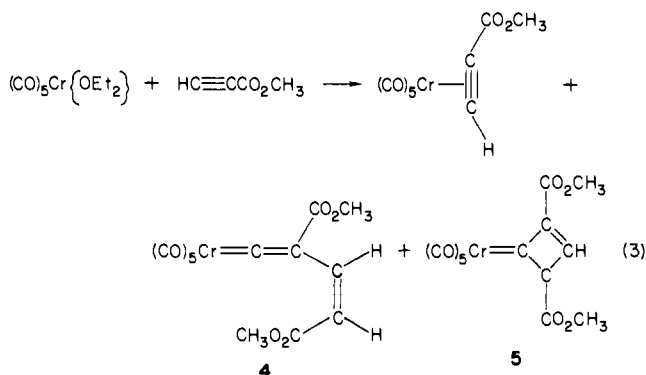


complex has been suggested to lead to alkyne dimerization. Berke and co-workers<sup>8a</sup> observed that addition of  $\text{HC}\equiv\text{CCO}_2\text{CH}_3$  to solutions of photogenerated  $(\text{CO})_5\text{Cr}\{\text{OEt}_2\}$  gave the products of eq 3, with **4** and **5** proposed to arise via intermediacy of the vinylidene complex  $(\text{CO})_5\text{Cr}=\text{C}=\text{C}(\text{CO}_2\text{CH}_3)\text{H}$ .



To test the mechanistic suggestion of eq 2, we attempted to generate the proposed vinylidene intermediate **3a** by protonation of  $[\text{PPN}][(\text{CO})_5\text{WC}\equiv\text{CPh}]$ ,<sup>9</sup> a well-established route to vinylidene complexes.<sup>7a,8b</sup> This complex forms at  $-77^\circ\text{C}$ , but it rapidly decomposes upon warm-up. In contrast, the vinylidene complex  $(\text{CO})_5\text{W}=\text{C}=\text{C}(\text{Me})\text{-}t\text{-Bu}$  (**6**), which was recently prepared by Mayr et al.<sup>8b</sup> by addition of  $[(\text{CH}_3)_3\text{O}]\text{BF}_4$  to  $[(\text{CO})_5\text{WC}\equiv\text{C-}t\text{-Bu}]^-$ , can be isolated as a dark green oil. We repeated the preparation of **6** and found by IR monitoring that no reaction occurred between **6** and excess  $\text{PhC}\equiv\text{CH}$  when these reagents were stirred together at  $22^\circ\text{C}$  for 1 h. However, 366-nm photolysis induced an immediate reaction as evidenced by the rapid green to red color change and the deposition of red poly(phenylacetylene). Thus the vinylidene complex **6** is capable of affecting alkyne polymerization, presumably by loss of CO, coordination of alkyne, and then entry into the mechanism of Scheme I. By analogy, the vinylidene complex **3a** should also initiate polymerization. In support of this suggestion, we find that complex **6**, like **1**,<sup>2</sup> cleanly loses CO upon 366-nm irradiation in  $\text{CH}_3\text{CN}$  solution to give UV and IR spectral changes indicative of formation of  $\text{cis}-(\text{CO})_4(\text{CH}_3\text{CN})\text{W}=\text{C}=\text{C}(t\text{-Bu})\text{CH}_3$ .<sup>10</sup>

Further evidence for the suggested mechanism comes from experiments with  $\text{CH}_3\text{C}\equiv\text{CCH}_3$ . Both Katz<sup>1</sup> and we<sup>2</sup> showed that poly(2-butyne) results when  $(\text{CO})_5\text{W}\{\text{C}(\text{OMe})\text{Ph}\}$  is heated or irradiated in the presence of 2-butyne. However, unlike  $\text{PhC}\equiv\text{CH}$ , 2-butyne cannot form a vinylidene complex upon interaction with photogenerated  $\text{W}(\text{CO})_5$  since it does not have an acidic hydrogen. Consistent with the proposed vinylidene intermediate in our mechanism, photolysis of  $\text{W}(\text{CO})_6$  in the presence of 2-butyne does not lead to polymer, but only to the  $\eta^2$ -2-butyne complex. However, when a trace of  $\text{PhC}\equiv\text{CH}$  (<1%) is added to the  $\text{W}(\text{CO})_6$ /2-butyne mixture, photoinduced polymerization of 2-butyne occurs after an induction period of 30–40 min. The vinylidene complex **3a** presumably forms under these conditions and initiates the polymerization of 2-butyne.

The most significant aspect of this study is the demonstration that an active carbene-containing catalyst can be generated from a simple carbonyl complex and free alkyne via the alkyne to vinylidene rearrangement. It should be noted that a similar initiation process may occur in the patented thermal ( $100$ – $150^\circ\text{C}$ ) polymerization of terminal alkynes by  $\text{W}(\text{CO})_6$  and a related series of group 6<sup>13</sup> metal carbonyls<sup>11</sup> as well as that reported to

occur upon heating (arene) $\text{M}(\text{CO})_3$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) with terminal alkynes.<sup>12</sup>

**Acknowledgment.** This research was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(12) Woon, P. S.; Farona, M. F. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1749.

(13) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III  $\rightarrow$  3 and 13.)

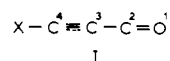
### Anti-Michael Carbolithiation of Silicon and Phenyl-Substituted $\alpha,\beta$ -Unsaturated Secondary Amides

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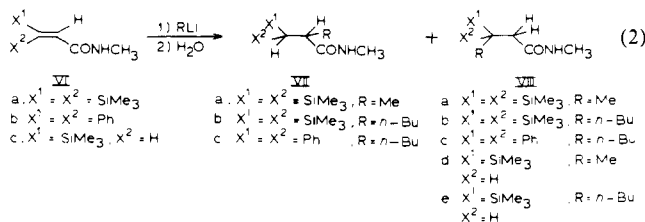
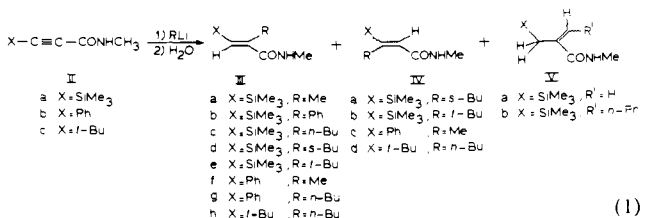
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The notion that  $\alpha,\beta$ -unsaturated carbonyl systems (I) add



nucleophiles *only* at C-2 and/or C-4 pervades organic texts.<sup>1</sup> We have observed attack at C-3 (anti-Michael addition) when we treated the ynamides II and the enamides VIa, b with  $\sigma$ -organolithiums. Subsequent hydrolysis gave III (sometimes accompanied by small amounts of the double-bond isomers V) and VII, either exclusively or together with the Michael isomers IV and VIII, respectively (eq I and 2, Table I). The Z isomers of IIIa–h could



not be detected. Deuterolysis of the reaction mixtures led to nearly quantitative incorporation of one carbon-bonded deuterium into

(1) (a) "Y- never attacks the 3 position": March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977; p 679. (b) See also: Eicher, T. In "The Chemistry of the Carbonyl Group"; Patai, S., Ed.; Interscience: New York, London, 1966; p 672. Posner, G. H. *Org. React.* **1972**, *19*, 1. Wakefield, B. J. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 7, p 28. (c) Faith in the generality of the "rule" expressed in the citation above may have prevented the detection of C-3 attack in earlier work: Wotiz, J. H.; Matthews, J. S.; Greenfield, H. *J. Am. Chem. Soc.* **1953**, *75*, 6343 and ref 3. A low yield (52%) of 4,4-diphenyl-3-buten-2-one and the appearance of a deep red color from  $\beta$ -phenylcinnamic acid and methylolithium were suggested to have arisen from competing anti-Michael addition (Jorgenson, M. J. *Org. React.* **1970**, *18*, 1, 18.

(8) (a) Berke, H.; Harter, P.; Huttner, G.; Zsolnai, L. *Z. Naturforsch.*, **B** **1981**, *36B*, 929. (b) Mayr, A.; Schaefer, K. C.; Huang, E. Y. *J. Am. Chem. Soc.* **1984**, *106*, 1517.

(9) Prepared via metathesis of  $\text{PPN}[(\text{CO})_5\text{WCl}]$  with  $\text{LiC}\equiv\text{CPh}$ . See: Schlientz, W. J.; Ruff, J. K. *J. Chem. Soc. A* **1971**, 1139.

(10) Isosbestic points were maintained in both the IR and UV-vis spectral changes observed upon photolysis of **6** in degassed  $\text{CH}_3\text{CN}$  solution. The final IR spectrum showed bands at 2020 w, 1939 w, 1900 s, and 1840 br,  $\text{cm}^{-1}$  indicative of a cis coordination of  $\text{CH}_3\text{CN}$ .<sup>2</sup>

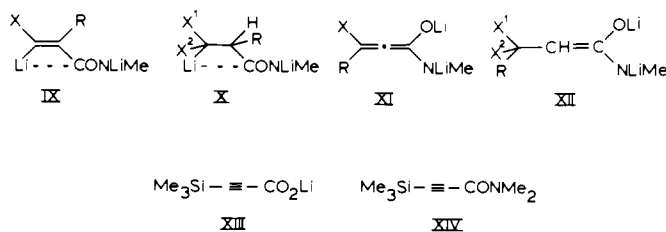
(11) Letto, J. R. U.S. Patent 3051.693, 1966.

Table I. Carbolithiations of Unsaturated Secondary Amides

entry	substrate	RLi (equiv)	yield, %		composition of product after hydrolysis, (%) <sup>a</sup>			reactn conditns <sup>b</sup>
			GC	isolated	anti-Michael	Michael	other	
1	IIa	MeLi (4)		40 <sup>c</sup>	IIIa <sup>d,e</sup> (94)		Va (6)	A, 3 h, 25 °C
2	IIa	PhLi (4)	17 <sup>c</sup>		IIIb <sup>d,e</sup> (100)			A, 10 min, 25 °C
3	IIa	<i>n</i> -BuLi (4)	60	58	IIIc <sup>e</sup> (92)		Vb (8)	A, 0.5 h, 0 °C
4	IIa	<i>s</i> -BuLi (4)	59	53	III <sup>d</sup> (98)	( <i>E</i> )-IVA (1) ( <i>Z</i> )-IVa (1)		A, 0.5 h, -40 °C
5	IIa	<i>t</i> -BuLi (4)	62		IIIe <sup>e</sup> (98)	( <i>E</i> )-IVb (1) ( <i>Z</i> )-IVb (1)		A, 0.5 h, -40 °C
6	IIb	MeLi (3)		61	III <sup>f</sup> (41)	( <i>E</i> )-IVc <sup>e,f</sup> (37) ( <i>Z</i> )-IVc <sup>e,f</sup> (5)	Iib (17)	A, 2 h, 25 °C
7	Iib	<i>n</i> -BuLi (3)		92	IIIg <sup>e,f</sup> (100)			A, 3 h, 25 °C
8	Iic	<i>n</i> -BuLi (4)	63		IIIh <sup>e</sup> (10)	( <i>E</i> )-IVd <sup>e</sup> (65) ( <i>Z</i> )-IVd <sup>e</sup> (25)		A, 1 h, 25 °C
9	VIa	MeLi (4)		60	VIIa (60)	VIIIa (15)	VIa (25)	B, 21 h, 25 °C
10	VIa	<i>n</i> -BuLi (4)		65	VIIb (90)	VIIIb (10)		A, 1.5 h, 25 °C
11	VIb	<i>n</i> -BuLi (4)	95	80	VIIc (14)	VIIIc (37)	VIb <sup>g</sup> (49)	A, 0.5 h, 0 °C
12	VIc	MeLi (4)	74			VIII <sup>d</sup> (100)		B, 70 h, 25 °C
13	VIc	<i>n</i> -BuLi (4)	75			VIII <sup>e</sup> (100)		B, 0.5 h, 25 °C
14	XV	<i>n</i> -BuLi (3)		78			XV (27) XVI (73)	A, 112 h, 25 °C

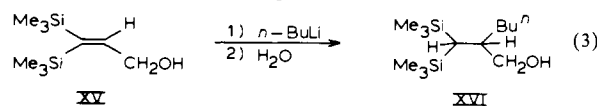
<sup>a</sup> Pure compounds were isolated by gas chromatography and had mass and NMR data consonant with the structures assigned. Additional evidence was obtained in many cases, as indicated below.<sup>d-f</sup> <sup>b</sup> Reactions were carried out in ether:alkane 1:1 [alkane/pentane (MeLi, PhLi, *t*-BuLi), hexane (*n*-BuLi), cyclohexane (*s*-BuLi)]. RLi was added to a solution of the amide at -40 (A) or 0 °C (B); the reaction mixture was then warmed up slowly to the temperature given in the table and kept at that temperature for the time indicated. <sup>c</sup> Extensive desilylation of the starting material was observed as a side reaction. <sup>d</sup> The hydrogenation product of this compound showed in its NMR spectrum a high-field ABX system of two diastereotopic protons ( $CH_2SiMe_3$ ) and one proton at lower field ( $CHRCONHMe$ ). <sup>e</sup> This product was photochemically (3000 Å, acetone, 15 h) equilibrated with its geometrical isomer. Differentiation between the *E* and *Z* isomer was achieved by LIS NMR experiments. <sup>f</sup> A mixture of *E/Z* isomers of this product was synthesized in an independent way. <sup>g</sup> This product originates from competing deprotonation of the starting material at C-2 as shown by quantitative D incorporation at C-2 in recovered VIb after D<sub>2</sub>O quench of the reaction mixture.

III(V), IV, VII and VIII, identifying lithium compounds IX and X, allenolate XI, and enolate XII as the precursors of III(V), VII,



IV, and VIII, respectively. Carboxylate XIII and tertiary amide XIV added *n*-BuLi in the 1,2-mode only.<sup>2</sup> An earlier report<sup>3</sup> on the reaction of Iib and MeLi does not mention the formation of III<sup>f</sup>. In the mixture obtained from Iic and *n*-BuLi Michael adduct (*E/Z*)-IV<sup>d</sup> was in considerable excess over its anti-Michael isomer III<sup>h</sup>, signifying that neither is steric inhibition of Michael addition a major factor in the favoring of anti-Michael addition by Iia,b nor is carbanion-stabilization by X the sole factor inducing anti-Michael addition of ynamides. In fact, irrespective of the nature of X, free energy lowerings by anti-Michael addition are always larger for  $C\equiv C-C=O$  than for  $HC=CH-C=O$ , while the converse holds for Michael additions.<sup>4</sup> Thus, a single carbanion-stabilizing group X can induce 100% anti-Michael addition in the case of ynamides Iia and Iib<sup>5</sup> and some anti-Michael addition is still observed with Iic. By contrast, in the enamides VIa,b even the combined action of two carbanion-stabilizing groups does not suffice for complete suppression of Michael addition and the monosubstituted enamide VIc undergoes Michael addition exclusively (cf. ref I3a). In the present reactions the carbanion-directing effect of  $\alpha$ -triorganosilyl is slightly stronger than that of  $\alpha$ -phenyl.<sup>6</sup> The contribution of the CONLiMe group to

the ease of anti-Michael addition is evidenced by the difference in rate between VIa and XV (eq 3, Table I, entries 10 and 14).<sup>7</sup>



Lowering of the alkene (alkyne) LUMO energy by CONLiMe and precoordination<sup>8</sup> of the organolithium reagent by the substrate through CONLiMe are obvious possible reasons. While the trans stereospecificity of the anti-Michael additions of Iia-c is in line with calculations,<sup>9</sup> we cannot rule out initial *cis* addition followed by stereoisomerization into the *E* isomer IX, which, undoubtedly, is stabilized by intramolecular  $Li\cdots NLiMeCO$  coordination.<sup>10</sup>

Earlier cases of anti-Michael addition seem to be limited to *tert*-butyl carbanionoids, which are prone to form *tert*-butyl radicals by single electron transfer (SET).<sup>11</sup> Absence of a primary alkyl lithium/tertiary alkyl lithium dichotomy in the present carbolithiations and the fact that similar carbolithiations can be performed with alkynes and alkenes substituted quite differently<sup>12</sup> suggest that *free* radicals are not involved in the formation of IX and X. When Iia was reacted with a large excess of different mixtures of 5-hexenyllithium (XVIII) and (cyclopentylmethyl)-

(6) Cf.; Eaborn, C.; Eidenschink, R.; Jackson, P. M.; Walton, D. R. M. *J. Organomet. Chem.* **1975**, *101*, C40. Eisch, J.; Galle, J. *J. Am. Chem. Soc.* **1976**, *98*, 4646. Calculations on  $XCH_2^-$  indicate higher stabilization by X = phenyl (Pross A.; DeFrees, D. J.; Levi, B. A.; Pollack, S. K.; Radom, L.; Hehre, W. J. *J. Org. Chem.* **1981**, *46*, 1693) than by X = SiH<sub>3</sub> (Hopkinson, A. C.; Lien, M. H. *Ibid.* **1981**, *46*, 998).

(7) In THF/hexane 3:1, 1,1-bis(trimethylsilyl)ethene adds *n*-BuLi rapidly; Seebach, D.; Burstinghaus, R.; Gröbel, B.-T.; Kolb, M. *Liebigs Ann. Chem.* **1977**, 830.

(8) Cf.; Al-Asser, M. A.; Beak, P.; Hay, D.; Kempf, J. D.; Mills, S.; Smith, S. G. *J. Am. Chem. Soc.* **1983**, *105*, 2080.

(9) Houk, K. N.; Strozier, R. W.; Rozeboom, M. D.; Nagase, S. *J. Am. Chem. Soc.* **1982**, *104*, 323 and references given there.

(10) Cf.; Beak, P.; Hunter, J. E.; Jun, Y. M. *J. Am. Chem. Soc.* **1983**, *105*, 6350.

(11) Holm, T.; Crossland, I.; Madsen, J. Ø. *Acta Chem. Scand., Ser. B* **1978**, *B32*, 754. Kruithof, K. J. H.; Mateboer, A.; Schakel, M.; Klumpp, G. W. *Recl. Trav. Chim. Pays-Bas*, in press.

(12) Cf.; Kruithof, K. J. H.; Schmitz, R. F.; Klumpp, G. W. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 3. Olsson, L.-I.; Claesson, A. *Acta Chem. Scand., Ser. B* **1976**, *B30*, 521. Richey, H. G., Jr.; Heyn, A. S.; Erickson, W. F. *J. Org. Chem.* **1983**, *48*, 3821. Crandall, J. K.; Clark, A. C. *J. Org. Chem.* **1972**, *37*, 4236 and earlier literature given there.

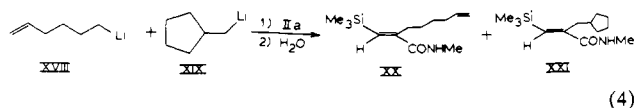
(2) Desilylation may have prevented the formation of addition product in the reactions of Iia with allyllithium, cyclopropyllithium, 1-pentynyllithium, and ethyl 2-lithioethanoate. In the latter two cases silylation of the reagent could be proven (results of M. Hogenboom).

(3) Klein, J.; Aminadav, N. *J. Chem. Soc. C* **1970**, 1380.

(4) Benson, S. W. "Thermochemical Kinetics"; Wiley: New York, London, Sydney, 1968.

(5) In the case of Iib this applies only to organolithiums more reactive than methyl lithium (see entries 6 and 7). At 0 °C Iia and *t*-BuLi gave 17% of Michael adduct IVb together with 83% of anti-Michael adduct IIIe.

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.<sup>13</sup> Anti-Michael adducts IX (X = SiMe<sub>3</sub>) are new members of the class of ( $\alpha$ -lithiovinyl)silanes that are of value in organic synthesis.<sup>14</sup>

(13) (a) Promotion of 1,4- over 1,2-addition: Baldwin, J. E.; Dupont, W. A. *Tetrahedron Lett.* **1980**, 21, 1881. Mpango, G. P.; Mahalanabis, K. K.; Mahdavi-Damghani, Z.; Snieckus, V. *Ibid.* **1980**, 21, 4823. Soai, K.; Ookawa, A.; Nohara, Y. *Synth. Commun.* **1983**, 13, 27. (b) Lithiations  $\beta$  to the carbonyl group of secondary and tertiary carboxamides: Gschwend, H. W.; Rodriguez, H. R. *Org. React.* **1979**, 26, 1. Fitt, J. J.; Gschwend, H. W. *J. Org. Chem.* **1980**, 45, 4257. Kempf, D. J.; Wilson, K. D.; Beak, P. *Ibid.* **1982**, 47, 1610. Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, 15, 306. Eaton, P. E.; Castaldi, G. J. *Am. Chem. Soc.* **1985**, 107, 724. See also ref 10. (c) Lithiations  $\alpha$  to the nitrogen of tertiary carboxamides: Reitz, D. B.; Beak, P.; Tse, A. *J. Org. Chem.* **1981**, 46, 4316. Seebach, D.; Lohmann, J.-J.; Syfrig, M. A.; Yoshifuji, M. *Tetrahedron* **1983**, 39, 1963 and earlier literature cited in these papers.

(14) Cf.: ref 2 and 3 in: Knorr, R.; von Roman, Th. *Angew. Chem.* **1984**, 96, 349.

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

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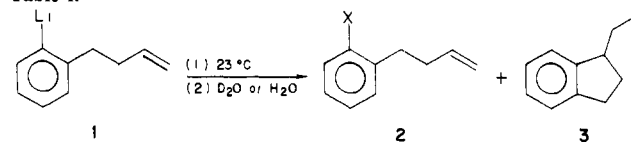
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Cyclization of *o*-(3-butenyl)phenyl radicals to 1-methylindanyl radicals has been used to detect radical intermediates in a variety of reactions.<sup>1</sup> Cyclization of 5-hexenyl radicals has also been used extensively for this purpose in the straight-chain case.<sup>1,2</sup> The possibility of anionic cyclization in these reactions has until recently been largely ignored.<sup>3-5</sup> 6-Hepten-2-yl radicals and anions both cyclize but the anion contribution can be distinguished by detailed product analysis.<sup>4</sup> 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. *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.  
 (3) Lee, K.-W.; San Filippo, J., Jr. *Organometallics* **1983**, 2, 906. Hill, E. A.; Richey, H. G., Jr.; Rees, T. C. *J. Org. Chem.* **1963**, 28, 2161 footnote 10.  
 (4) Garst, J. F.; Hines, J. B., Jr. *J. Am. Chem. Soc.* **1984**, 106, 6443 and references therein. Also see: Garst, J. F.; Pacifici, J. A.; Felix, C. C.; Nigam, A. J. *J. Am. Chem. Soc.* **1978**, 100, 5974.  
 (5) Bailey, W. F.; Patricia, J. J.; DelGobbo, V. C.; Jarret, R. M.; Okarma, P. J. *J. Org. Chem.* **1985**, 50, 1999.

Table I.



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

<sup>a</sup>One 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. <sup>b</sup>At the end of the reaction period 1 mL of D<sub>2</sub>O or H<sub>2</sub>O was added. <sup>c</sup>Two equivalents of TMEDA were added at room temperature at time = 0. <sup>d</sup>Deuterium was shown to be on the ring by the MS fragmentation pattern and probably ortho by deuterium NMR. <sup>e</sup>MS showed the deuterium was all in the methyl group.

*o*-(3-Butenyl)bromobenzene was treated with 2 equiv of *n*-butyllithium<sup>6</sup> 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 D<sub>2</sub>O or H<sub>2</sub>O. 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<sub>1</sub> 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.<sup>3</sup> 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.<sup>7</sup> When a less polar solvent, diethyl ether, was used, the cyclization rate slowed under comparable conditions (31% in Et<sub>2</sub>O compared to 89% in THF after 30 min). Addition of tetramethylethylenediamine (TMEDA) to the Et<sub>2</sub>O reaction solution increased the cyclization rate to that observed in THF (31% in Et<sub>2</sub>O compared to 94% in Et<sub>2</sub>O/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,<sup>8</sup> effectively making the "ion pair" looser. The effect of the more polar solvent, THF, is similar.<sup>9-11</sup> The deuterium contents for both Et<sub>2</sub>O 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.

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(10) Recent work on the nature of butyllithium aggregates<sup>11</sup> 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 intermediate<sup>9</sup> and the intramolecular reaction remains anion-like rather than radical.

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