

Table I. Products Evolved during Hydrogenation and Hydrolysis of a Nonferromagnetic Ni-Pentane Powder (Ni:C:H, ~2:1:2)

temp, °C	products, mol % ^a					
	CH ₄	CO ₂ ^c	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂
25			H ₂ ^b			
		1.8	0.9	3.6	5.4	8.0
300	10	38	22	7.4	2.5	1.5
			H ₂ O ^d			
75	<i>e</i>	9.0	2.2	17	23	48

^a Overall percent for 25 and 300 °C treatments. ^b 150 Torr of H₂, 30 h, 25 °C; 60 Torr of H₂, 6 h, 300 °C; 150 mg of Ni-pentane. ^c Variable, dependent upon airless care during workup. ^d 2-mL H₂O reflux with 300 mg of Ni-pentane for 1 h. ^e Not measured but non-condensable gas observed.

addition and/or abstraction processes with (Ni)_n and C₅H₁₂ increase and become more and more competitive, and, when stable molecular structures are forced to be attained by warming to room temperature, the final Ni-organic composition depends on the experimental warm-up rate. Currently we doubt that nickel atoms are actually reacting with pentane for several reasons: (1) metal atoms including Ni are known to form clusters readily in inert matrices even as low as 10 K;^{4,5} (2) we can visually observe the formation of Ni particles in the -196 to -130 °C range and feel certain that no Ni atoms exist at 130 °C (pentane liquid), the temperature where pentane reaction is obviously occurring at a very competitive rate; and (3) the only data yet reported on metal atom-alkane codepositions⁶ indicate that V atom-alkane reactions are not occurring at the temperature where V clustering is taking place.

What is the form of the organic material in the "pseudo Ni-organometallic"? This question becomes exceedingly important for two reasons: (1) learning the structure of the R group attached to the nickel clusters should teach us a great deal about how the low temperature reactions occur, and (2) the presence of more organics allows the preparation of smaller crystallite nonferromagnetic nickel particles that are more stable to sintering and more active in some catalytic processes than the larger particle (less organics) ferromagnetic samples (nonferro, 260-280 °C with gross sintering; ferro, 220-240 °C).³ These results indicate that the carbonaceous species stabilize the nearly amorphous nickel framework.

ESCA studies incorporating first surface analysis of "as is" samples followed by sputtering to several different depths and then further analyses have demonstrated that the carbon is homogeneously dispersed throughout the nickel, and that the carbon is not in the form of carbides but rather more likely sp²- and sp³-bound carbon species. Addition of H₂ or H₂O to the Ni-pentane powder yields distributions of evolved organics that are very similar, identified as CH₄, C₂H₆, C₃H₈, C₄H₁₀, and C₅H₁₂ (cf. Table I). No organics containing more than five carbons were found. The similarity of product distributions for hydrogenation and hydrolysis and the mild conditions employed strongly suggest that the pentane cleavage reactions are not occurring during the workup, but occurred during the Ni-pentane codeposition—warm-up procedure as previously discussed.

These results clearly demonstrate cleavage of pentane by nickel clusters at very low temperatures and retention of organic fragments to produce thermally stable catalytically active "organometallic" powders. The Ni-Ni framework is stabilized toward sintering by strongly bound fragments of the alkane, which apparently are present as alkyl radical and carbenoid-like species.

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helpful discussions and ESCA work by Curt White and Charles Kibby of the Pittsburgh Energy Research Center are greatly appreciated.

References and Notes

- (1) Part 6 of this series: K. J. Klabunde, D. Ralston, R. Zoellner, H. Hattori, and Y. Tanaka, *J. Catal.*, in press.
- (2) K. J. Klabunde, H. F. Efner, T. O. Murdock, and R. Ropple, *J. Am. Chem. Soc.*, **98**, 1021 (1976).
- (3) K. J. Klabunde, S. C. Davis, H. Hattori, and Y. Tanaka, *J. Catal.*, in press.
- (4) M. Moskovits and G. A. Ozin, Ed., "Cryochemistry", Wiley-Interscience, New York, N.Y., 1976, p 395.
- (5) M. Moskovits and J. Hulse, *Surf. Sci.*, **57**, 125 (1976).
- (6) W. E. Klotzbucher, S. A. Mitchell, and G. A. Ozin, *Inorg. Chem.*, **16**, 3063 (1977).

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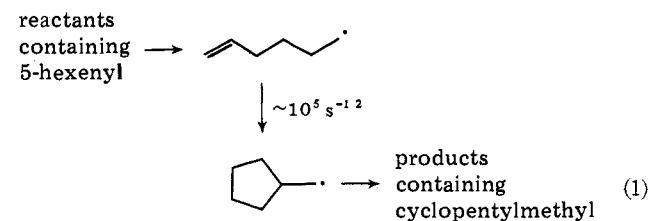
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Intramolecular 1,4 Proton Transfer in the 5-Hexenyl Anion. The 5-Hexenyl Probe as a Detector of Both Alkyl Radical and Anion Intermediates

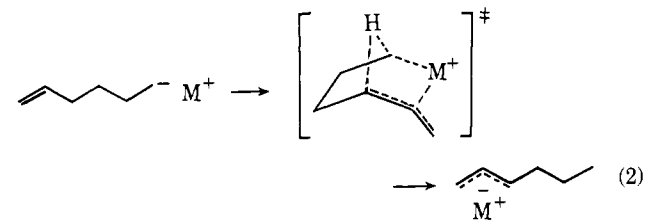
Sir:

The cyclization of 5-hexenyl to cyclopentylmethyl radicals (eq 1) is a valuable probe for alkyl radical reaction interme-



diates.¹ Because the corresponding cyclization of 5-hexenyl anions often occurs to a negligible or limited extent, this probe is especially useful when both alkyl radicals and anions may be intermediates.

During one such application, we obtained unexpected products that point to isomerization of the 5-hexenyl anion by an intramolecular 1,4 proton transfer (eq 2). While this ra-



tional but unprecedented reaction complicates slightly the interpretation of results, it also extends the usefulness of the probe. Under favorable circumstances, the 5-hexenyl probe detects both radical and anion intermediates separately and specifically.

The expected products of reactions of 5-hexenyl chloride in ethers with alkali metals were 1-hexene and methylcyclopentane. In addition, there were formed 2-hexenes and dimers **1** and **2**. As anticipated, the normal Wurtz coupling product, 1,11-dodecadiene, was not formed in significant amounts.³

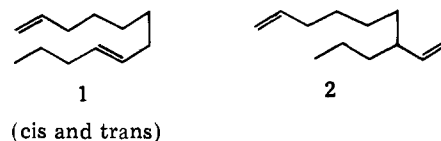


Table 1. Products of Reactions of 5-Hexenyl Chloride in Ethers with Alkali Metals^a

metal	solvent	MCP	1-hex	2-hex	1 + 2
Na	DME	2	94	4	<1
Na	THF	3	85	3	9
Na	diethyl ether	6	94	<1	0
Na	dioxane	1	98	1	0
Cs	DME	44	10	12	34 ^b
Cs	THF	18	7	18	57
Cs	diethyl ether	10	5	16	69
Cs	dioxane	4	67	30	<1

^a Yields are mole percent of the products shown. No others were detected at significant levels. MCP = methylcyclopentane; 1-hex = 1-hexene; 2-hex = 2-hexene. Reactions were carried out at 25.0 ± 0.3 °C in sealed vessels under solvent vapor pressure. Solutions of 5-hexenyl chloride, initially 0.005–0.01 M, were agitated over metal mirrors for ~18 h and then neutralized with acetic acid. Analyses were by VPC using internal standards. The conditions used separated 1-hexene, *cis*- and *trans*-2-hexenes, *cis*- and *trans*-3-hexenes, methylcyclopentane, cyclohexane, hexane, and 1,5-hexadiene. **1** and **2** were collected by preparative VPC and characterized by their C,H analyses and off-resonance decoupled ¹³C NMR spectra. ^b For Cs in DME the reaction time was 5 min. Alkene isomerizations were found to occur over a period of hours for products left in contact with a Cs mirror in DME.

3-Hexenes were absent and 1,5-hexadiene was formed in no more than trace quantities (distinctly <1%). Table I gives the product distributions for experiments with sodium and cesium, which represent the extremes observed for sodium, potassium, rubidium, and cesium, in THF, DME, diethyl ether, and dioxane.

The unexpected products imply 1-propylallyl intermediates: radicals, anions, or both. Isomerization of 5-hexenyl to 1-propylallyl radicals has not been found; instead, 5-hexenyl radicals cyclize as depicted in eq 1.⁴ The possibility that surface-adsorbed radicals behave differently from solution radicals and are responsible for the isomerization observed is ruled out by the fact that the 1-propylallyl-derived products are also found from reactions of homogeneous solutions of alkali naphthalenes, potassium benzene, and alkali metals (i.e., solutions of M⁺ and e⁻) with 5-hexenyl chloride.

Intermediate 1-propylallyl anions would protonate to 2-hexenes (as well as 1-hexene), and they would react with 5-hexenyl chloride to give **1** and **2**, thus rationalizing these products. Control experiments show that alkenes are not isomerized under the reaction conditions employed. Thus, a mixture of hexyl chloride and 1-hexene in THF reacts with K or Cs to give only hexane and 1-hexene. Further, when product isomerization is deliberately allowed to occur (by prolonged reaction of the Cs/5-hexenyl chloride/DME system), additional peaks appear in the C₁₂ region of the VPC traces, but such peaks are absent for the product mixtures reported in Table I. This militates against intermolecular base- or metal-promoted reactions of 1-hexene as sources of 1-propylallyl anions, leaving the intramolecular process (eq 2) as the only reasonable possibility.

It is significant, we believe, that there exists a possible transition state for the 1,4 proton transfer of a 5-hexenylalkali in which the metal ion is simultaneously in good contact with both the original and the developing centers of negative charge in the anion (see eq 2).

Since isomerization of 5-hexenylsodium is a minor process, the conclusions of previous studies, in which the 5-hexenyl probe was applied to reductions of alkyl halides by sodium arenes and related species, are left unchanged.^{1a-h}

Users of the 5-hexenyl probe should be aware that 5-hexenyl anions can isomerize prototropically. Products derived through 1-propylallyl anions must be included in the reckoning of the yield of 5-hexenyl anions.

Another caveat is appropriate here: cyclization of 5-hexenyl anions is not always negligible. It competes with the other reactions of 5-hexenyl anions, and since all of these may be affected by counterion, solvent, and temperature, the extent of anion cyclization can be expected to depend on these conditions.⁵ We have found situations with the higher alkali metals and solvents containing crown ethers in which 5-hexenyl anions cyclize to an extent of ~6%.

Anion cyclization cannot account for the large yield of methylcyclopentane found in the reaction of 5-hexenyl chloride with Cs in DME (Table I) unless such cyclization is dependent on the heterogeneity of the system or some other detail of reaction conditions. When 5-hexenylcesium is produced in DME by the reduction of 5-hexenyl chloride with cesium naphthalene, <3% of the reduction products is methylcyclopentane.⁶

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References and Notes

- (a) J. F. Garst, P. W. Ayers, and R. C. Lamb, *J. Am. Chem. Soc.*, **88**, 4260 (1966); (b) R. C. Lamb, P. W. Ayers, M. K. Toney, and J. F. Garst, *ibid.*, **88**, 4261 (1966); (c) J. F. Garst and F. E. Barton, II, *Tetrahedron Lett.*, 587 (1969); (d) J. F. Garst and C. D. Smith, *J. Am. Chem. Soc.*, **95**, 6870 (1973); (e) J. F. Garst and F. E. Barton, II, *ibid.*, **96**, 523 (1974); (f) J. F. Garst and C. D. Smith, *ibid.*, **98**, 1520 (1977); (g) J. G. Garst and C. D. Smith, *ibid.*, **98**, 1526 (1976); (h) J. F. Garst, R. D. Roberts, and J. A. Pacifici, *ibid.*, **99**, 3528 (1977); (i) J. K. Kochi and J. W. Powers, *ibid.*, **92**, 137 (1970); (j) H. W. H. J. Bodewitz, C. Blomberg, and F. Bickelhaupt, *Tetrahedron*, **31**, 1053 (1975); (k) E. C. Ashby and J. S. Bowers, Jr., *J. Am. Chem. Soc.*, **99**, 8504 (1977).
- (a) D. Lal, D. Griller, S. Husband, and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 6355 (1974); (b) D. J. Carlsson and K. U. Ingold, *ibid.*, **90**, 7047 (1968).
- Many previous experiments have shown that no normal Wurtz coupling results when simple primary alkylsodiums, e.g., hexyl- and 5-hexenylsodium, are generated from corresponding alkyl chlorides.^{1a} Clearly, such alkylsodiums are protonated by the solvent rapidly compared with their reactions with their parent alkyl chlorides.
- (a) R. C. Lamb, P. W. Ayers, and M. K. Toney, *J. Am. Chem. Soc.*, **85**, 3483 (1963); (b) C. Walling and M. S. Pearson, *ibid.*, **86**, 2262 (1964); (c) C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, *ibid.*, **88**, 5361 (1966).
- In fact, cyclization of 5-hexenylmagnesium halides to cyclopentylmethylmagnesium halides is well known and intensely studied. See H. G. Richey, Jr., and H. S. Veale, *J. Am. Chem. Soc.*, **96**, 2641 (1974). See also, for additional background and related material, E. A. Hill, *Adv. Organomet. Chem.*, **16**, pp 131–165 (1977), and E. A. Hill, *J. Organomet. Chem.*, **91**, 123 (1975).
- For example, 10⁻¹ M cesium naphthalene in DME reacts with 3.5 × 10⁻² M 5-hexenyl chloride to give reduction products consisting of <3% methylcyclopentane: F. E. Barton, II, Dissertation, University of Georgia, 1969.

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Mechanism of Lipid-Protein Interaction in Lipoproteins. A Synthetic Peptide-Lecithin Vesicle Model

Sir:

We are engaged in an investigation of the relationship between structure and function in lipoproteins, exploring the mechanism by which small fragments of a protein molecule may exhibit some of the fundamental properties of the native protein itself. The tertiary structure of an enzyme is known to bring into close proximity the functional groups necessary for catalysis but far apart in the linear sequence of amino acids. Therefore, making the assumption that the catalytic activity of an enzyme could be imitated by a small synthetic portion of it surrounding one active site residue would be naive, in general. In contrast, the functional units of structural proteins