Table II. Kinetic Activation Parameters for Some Representative Substituents in the Retro-Diels-Alder Reaction of Anthracene Adducts in Diphenyl Ether

R	compd	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	T(av), °C
H	1a	34.8 ± 1.4	−7.9 ± 2.7	230
Me	1b	37.8 ± 1.9	0.4 ± 3.9	223
Et	1c	36.1 ± 3.5	−0.1 ± 7.2	210
i-Pr	1d	35.7 ± 0.9	−3.7 ± 1.9	220
CHO	1f	40.0 ± 1.1	6.5 ± 2.3	215
OCH_3	1k	32.3 ± 1.0	−5.5 ± 2.0	215
OPh	1l	36.2 ± 1.2	4.6 ± 2.6	195
OH	1n	49.8 ± 4.6	39 ± 10	165
$-CH_2S(CH_2)_8SCH_2-$	1u	32.6 ± 0.4	−6.0 ± 0.9	210
$-CH_2S(CH_2)_{10}SCH_2-$	1v	37.2 ± 4.2	3.1 ± 8.5	215

these data with the di-*tert*-butyl adduct, we have to date been unable to prepare the highly strained 9,10-di-*tert*-butylanthracene. Instead, one may consider (with appropriate reservation)[22] the reactivity of disilyl adduct **1e**, which is again slower than diisopropyl adduct **1d**. Our analysis of this bell-shaped reactivity relationship centers on the question: how much does the transition structure "know" about steric problems in the anthracene it is going to? It is reasonable to conclude, on the basis of molecular-mechanics calculations and examinations of space-filling models, that increasing steric bulk of the substituents results in greater strain energies of *both* adducts and anthracenes. However, steric strain in the adducts, in which a "gear-like" orientation between substituent and adduct framework can exist, is less than strain in the anthracenes, in which bad contacts with the peri hydrogens cannot be avoided *beginning with the isopropyl group*. In other words, at some hypothetical point between ethyl and isopropyl groups, the generation of strain in the transition structure wins out over the release of strain in the starting material, and the reaction slows. On the basis of entries **1u-x**, our notion that strain induced by bridging substituents would accelerate cycloreversions significantly appears unfounded, perhaps for the same reasons described above.

One additional set of results is pertinent to a discussion of the mechanism of the retro-Diels-Alder reaction. As shown in Table II, the activation entropies of most cycloreversion reactions fall near 0 eu, as is consistent with the picture of the retro-Diels-Alder transition structure resembling that of the adduct.[23] However, cycloreversion of the dihydroxy adduct **1n** shows surprisingly large positive values for both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. The observation that cycloreversion of the dihydroxy adduct uniquely exhibits a substantial deceleration in less polar solvent[24] suggests that deprotonation (either full or partial) of a tertiary alcohol in **1n** is the rate-limiting step. Dramatic acceleration of the retro-Diels-Alder reaction by alkoxide substituents has been reported previously by Grimme,[3b] and we observe the same effect. A THF solution of dihydroxy adduct **1n** at reflux (66 °C) shows no (less than 1%) cycloreversion after 120 h. After cooling to room temperature, addition of excess NaH results in rapid cycloreversion ($t_{1/2}$ about 11 min). It therefore seems likely that the activation parameters determined for **1n** reflect a deprotonation step rather than a cycloreversion.

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(22) Because the Si-C bond is longer than the C-C bond, the purely steric effect of a $Si(CH_3)_3$ group is expected to be smaller than that of a $C(CH_3)_3$ group; the inductive electronic effects are predicted to be similar, based on σ_p values. It is difficult to predict what the resonance effect of the vacant silicon d orbital would be, although as a rDA dienophile substituent, $Si(CH_3)_3$ is faster than $C(CH_3)_3$ by about 22-fold at 250 °C (cf. ref 4).

(23) It is sometimes said that the forward Diels-Alder reaction is "entropy late and enthalpy early"; the converse would state that the retro-Diels-Alder is "enthalpy late and entropy early".

(24) When pentadecane (nonpolar) and diphenyl ether (more polar) are used at 200 °C, the relative reaction rates are as follows: R = Et, 1.00, 1.38; R = NMe_2, 1.00, 1.09; R = $OSiMe_3$, 1.00, 1.19; R = OH, 1.00, 12.0. It was not possible to obtain a highly accurate rate constant for cycloreversion of the R = NH_2 adduct at 200 °C in pentadecane because oxidation was no longer very fast as compared to cycloreversion. By following the appearance and disappearance of the peak at 402 nm due to diaminoanthracene (maximum absorbance at 35 s), we could then use a curve-fitting algorithm to estimate the rate constant for cycloreversion in pentadecane as 3.5×10^{-2} s^{-1}. This number is probably indistinguishable from the rate constant determined for 9,10-bis(dimethylamino)anthracene (4.0×10^{-2} s^{-1}).

Anionic Cyclizations of α-Alkoxy Lithiums. New, Stereoselective Routes to Substituted Tetrahydrofurans

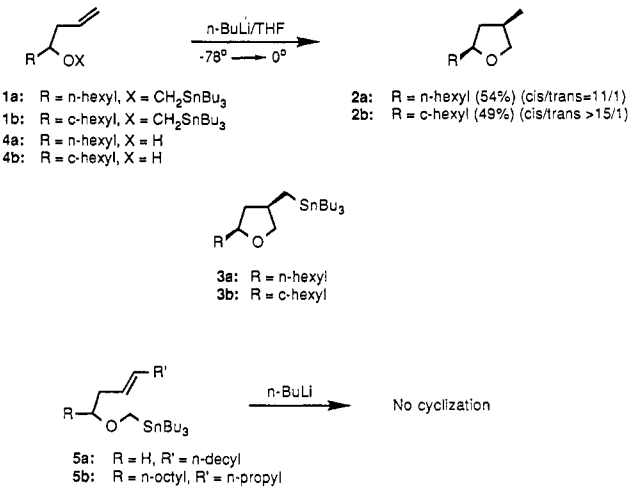
Summary: Treatment of the (tri-*n*-butylstannyl)methyl ethers of alkyl allyl carbinols with *n*-BuLi in THF at −78 °C gives the corresponding α-alkoxy lithiums. On warming, these species undergo anionic cyclization to afford cis-2,4-disubstituted tetrahydrofurans. A useful variant of this method, which employs allylic ethers as cyclization terminators, is also described.

Sir: The cyclization reactions of 5-hexenyl radicals have formed the basis for a wide variety of synthetic methods introduced during recent years.[1] It has been known for some time that 5-hexenyl carbanions can undergo a similar

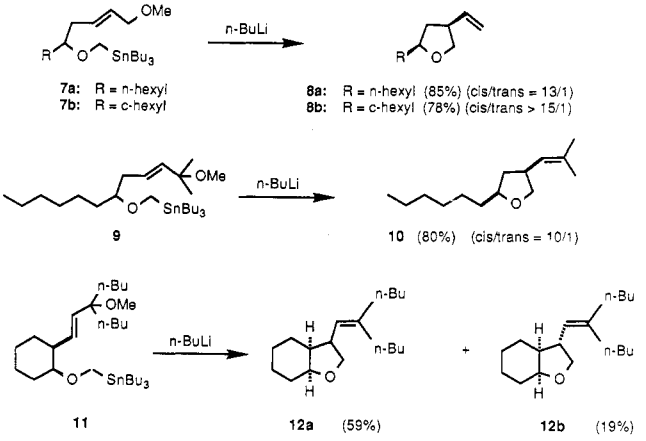
(1) Hart, D. J. *Science (Washington D. C.)* **1984**, *223*, 883.

0022-3263/88/1953-1336$01.50/0

Scheme I



Scheme II



regioselective closure, affording cyclopentylmethyl organometallics,[2] and these transformations are themselves beginning to find acceptance within the synthetic community.[3] We have discovered that α-alkoxy lithium reagents, generated from the (tri-*n*-butylstannyl)methyl ethers[4] of several homoallylic alcohols, undergo facile and highly stereoselective cyclization to afford substituted tetrahydrofurans.[5]

Treatment of stannanes **1a,b**[6] with a slight excess of *n*-BuLi in THF at −78 °C gave rise to the expected α-alkoxy lithiums in accord with the results of Still. Upon warming to 0 °C these anions underwent cyclization to produce, after aqueous workup, the corresponding tetrahydrofurans **2a,b** in quite poor (~20%) yield. Among the byproducts were the new stannanes **3a,b**, which presumably form upon reaction of the incipient tetrahydrofurylmethyl anions with $(n\text{-Bu})_4\text{Sn}$. This transmetalation is apparently reversible, and the equilibrium could be shifted in favor of products **2a,b** by performing the cyclization in the presence of a large excess of *n*-BuLi. In practice, the use of 5 equiv of *n*-BuLi effectively suppressed formation of the unwanted products **3a,b**.[7] Under these conditions, **2a,b** could be obtained in the yields reported below (Scheme I). The other major byproducts of these reactions were the alcohols **4a,b**, from which the stannanes themselves had originally been prepared. The decomposition of α-alkoxy lithiums and related species via this type of α-elimination pathway is precedented.[8,9] Interestingly, the products of Wittig rearrangement[4b] and β-elimination[9] were not formed in significant amounts.

These reactions are remarkable for the high degree of stereoselectivity they exhibit. In order to be certain of the stereochemistry of **2a,b**, independent syntheses of *cis*-**2a** and *trans*-**2a** from γ-decanolactone were carried out using established methods.[10] The ^{1}H and ^{13}C NMR spectral data obtained from these compounds enabled us to determine the stereochemistry of the other tetrahydrofurans and also the cis/trans ratios in a straightforward manner.[11] The stereochemical outcome of these cyclizations is similar to that which would be reasonably expected[12] for the corresponding radical-mediated process although the degree of selectivity is unusually high. As with the radical reactions, this stereoselectivity may be taken to imply a chair-like transition state (**6**), although the situation here is rendered more complex by the possibility that the reacting species is not monomeric but, instead, an aggregate. Complexation of lithium by the solvent (THF) may also

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(4) (a) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481. (b) Still, W. C.; Mitra, A. *J. Am. Chem. Soc.* **1978**, *100*, 1927.

(5) We are aware of only a few other instances of anionic cyclizations leading to a tetrahydrofuran system. One involved the cyclization of 5-*endo*-norbornenyl benzyl ether upon treatment with MeLi (Lansbury, P. T.; Caridi, F. J. *J. Chem. Soc., Chem. Commun.* **1970**, 714). Similar reactions were also observed with the benzyl and allyl ethers of 7-norbornenol (Klumpp, G. W.; Schmitz, R. F. *Tetrahedron Lett.* **1974**, 2911). Interestingly, the benzyl ether corresponding to **1a** failed to cyclize upon treatment with MeLi, giving instead the Wittig rearrangement product. Conversely, the stannylmethyl ether of 5-*endo*-norbornenol failed to cyclize upon transmetalation.

(6) Stannanes were prepared by the method of Still (KH, Bu_3SnCH_2I, THF) (ref 4) and purified chromatographically prior to treatment with *n*-BuLi. The stannanes and their cyclization products were characterized by ^{1}H NMR, IR, HRMS, and, in most cases, ^{13}C NMR.

(7) General experimental procedure: A solution of the stannane (0.3 mmol) in 4 mL of THF was cooled to −78 °C and treated with 0.95 mL of 1.6 M *n*-BuLi in hexane (1.5 mmol). After 5 min the dry ice–acetone bath was replaced by an ice bath and the reaction allowed to proceed for 20–30 min. The reaction was quenched with water and the product isolated by ether extraction and purified by flash chromatography on silica gel.

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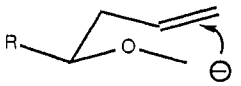
(11) *cis*-**2a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.84 (t, 1 H, J = 7 Hz), 3.80 (m, 1 H), 3.32 (t, 1 H, J = 7 Hz), 2.30 (m, 1 H), 2.13 (m, 1 H), 1.60–1.20 (m, 10 H), 1.01 (d, 3 H, J = 6 Hz), 0.85 (t, 3 H, J = 6 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 80.2, 74.3, 40.9, 36.1, 34.2, 31.8, 29.4, 26.3, 22.5, 17.9, 14.0. *trans*-**2a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.96 (t, 1 H, J = 7 Hz), 3.87 (m, 1 H), 3.23 (t, 1 H, J = 7 Hz), 2.30 (m, 1 H), 1.65–1.15 (m, 11 H), 1.00 (d, 3 H, J = 6 Hz), 0.86 (t, 3 H, J = 6 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 78.8, 74.8, 39.6, 36.2, 33.2, 31.9, 29.4, 26.3, 22.6, 18.0, 14.0. The chemical shifts of the oxymethylene protons and the ^{13}C chemical shifts of the oxygen-bearing carbons appear to be stereochemically diagnostic for these systems. The values obtained for *cis*- and *trans*-**2a** parallel closely those obtained for related 2,4-disubstituted tetrahydrofurans whose stereochemistry has been assigned (ref 10). The vinyltetrahydrofurans were hydrogenated (H_2, Pd/C, MeOH) to give products whose spectra could be more directly compared with those of *cis*- and *trans*-**2a**.

(12) (a) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073. (b) Spellmeyer, D. C.; Houk, K. N. *J. Org. Chem.* **1987**, *52*, 959.

play an important role since, in Et_2O, these cyclizations fail to occur.



6

Employing our standard conditions, we have been unable to effect the cyclization of α-alkoxy lithiums derived from stannanes (exemplified by **5a,b**) in which the double bond bears a second alkyl substituent. These results are in keeping with the observations of Bailey[3c] and presumably reflect the fact that cyclization, in such cases, would lead to the generation of a relatively unstable secondary carbanion. The failure of these anions to cyclize is significant since it argues against the possible involvement of radical intermediates in the successful cyclizations. If these reactions were mediated by transient radical species derived from the α-alkoxy lithiums, the presence of alkyl substituents at the double bond terminus would be expected to facilitate rather than impede cyclization.[13]

In striking contrast to the behavior of **5a,b**, the methoxy-substituted stannanes **7a,b**, **9**, and **11** undergo cyclization, giving vinyl tetrahydrofurans in excellent yield (Scheme II). The facility of these reactions may be due to the fact that, in the transition state, anionic character can be partially displaced onto oxygen. From a synthetic standpoint these cyclization–eliminations are far more valuable than the simple cyclizations outlined in Scheme I. They not only proceed in better yield but give rise to versatile olefinic substituents suitable for further manipulation. An attractive feature of this method is its employment of the stable and easily generated methoxy unit as a leaving group.[14] In these cyclizations only a slight excess of *n*-BuLi need be employed since the formation of products analogous to **3a,b** is precluded by the rapid elimination of methoxide.

Although there appear to be certain limitations to its scope, the anionic cyclization of α-alkoxy lithiums provides an expedient and stereoselective route to a variety of tetrahydrofurans not easily accessible by other means. At the present time we are continuing to explore the generality of this new method and also attempting to adapt it for the preparation of pyrrolidines[15] from stannylmethyl amines.[16] The results of these investigations will be communicated in due course.

Acknowledgment. We thank the Research Board of the University of Illinois, Research Corporation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support of this work.

(13) Beckwith, A. L. J.; Blair, I. A.; Phillipou, G. *Tetrahedron Lett.* **1974**, 2251.

(14) Compare: (a) Stork, G.; Schoofs, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 5081. (b) Abeywickrema, A. N.; Beckwith, A. L. J.; Gerba, S. *J. Org. Chem.* **1987**, *52*, 4072. (c) Ishii, T.; Kawamura, N.; Matsubara, S.; Utimoto, K.; Kozima, S.; Hitomi, T. *J. Org. Chem.* **1987**, 52, 4416.

(15) Padwa has recently investigated a conceptually related approach to pyrrolidines involving an azahexenyl radical cyclization. (a) Padwa, A.; Nimmesgern, H.; Wong, G. S. K. *Tetrahedron Lett.* **1985**, 957. (b) Padwa, A.; Nimmesgern, H.; Wong, G. S. K. *J. Org. Chem.* **1985**, *50*, 5620.

(16) Peterson, D. J. *J. Am. Chem. Soc.* **1971**, *93*, 4027.

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Allene Epoxidation. Efficient Synthesis and Synthetic Conversions of 1,4-Dioxaspiro[2.2]pentanes[1]

Summary: The oxidation of simple allenes with dimethyldioxirane provides the corresponding 1,4-dioxaspiro[2.2]pentanes in good to excellent isolated yields; subsequent addition of various nucleophiles proceeds regioselectively to generate highly functionalized products of type **2**.

Sir: Earlier studies of the peracid oxidation of allenes has established the involvement of 1,4-dioxaspiro[2.2]pentanes (**1**) as one of several novel reactive intermediates that lead to an array of isolated products.[2-4] The overall conversion of allenes to ketones of structure **2** by the addition of nucleophiles to these spirodioxides **1** constitutes an attractive synthetic scheme that generates functionality at each of the three allenic carbons (Scheme I). However, spirodioxides have been isolated and characterized in only three instances to date, each of which involves a sterically hindered allene.[3,5] Furthermore, products of type **2** are not generally formed in acceptable yields, owing to the various reaction pathways in competition under the conditions of the peracid oxidations. In this paper we report on a method for the efficient generation of spirodioxides **1** and examine their reactions with various nucleophiles.

The recent discovery by Murray[6] that dimethyldioxirane (**3**) can be obtained as a dilute solution in acetone provided the key to our search for a suitable oxidant.[7] Use of this extraordinary reagent[8] in the presence of solid K_2CO_3 as a buffering agent provides the neutral, nonnucleophilic conditions that permit the isolation of spirodioxides. Thus, treatment of 2,5,5-trimethyl-2,3-hexadiene (**4a**) with 5 equiv of **3** for 10 min at room temperature, followed by removal of solvent in vacuo, gave the known[3] spirodioxide **5a** as a single diastereomer in good yield (84%) and purity.[9] In a similar manner, the less hindered allene **4b** was transformed to **5b** in 95% yield by 3.5 equiv of **3**. In this case a 9:1 ratio of stereoisomers was observed.[10] These

(1) This work was first presented at the 194th National Meeting of the American Chemical Society, New Orleans, LA, August 30–September 4, 1987. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and a Public Health Service Biomedical Research Support Grant administered by Indiana University for partial support of this work. Departmental equipment grants aided in the purchase of the Varian 300 NMR (PHS-SID-RR-1882-01) and the Kratos MS 80 (CHE-81-11957) instruments used in this work.

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(5) Wolff, S.; Agosta, W. C. *Can. J. Chem.* **1984**, *62*, 2429–2434.

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(7) Dimethyldioxirane solutions in acetone have been shown to epoxidize olefins in a syn-stereospecific manner.[6] An in situ method behaves similarly: Curci, R.; Fiorentino, M.; Troisi, L. *J. Org. Chem.* **1980**, *45*, 4758–4760.

(8) For other interesting reactions of **3**, see: Murray, R. W.; Jeyaraman, R.; Molan, L. *J. Am. Chem. Soc.* **1986**, *108*, 2470–2472. Murray, R. W.; Jeyaraman, R.; Molan, L. *Tetrahedron Lett.* **1986**, *27*, 2335–2336. Jeyaraman, R.; Murray, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 2462–2463.

(9) Compound **5a** showed the following:[3] IR 1635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.52 (s, 1), 1.53 (s, 3), 1.50 (s, 3), 0.97 (s, 9); ^{13}C NMR ($CDCl_3$) δ 88.3 (s), 69.4 (dm, J = 171, 5 Hz), 63.4 (m, J = 5 Hz), 31.1 (m, J = 4 Hz), 25.6 (qm, J = 125, 4 Hz), 22.4 (qd, J = 128, 4 Hz), 20.2 (qd, J = 128, 4 Hz).

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