrogen adsorption on the metal. Its origin has been related to the formation of metal-titania bonding and/or to the coverage of metal by TiO_x species;¹⁻²⁰ however, the nature of this phe-

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