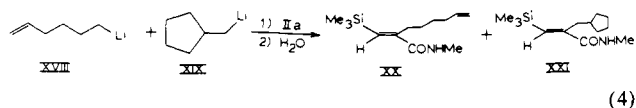


lithium (XIX) (eq 4) the graph of [XXI]/[XX] vs. [XIX]/[XVIII] ($-20\text{ }^{\circ}\text{C}$, ether/pentane 1:1, [XXI]/[XX] = 1.65, [XIX]/[XVIII]) indicated that no XXI is formed from XVIII. Therefore, if SET takes place in the reactions of IIa with primary alkylolithiums at all, the rate of radical-radical anion coupling must be much higher than the rate of cyclization of the 5-hexenyl radical.



The present findings extend the scope within which CONLiMe can be used as a tool for controlling reactivity and selectivity in organolithium chemistry.¹³ Anti-Michael adducts IX (X = SiMe₃) are new members of the class of (α -lithiovinyl)silanes that are of value in organic synthesis.¹⁴

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Cyclization of *o*-(3-Butenyl)bromobenzene via the Aryllithium Derivative

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Cyclization of *o*-(3-butenyl)phenyl radicals to 1-methylindanyl radicals has been used to detect radical intermediates in a variety of reactions.¹ Cyclization of 5-hexenyl radicals has also been used extensively for this purpose in the straight-chain case.^{1,2} The possibility of anionic cyclization in these reactions has until recently been largely ignored.³⁻⁵ 6-Hepten-2-yl radicals and anions both cyclize but the anion contribution can be distinguished by detailed product analysis.⁴ In the case of *o*-(3-butenyl)phenyl anion the possibility of cyclization has not been considered nor would it be possible to apply the same methodology as in the open-chain case. We wish to report that the phenyllithium derivative cyclizes with the *o*-(3-butenyl) double bond, that cyclization can be prevented at low temperature, but that the corresponding radical cyclizes under the same conditions. These results define conditions where a valid radical test can be made.

(1) Beckwith, A. L. *J. Tetrahedron* **1981**, 37, 3073.

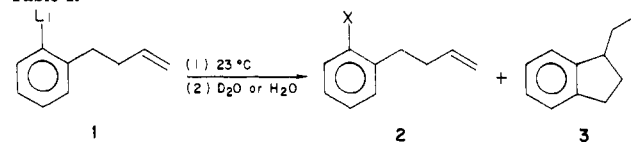
(2) Beckwith, A. L. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1535. Al-najjar, M. S.; Kuivila, H. G. *J. Am. Chem. Soc.* **1985**, 107, 416. Ashby, E. C.; Wenderoth, B.; Pham, T. N.; Park, W.-S. *J. Org. Chem.* **1984**, 49, 4505.

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Table I.



X = H or D			
solvent	reactn ^b time/ temp, min/ $^{\circ}\text{C}$	% 2 (% d_1) ^d	% 3 (% d_1) ^e
THF	120/-78	100 (100)	0
	5/23	58 (75)	42 (74)
	10/23	38 (52)	62 (52)
	30/23	13 (10)	89 (10)
	60/23	12 (<1)	90 (<1)
Et ₂ O	30/23	69 (100)	31 (84)
	60/23	42 (100)	60 (64)
Et ₂ O/TMEDA ^c	60/-78	101 (100)	0
	10/23	32 (90)	67 (92)
	30/23	8 (49)	94 (85)

^aOne equivalent (0.3-0.5 mmole) of ArBr, 2 equiv of BuLi for 30 min at dry ice/acetone temperature ($-78\text{ }^{\circ}\text{C}$) in the solvent indicated (15 mL) under argon. ^bAt the end of the reaction period 1 mL of D₂O or H₂O was added. ^cTwo equivalents of TMEDA were added at room temperature at time = 0. ^dDeuterium was shown to be on the ring by the MS fragmentation pattern and probably ortho by deuterium NMR. ^eMS showed the deuterium was all in the methyl group.

o-(3-Butenyl)bromobenzene was treated with 2 equiv of *n*-butyllithium⁶ at $-78\text{ }^{\circ}\text{C}$ (dry ice-acetone bath) in THF or diethyl ether. After 30 min at $-78\text{ }^{\circ}\text{C}$ the solutions were warmed to room temperature ($23\text{ }^{\circ}\text{C}$) for a period of time and then quenched by injection of an excess of D₂O or H₂O. The products were analyzed by GC and by GC-MS (for deuterium incorporation). The results are shown in Table I. Preparation of a stable aryllithium derivative at low temperature obviated electron-transfer processes so that radical reactions did not intercede.

When the reaction was carried out in THF, held at $-78\text{ }^{\circ}\text{C}$ for 2 h, then quenched, the yield of uncyclized 2 was 100% with 100% d_1 incorporation, indicating no cyclization or other reaction of the aryllithium reagent 1 at this temperature. Warming this solution to room temperature and quenching at various times indicated the slow cyclization of 1 to the indan 3.³ The decrease in deuterium incorporation for both 2 and 3 as the reaction time increased is consistent with slow attack by RLi on THF at room temperature.⁷ When a less polar solvent, diethyl ether, was used, the cyclization rate slowed under comparable conditions (31% in Et₂O compared to 89% in THF after 30 min). Addition of tetramethylethylenediamine (TMEDA) to the Et₂O reaction solution increased the cyclization rate to that observed in THF (31% in Et₂O compared to 94% in Et₂O/TMEDA). Both the solvent effects and the effect of TMEDA are expected for a reaction involving charge separation in the activated complex. TMEDA is known to increase the basicity of lithium alkyls,⁸ effectively making the "ion pair" looser. The effect of the more polar solvent, THF, is similar.⁹⁻¹¹ The deuterium contents for both Et₂O reaction conditions show less solvent proton abstraction than in THF. These results can be interpreted by the anion-like cyclization of the aryllithium reagent to the double bond at $23\text{ }^{\circ}\text{C}$. The

(6) When a 1:1 ratio of BuLi to ArBr was used, the products were largely contaminated by butyl-group incorporation into both 2 and 3 by nucleophilic displacement on butyl bromide formed from the exchange lithiation. A 2:1 BuLi to ArBr ratio prevented this reaction.

(7) Jung, M. E.; Blum, R. B. *Tetrahedron Lett.* **1977**, 3791.

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(9) Cyclization of the 5-hexenyl radical is totally independent of solvents effects: Citterio, A.; Arnoldi, A.; Minisci, F. *J. Org. Chem.* **1979**, 44, 2674.

(10) Recent work on the nature of butyllithium aggregates¹¹ which may be applicable to aryllithium derivatives does not invalidate this interpretation. However, the basis for the change of reactivity with solvent and TMEDA may be a change in the hexamer/tetramer/dimer ratios. These solvent effects are not expected for a radical intermediate⁹ and the intramolecular reaction remains anion-like rather than radical.

(11) McGarrity, J. F.; Ogle, C. A. *J. Am. Chem. Soc.* **1985**, 107, 1805. McGarrity, J. F.; Ogle, C. A.; Brich, Z.; Loosli, H.-R. *Ibid.* **1985**, 107, 1810.

solvent polarity, the TMEDA effect, and the deuterium labeling are all consistent with this interpretation. The presence of adventitious oxygen would have been detected by cyclization at -78 °C from the radical but this was not observed.¹²

In order to show that a valid radical test can be made at -78 °C, the *o*-(3-butenyl)phenyl radical was generated from the corresponding bromide with lithium naphthalene¹⁴ at -78 °C, held at this temperature for 1 h then quenched and worked up to give 52% **3** (X = H) and 46% **2** (X = H). This result indicates the intermediacy of the radical in this reaction because the anion with the same counter ion (Li^+) and in the same solvent (THF) is stable at this temperature.

Verification of the anionic cyclization at room temperature has been carried out by a series of electrochemical experiments. Electrochemical reduction of *o*-(3-butenyl)bromobenzene carried out at an electrode surface generated an anion which can cyclize to the methylindan derivative.¹⁵ This process was shown to be prevented by introduction of water which protonated the intermediate anion. Alternately, the cyclization was facilitated by use of a mediator to allow reduction to the radical anion which decomposed rapidly to the aryl radical and cyclized before further reduction could occur. These results will be reported in detail shortly.

Radical tests by cyclization of alkene substrates must be carried out at low temperature in nonpolar solvents or under conditions where it has been shown that the anion does not cyclize.

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(12) The possibility that a small amount of oxygen might oxidize the aryllithium reagent to the radical¹³ with subsequent cyclization was examined by introduction of dry air at -78 °C. Quenching after 5 min gave no **3** but ca. 5% of a product which was tentatively assigned the 1-(hydroxymethyl)indan (**4**) structure. On longer treatment more of this product was observed, but no **3**. Thus, the aryllithium reagent was oxidized to the radical which cyclized at -78 °C and was oxygenated leading ultimately to **4**.

(13) Beckwith, A. L. J.; Goh, S. H. *J. Chem. Soc., Chem. Commun.* **1983**, 905.

(14) Garst, J. F.; Barbas, J. T. *J. Am. Chem. Soc.* **1974**, *96*, 3239.

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Mass Spectrometry of Microscale Chemical Reaction Products Produced at the Surface of Organic Solids

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Chemical reactions that take place at the surface of organic solids are of interest in a wide range of fields. We here report a new technique for detecting such reactions. During the course of a ^{252}Cf ionization¹ mass spectrometric investigation² of the triphenylmethane dye crystal violet,³ we inadvertently exposed a thin solid film⁴ of the dye to light in the presence of air following the essentially nondestructive⁵ mass spectrometric analysis. Subsequent mass spectrometric reanalysis of the dye film demonstrated with great clarity that the compound had undergone extensive chemical transformations.

(1) Macfarlane, R. D.; Torgerson, D. F. *Science (Washington, D.C.)* **1976**, *191*, 920-925. Chait, B. T.; Agosta, W. C.; Field, F. H. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *39*, 339-336.

(2) Chait, B. T. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *53*, 227-242.

(3) *N*-[4-[Bis[4-(dimethylamino)phenyl]methylene]-2,5-cyclohexadiene-1-ylidene]-*N*-methylmethanaminium chloride.

(4) The thin film was produced by electrodepositing 1 μg of crystal violet dissolved in methanol onto a circular disk of aluminized polyester with an area of 1 cm^2 as described by: McNeal, C. J.; Macfarlane, R. D.; Thurston, E. L. *Anal. Chem.* **1979**, *51*, 2036-2039.

(5) We estimate that only 10^{-6} of the sample is consumed by the ionization process during a typical measurement.

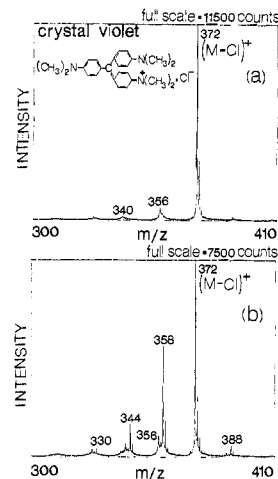


Figure 1. Partial positive ion ^{252}Cf time-of-flight mass spectra of a film of crystal violet (a) unirradiated and (b) irradiated with visible-wavelength photons.

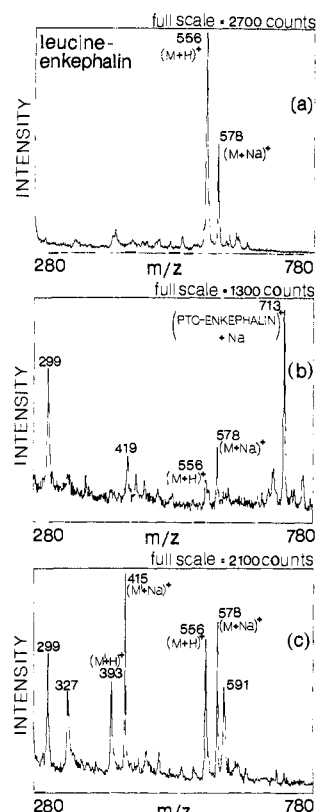


Figure 2. (a) Partial positive ion ^{252}Cf mass spectrum of a film of untreated leucine-enkephalin. (b) Mass spectrum of the film after exposure to phenyl isothiocyanate, tributylamine, and H_2O vapors. (c) Mass spectrum of the film after subsequent exposure to trifluoroacetic acid vapor. PTC = phenylthiocarbonyl. M denotes the mass of leucine-enkephalin. M' denotes the mass of leucine-enkephalin minus the N-terminal tyrosine residue.

To establish the generality of the procedure the surface reactions of several organic solids were investigated with three major reagent classes:

(1) **Photons.** Figure 1a shows the high-mass portion of the mass spectrum of crystal violet prior to irradiation of the dye film. The spectrum exhibits an intense intact cation peak at m/z 372 and several less intense fragment ion peaks (e.g., at m/z 356 and 340) arising from successive loss of methane.⁵ Figure 1b shows the spectrum obtained from the same sample film after a brief irra-

(6) Schelfers, S. M.; Verma, S.; Cooks, R. G. *Anal. Chem.* **1983**, *55*, 2260-2266. Pannell, L. K.; Sokoloski, E. A.; Fales, H. M.; Tate, R. L. *Anal. Chem.* **1985**, *57*, 1060-1067.