

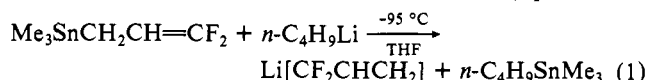
gem-(Difluoroallyl)lithium: Preparation by Lithium-Halogen Exchange and Utilization in Organosilicon and Organic Synthesis

Dietmar Seyferth,* Robert M. Simon, Dennis J. Sepelak, and Helmut A. Klein

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received January 17, 1983

Abstract: *gem*-(Difluoroallyl)lithium may be generated by lithium-bromine exchange between *n*-butyllithium and $\text{CH}_2=\text{CHCF}_2\text{Br}$ at -95°C by using an in situ procedure. When this $\text{Li}[\text{CF}_2\text{CHCH}_2]$ preparation is carried out in the presence of chlorosilanes, aldehydes, ketones, and esters, products of the type $\text{R}_3\text{SiCF}_2\text{CH}=\text{CH}_2$, $\text{RCH}(\text{OH})\text{CF}_2\text{CH}=\text{CH}_2$, and $\text{RR}'\text{C}(\text{OH})\text{CF}_2\text{CH}=\text{CH}_2$, respectively, are formed, often in good yield. The factors determining the regioselectivity in additions to $\text{C}=\text{O}$ of unsymmetrically substituted allylic lithium reagents are discussed.

In earlier work we reported the preparation of *gem*-(difluoroallyl)lithium (1) by the transmetalation reaction (eq 1).¹ This



reagent is not stable in solution, even at -95°C , so that conventional organolithium methodology is not applicable. However, because the Si-Cl bond of triorganosilanes reacts only slowly with organolithium reagents at low temperature, slow addition of an *n*-butyllithium solution to a solution containing (3,3-difluoroallyl)trimethyltin as well as an excess of the triorganochlorosilane (i.e., an in situ procedure) was an alternate procedure which could be applied successfully to the synthesis of $\text{R}_3\text{SiCF}_2\text{CH}=\text{CH}_2$ compounds in good yield. This in situ procedure, however, had serious limitations. When a diorganodichlorosilane (e.g., Me_2SiCl_2) was used instead of an R_3SiCl compound, disubstitution could not be effected. The first Si-Cl bond of Me_2SiCl_2 is more reactive than the Sn-C bond of $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CF}_2$, so the product that was formed when disubstitution of Me_2SiCl_2 was sought was $\text{Me}_2\text{Si}(n\text{-C}_4\text{H}_9)(\text{CF}_2\text{CH}=\text{CH}_2)$ rather than $\text{Me}_2\text{Si}(\text{CF}_2\text{CH}=\text{CH}_2)_2$. Moreover, the in situ procedure could not be applied to the synthesis of alcohols containing the CF_2CHCH_2 substituent by reaction of $\text{Li}[\text{CF}_2\text{CHCH}_2]$ with aldehydes or ketones. Under the experimental conditions, the rate of the addition of *n*-butyllithium to the $\text{C}=\text{O}$ bond of the substrate was faster than its reaction with $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CF}_2$ and most of the latter was recovered unchanged. In an in situ reaction in which 3-pentanone was the carbonyl compound used, the desired product, $(\text{C}_2\text{H}_5)_2\text{C}(\text{OH})\text{CF}_2\text{CH}=\text{CH}_2$, was obtained in only 10% yield. The tedious and cumbersome method of alternate, incremental additions could be applied to the preparation of $(\text{C}_2\text{H}_5)_2\text{C}(\text{O}-\text{H})\text{CF}_2\text{CH}=\text{CH}_2$ in 75% yield, but failed to give a good product yield when benzaldehyde was the substrate used.

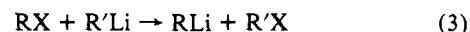
The difluoroallyl group, with its two C-F bonds and its reactive $\text{C}=\text{C}$ bond, is a potentially interesting substituent in both organic and organometallic systems. Therefore, it was of interest to improve, if possible, the procedures for the generation and utilization of *gem*-(difluoroallyl)lithium.

Results and Discussion

The preparation of organolithium reagents by transmetalation, in which a suitable organolithium reagent is allowed to react with an organic derivative of another metal (usually tin, lead, or mercury) (eq 2), is believed to involve nucleophilic displacement of R from M, a polar process.² As such, it may be expected to



be relatively slow at low temperature, slower than $\text{R}'\text{Li}$ addition to the $\text{C}=\text{O}$ bond of aldehydes and ketones. In contrast, the lithium-halogen exchange reaction, which finds many applications in organolithium preparation (eq 3),³ according to available ev-

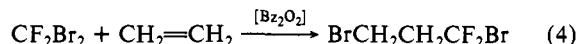


(X usually Br)

idence,⁴ proceeds by an electron-transfer mechanism. As such, it should be rapid even at low temperature in ether solvents, especially in the case of polyhalomethanes.

This reasoning led us to examine $\text{CH}_2=\text{CHCF}_2\text{Br}$ as an alternate precursor of *gem*-(difluoroallyl)lithium. It was hoped that the $\text{CH}_2=\text{CHCF}_2\text{Br}/n\text{-C}_4\text{H}_9\text{Li}$ reaction proceeds at a rate comparable to or even faster than that of *n*-butyllithium addition to the carbonyl substrate when the in situ procedure is used.

A precursor of the required halide, $\text{CH}_2=\text{CHCF}_2\text{Br}$, had been prepared by Tarrant and Lovelace by the benzoyl peroxide induced addition of dibromodifluoromethane to ethylene in an autoclave at 80°C (eq 4).⁵ The reported runaway exotherm which resulted



in loss of most of the contents of the autoclave through the rupture disk (designed to withstand 1250 psi)⁵ was somewhat disquieting. However, these workers used an unusually large amount of benzoyl peroxide to initiate the addition⁶ and we found this reaction to be a safe and useful preparation of $\text{BrCH}_2\text{CH}_2\text{CF}_2\text{Br}$ when smaller amounts of benzoyl peroxide were used. Dehydrobromination of $\text{BrCH}_2\text{CH}_2\text{CF}_2\text{Br}$ with use of a saturated aqueous solution of KOH at $120\text{--}150^\circ\text{C}$ gave a $\sim 5:2$ mixture of $\text{CH}_2=\text{CHCF}_2\text{Br}$ and $\text{CF}_2=\text{CHCH}_2\text{Br}$ in yields as high as 93%. Slow distillation of this mixture through a glass-helices-packed column increased the $\text{CH}_2=\text{CHCF}_2\text{Br}/\text{CF}_2=\text{CHCH}_2\text{Br}$ ratio to 20:1, and this material was used in our subsequent studies.

The lithium-halogen exchange reaction, as expected, could be applied to good advantage to the in situ generation of *gem*-(difluoroallyl)lithium. When the $\text{CH}_2=\text{CHCF}_2\text{Br}/n\text{-C}_4\text{H}_9\text{Li}$ reaction was carried out in a 5:1:1 (by volume) mixture of THF/ Et_2O /pentane at -95°C under nitrogen in the presence of

(3) (a) Wakefield, B. J. "The Chemistry of Organolithium Compounds"; Pergamon Press; Oxford, 1974, Chapter 4. (b) Reference 2b, pp 148-160.

(4) (a) Reference 3a, pp 51 and 52. (b) Ward, H. R.; Lawler, R. G.; Loken, H. Y. *J. Am. Chem. Soc.* **1968**, *90*, 7359. (c) Ward, H. R.; Lawler, R. G.; Cooper, R. A. *Ibid.* **1969**, *91*, 746. (d) Lepley, A. R. *J. Chem. Soc., Chem. Commun.* **1969**, 64. (e) Lepley, A. R.; Landau, R. L. *J. Am. Chem. Soc.* **1969**, *91*, 749.

(5) Tarrant, P.; Lovelace, A. M. *J. Am. Chem. Soc.* **1954**, *76*, 3466.


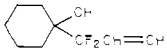
(6) Twelve times more (in terms of molar equivalents) of benzoyl peroxide was used than previous workers⁷ had used in similar Bz_2O_2 -catalyzed addition of CCl_4 to ethylene.

(7) Joyce, R. M.; Hanford, W. E.; Harmon, J. *J. Am. Chem. Soc.* **1948**, *70*, 2529.

(1) Seyferth, D.; Wursthorn, K. R. *J. Organomet. Chem.*, **1979**, *182*, 455.

(2) (a) Seyferth, D.; Weiner, M. A. *J. Am. Chem. Soc.* **1962**, *84*, 361. (b) Schöllkopf, U. In "Houben-Weyl Methoden der Organischen Chemie", Müller, E., Ed.; Georg Thieme-Verlag: Stuttgart, 1970; Vol. XIII/1, pp 130-134.

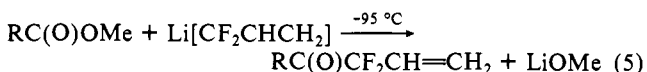
Table I. Reactions of in Situ Generated *gem*-(Difluoroallyl)lithium

reactant	product	yield, %
Me ₃ SiCl	Me ₃ SiCF ₂ CH=CH ₂	27
Et ₃ SiCl	Et ₃ SiCF ₂ CH=CH ₂	51
<i>n</i> -Pr ₃ SiCl	<i>n</i> -Pr ₃ SiCF ₂ CH=CH ₂	50
PhMe ₂ SiCl	PhMe ₂ SiCF ₂ CH=CH ₂	71
Me ₂ SiCl ₂	Me ₂ Si(CF ₂ CH=CH ₂) ₂	74
<i>n</i> -C ₄ H ₉ CH=O	<i>n</i> -C ₄ H ₉ CH(OH)CF ₂ CH=CH ₂	87
(CH ₃) ₃ CCH=O	(CH ₃) ₃ CCH(OH)CF ₂ CH=CH ₂	95
CH ₂ =CH-CH=O	CH ₂ =CHCH(OH)CF ₂ CH=CH ₂	20
PhCH=O	(CH ₂ =CHCH(OH)C ₆ H ₅) _{<i>n</i>}	51
	PhCH(OH)CF ₂ CH=CH ₂	15
	(PhCH(OH)(CH ₂) ₃ CH ₃) _{<i>n</i>}	78
(CH ₃) ₂ C=O	(CH ₃) ₂ C(OH)CF ₂ CH=CH ₂	42
(C ₂ H ₅) ₂ C=O	(C ₂ H ₅) ₂ C(OH)CF ₂ CH=CH ₂	70
		59
PhC(O)CH ₃	PhC(Me)(OH)CF ₂ CH=CH ₂	73
ClCH ₂ CO ₂ Me	ClCH ₂ C(O)CF ₂ CH=CH ₂	95
(CH ₃) ₂ CHCO ₂ Me	(CH ₃) ₂ CHC(O)CF ₂ CH=CH ₂	62
(CH ₃) ₃ CCO ₂ Me	(CH ₃) ₃ CC(O)CF ₂ CH=CH ₂	49

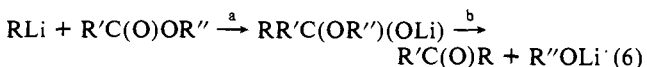
an excess of a triorganochlorosilane, good yields of the expected R₃SiCF₂CH=CH₂ were obtained (Table I). Although the (difluoroallyl)lithium is generated by reaction at the CF₂ terminus of the difluoroallyl precursor in the CH₂=CHCF₂Br/*n*-C₄H₉Li reaction, vs. the CH₂ terminus in the case of the Me₃SnCH₂CH=CF₂/*n*-C₄H₉Li reaction, the reagent formed in these different reactions appears to be the same: R₃SiCF₂CH=CH₂ is formed in either case. No trace of the other isomer,⁸ R₃SiCH₂CH=CF₂, was observed. Noteworthy is the fact that Me₂Si(CF₂CH=CH₂)₂ was obtained in 73% yield when Me₂SiCl₂ was the silicon halide used. Thus, in this application, the lithium/halogen exchange synthesis of *gem*-(difluoroallyl)lithium is far superior to that using the transmetalation reaction.

The in situ lithium-halogen exchange route to *gem*-(difluoroallyl)lithium made possible the difluoroallylation of aldehydes and ketones as well. Dialkyl ketones (Me₂CO, Et₂CO, and cyclohexanone) and an alkyl aryl ketone (acetophenone) were found to give products of the type R₂C(OH)CF₂CH=CH₂ in good to fair yield (Table I), but no difluoroallyl product was obtained with benzophenone. Aliphatic aldehydes could be converted to alcohols of the type RCH(OH)CF₂CH=CH₂ in good yield (Table I), but competing *n*-butyllithium addition became important when the C=O bond was more reactive, as in the case of acrolein and benzaldehyde (Scheme I). Thus there are some limits to the applicability of this procedure. The C=O bond reactivity toward nucleophiles can vary widely as the substituents on the carbon atom are changed. It appears that aromatic substituents result in a C=O group reactive enough to trap most of the *n*-butyllithium before it can undergo the electron-transfer reaction with CH₂=CHCF₂Br.

gem-(Difluoroallyl)lithium also was found to allylate esters when the in situ procedure was used (eq 5). The yields of 1,1-difluoroallyl ketones obtained were good (Table I).



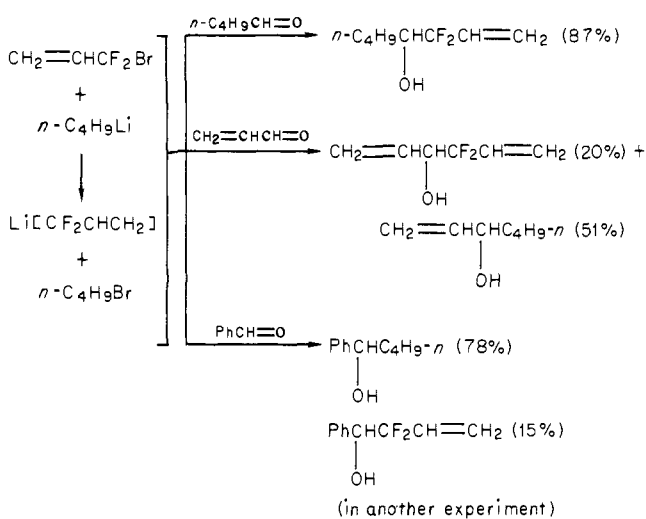
The alkylation of esters by organolithium compounds to give ketones proceeds via initial addition of RLi to the C=O function, followed by elimination of lithium alkoxide (eq 6). In our in situ



difluoroallylation of ketones the elimination step b apparently does not occur at the low reaction temperature, rather during the warmup period. This was shown in a reaction in which it was

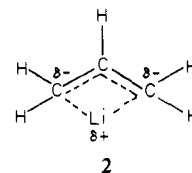
(8) Seyferth, D.; Wursthorn, K. R.; Lim, T. F. O.; Sepelak, D. J. *J. Organomet. Chem.* **1981**, *205*, 301.

Scheme I. Reactions of *gem*-(Difluoroallyl)lithium with Aldehydes

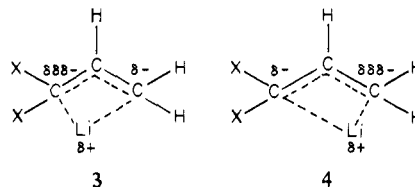


attempted to prepare ClCH₂C(OH)(CF₂CH=CH₂)₂ by treating methyl chloroacetate with 2 molar equiv of *gem*-(difluoroallyl)lithium. When this reaction mixture was treated with trimethylchlorosilane prior to warming to room temperature, the product was not the trimethylsilyl derivative of the expected carbinol, rather it was ClCH₂C(OMe)(OSiMe₃)CF₂CH=CH₂. Thus it was the first intermediate, ClCH₂C(OMe)(OLi)CF₂CH=CH₂, that was the major species present when the trimethylchlorosilane was added.

As Table I shows, all products obtained in reactions of *gem*-(difluoroallyl)lithium with aldehydes, ketones, and esters were the ones in which the new C-C bond had been formed at the CF₂ terminus of the reagent. This observation requires some discussion. First we must consider the nature of the *gem*-(difluoroallyl)lithium species. The most recent work suggests that allyllithium exists in ethereal solvents in the form of symmetrically bridged species **2**,⁹ a tight ion pair in which covalent contributions are important.



A terminally disubstituted lithium reagent, Li[CX₂CHCH₂], should have an unsymmetrical charge distribution, **3** or **4**, with

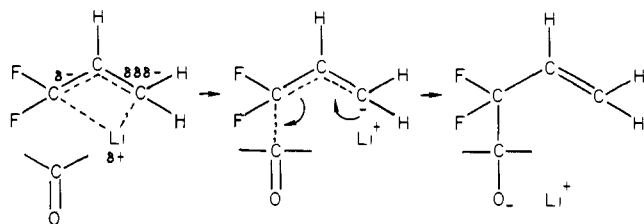


the lithium ion no longer bridging the terminal carbon atoms in a symmetrical fashion. Of the two extrema, **3** and **4**, we expect **4** (X = F) to best describe *gem*-(difluoroallyl)lithium in solution. Although the -I inductive effect of the fluorine substituents might be expected to stabilize a carbanion center, this effect will be cancelled in large part by the destabilizing repulsion between the lone-pair electrons on the fluorine substituents and the electrons in the carbanion orbital.¹⁰ The work of Streitwieser and Mares¹¹

(9) (a) Neugeberger, W.; Schleyer, P. v. R. *J. Organomet. Chem.* **1980**, *198*, C1. (b) Brownstein, S.; Bywater, S.; Worsfold, D. J. *Ibid.* **1980**, *199*, 1. (c) Bywater, S.; Patmore, D. J.; Worsfold, D. J. *Ibid.* **1977**, *135*, 145.

(10) (a) Cram, D. J. "Fundamentals of Carbanion Chemistry"; Academic Press: New York, 1965; Chapter II. (b) Sheppard, W. A.; Sharts, C. M. "Organic Fluorine Chemistry"; W. A. Benjamin: New York, 1969; pp 308 and 309.

Scheme II



on the relative stabilizing effects of a 9-F vs. a 9-CF₃ substituent in the fluorenyl anion may be noted in this connection. Also pertinent is the observation by Hine et al.¹² that one fluorine substituent on the α -carbon atom of ethyl acetate (i.e., in CF₂HCO₂Et) slightly increases the acidity of the remaining hydrogen atoms of the methyl group, but that substitution of a second fluorine atom (to give CF₂HCO₂Et) decreases the acidity of the remaining hydrogen atom by a factor of 1000 vs. CH₃CO₂Et itself.

If **4** best describes *gem*-(difluoroallyl)lithium, i.e., if most of the negative charge resides at the CH₂ terminus than at the CF₂ terminus,¹³ how can one reconcile this with the observation that the products which result are those in which the new bond to the electrophile is formed at the CF₂ terminus? We suggest that the lithium counterion must be considered in any explanation that is offered. If allylic lithium reagents exist in ether solvents in the form of tight ion pairs in which there is a significant covalent bonding contribution, as indicated in **2**, **3**, and **4**, then the lithium ion would be expected to be coordinated at the site of greatest negative charge, i.e., at the CH₂ terminus in the case of Li[CF₂CHCH₂]. This would serve to block the CH₂ terminus from attack by an electrophile relative to the "free" CF₂ terminus. An S_E2' process would result in most cases (Scheme II). In Scheme II attack at a C=O group is shown, but the same considerations are applicable to attack at the Si atom of a chlorosilane.

This explanation for the observed regioselectivity of the reactions of *gem*-(difluoroallyl)lithium may be applied to the reactions of other terminally substituted allylic lithium reagents. For instance, a much more complicated picture had emerged in our study of the reactions of *gem*-(dichloroallyl)lithium with aldehydes and ketones.¹⁴ In the case of *gem*-(dichloroallyl)lithium, we suggest that, for the same reasons, the charge density will be greater at the CH₂ terminus than at the CCl₂ end, but that this charge density difference will not be as great. It is known that chlorine atoms, while showing some effects of Cl lone-pair repulsion of the negative charge at adjacent sp² carbanion centers, do so to a lesser degree.¹⁵ As the charge density at the CH₂ terminus decreases on going from Li[CF₂CHCH₂] to Li[CCl₂CHCH₂], the Li⁺ ion will be displaced less from the symmetrical position of unsubstituted allyllithium. Thus, the CH₂ terminus will be less blocked to attack, especially to attack by the stronger electrophiles. It is then no surprise that substrates with more reactive C=O bonds such as hexafluoroacetone, 1,1,1-trifluoroacetone, trifluoromethyl phenyl ketone, benzophenone, acrolein, and acetophenones with electron-withdrawing substituents on the phenyl ring react with *gem*-(dichloroallyl)lithium to form the new C-C bond at the CH₂ terminus. This is, after all, the site of greater electron density. On the other hand, *gem*-(dichloroallyl)lithium reacted with dialkyl ketones, which have a less reactive carbonyl group, to form products of the type R₂C(OH)CCl₂CH=CH₂ (after hydrolytic workup). Aliphatic aldehydes and acetophenone reacted to give mixtures of both types of products, RCH(OH)CCl₂CH=CH₂ and RCH(OH)CH₂CH=CCl₂, in the case of

aldehydes. Unfortunately, the regioselectivity of *gem*-(difluoroallyl)lithium could not be probed to the limit of the highly reactive carbonyl compounds since, as noted above, with these the addition of *n*-butyllithium to the C=O bond was faster than its reaction with CH₂=CHCF₂Br. In our report on *gem*-(dichloroallyl)lithium¹⁴ we attempted to rationalize the observed regioselectivity of this reagent, which obviously showed the operation of an electronic effect, in terms of the hard/soft-acid/base approach. That, however, was merely a rationalization, not an explanation. The present approach, we feel, is much more satisfactory.

The regioselectivities of three other allylic lithium reagents which bear a chlorine substituent on one of the terminal carbon atoms also are of interest: *gem*-(chloromethylallyl)lithium (Li[CH₂CClCHCH₂]),¹⁶ (chloroallyl)lithium (Li[ClCHCHCH₂]),¹⁷ and *gem*-(chloro(trimethylsilyl)allyl)lithium (Li[Me₃SiCClCHCH₂]).¹⁸ In the first of these, the methyl group will inductively destabilize a negative charge at the carbon atom to which it is attached and the chlorine substituent will cause some destabilization as well by the lone-pair effect discussed above. The observed formation of *only* products of the type R₂C(OH)C(CH₃)(Cl)CH=CH₂ in reactions of *gem*-(chloromethylallyl)lithium with cyclohexanone, methyl isopropyl ketone, acetophenone, and benzophenone is easily understood on this basis. Only when steric effects become prohibitive, as in the case of methyl *tert*-butyl ketone, was C-C bond formation at the CH₂ terminus observed.

In (chloroallyl)lithium, destabilization by only one chlorine substituent on one of the terminal carbon atoms is operative. One might then expect to find C-C bond formation at the CH₂ terminus more favorable than in the case of Li[CCl₂CHCH₂]. This is what was observed.¹⁷ For instance, in the reaction of (chloroallyl)lithium with Et₂C=O, the CH₂/CHCl terminus attack ratio was 3. In comparison, Li[CCl₂CHCH₂] reacted with this ketone to give only Et₂C(OH)CCl₂CH=CH₂.¹⁴ In the case of aldehydes, the formation of RCH(OH)CH₂CH=CHCl is highly favored, which stands in marked contrast to the regioselectivity observed in Li[CCl₂CHCH₂]/RCHO reactions.¹⁴

In the case of *gem*-((trimethylsilyl)chloroallyl)lithium the trimethylsilyl group brings two effects: the well-known stabilization of an adjacent negative charge (by d_π-p_π bonding and/or by polarization effects) and a fairly substantial steric effect. Thus, while the electronic effect of the Me₃Si group would work against that of the chlorine substituent, its steric effect would hinder C-C bond formation at the substituted terminus of the allylic reagent. On reaction with 1,1,1-trifluoroacetone, only (CH₃)(CF₃)C(OH)CH₂CH=C(Cl)(SiMe₃) was formed, but with cyclohexanone and acetophenone both possible isomeric products were obtained.

Similar, previously reported dramatic differences in regioselectivity in reactions of alkyl-substituted allylic lithium reagents vis-à-vis acetone and hexafluoroacetone¹⁹ now find a ready explanation. As noted already, an alkyl group will inductively destabilize an adjacent negative charge. That this is so in terminally alkyl-substituted allyllithium reagents has been demonstrated experimentally by ¹³C NMR studies.²⁰ Thus, the tight ion pair found for (alkylallyl)lithium reagents in ether solvents should be best described by **5**. Barring prohibitive steric factors, formation of the new C-C bond on reaction with aldehydes and ketones at the substituted terminus should be favored. This has been found to be generally true,²¹ and we cite only some results from our own previous work¹⁸ (eq 7-9). As expected on the basis

(11) Streitwieser, A.; Mares, F. *J. Am. Chem. Soc.* **1968**, *90*, 2444.

(12) Hine, J.; Mahone, L. G.; Liotta, C. L. *J. Am. Chem. Soc.* **1967**, *89*, 5911.

(13) In support of this idea, we note that CNDO/2MO calculations have indicated that in Li[CF₂CHCH₂]₂Me₂O the total charge density at the CH₂ terminus is much greater than at the CF₂ terminus: Prof. J. F. Sebastian (Miami University), private communication, October 1974.

(14) Seyferth, D.; Murphy, G. J.; Mauzé, B. *J. Am. Chem. Soc.* **1977**, *99*, 5317.

(15) Adolph, H. G.; Kamlet, M. J. *J. Am. Chem. Soc.* **1966**, *88*, 4761.

(16) Mauzé, B. *J. Organomet. Chem.* **1979**, *170*, 265.

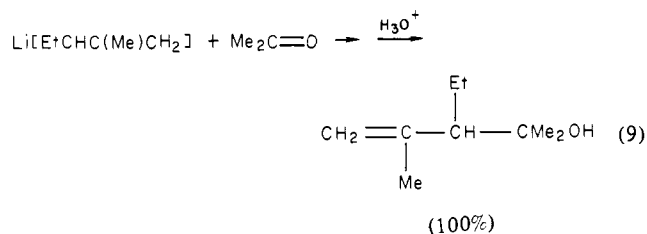
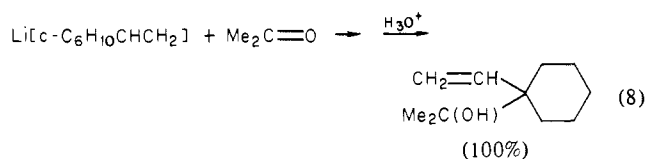
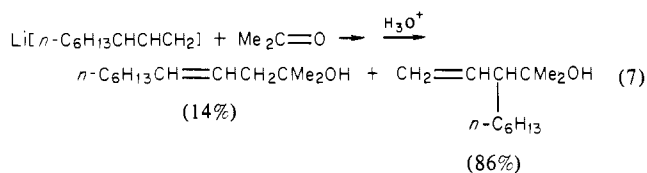
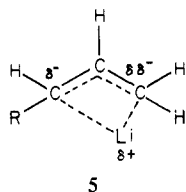
(17) Doucoure, A.; Mauzé, B.; Miginiac, L. *J. Organomet. Chem.* **1982**, *236*, 139.

(18) Seyferth, D.; Mammarella, R. E. *J. Organomet. Chem.* **1978**, *156*, 279.

(19) Seyferth, D.; Mammarella, R. E. *J. Organomet. Chem.* **1979**, *177*, 53.

(20) (a) van Dongen, J. P.; van Dijkman, H. W.; de Bie, M. *J. Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 29. (b) Bywater, S.; Lachance, P.; Worsfold, D. *J. J. Phys. Chem.* **1975**, *79*, 2148. (c) Bywater, S.; Worsfold, D. *J. Organomet. Chem.* **1978**, *159*, 229.

(21) Courtois, G.; Miginiac, L. *J. Organomet. Chem.* **1974**, *69*, 1.



of the ideas developed above, all three reagents shown in eq 6–8 reacted with hexafluoroacetone to favor formation of the product alcohol with the new C–C bond at the CH₂ terminus. With (*n*-hexylallyl)lithium 68%, with Li[c-C₆H₁₀CHCH₂] 100%, and with Li[EtCHC(Me)CH₂] 65% of the product was formed at the CH₂ end of the reagent.

These considerations lead us to conclude that much remains to be done in the area of allylic lithium reagent chemistry. If the tight binding between the allyl anion and the lithium ion even in Et₂O and THF solution indeed is the crucial factor that determines the observed regioselectivities with the various electrophiles used, then the effect of strong Lewis base additives, such as Me₂NCH₂CH₂NMe₂, (Me₂N)₃PO, crown ethers, cryptands, etc., which might compete in the binding of Li⁺, would be a fruitful area of study, both from the mechanistic and the synthetic point of view. Such a study might be carried out with *gem*-(dichloroallyl)lithium, whose reactivity as an ambident nucleophile in the absence of additives has been well mapped.¹⁴

This research, then, has provided a new and useful route to *gem*-(difluoroallyl)lithium which allows the synthesis of α,α-difluoroallyl-substituted secondary and tertiary alcohols, ketones, and silicon compounds. In addition, a useful explanation of the regioselectivities observed in the reactions of all kinds of substituted allylic lithium reagents with various electrophiles has been proposed.

The introduction of fluorine in place of hydrogen in organic compounds can cause profound (and, in some cases, useful) changes in biological effects²² and the availability of the difluoroallyl anion as a reagent offers a new method of introducing fluorine into compounds of biological interest. The difluoroallylic alcohols prepared in this study may themselves be of interest as potential antimetabolites.

Experimental Section

General Comments. All reactions of *gem*-(difluoroallyl)lithium were carried out under an inert atmosphere in flame-dried glassware. THF and diethyl ether were purified by distillation from sodium benzophenone ketyl under an inert atmosphere. Pentane was similarly distilled, but from LiAlH₄. Solvents were stored under an inert atmosphere prior to use, and diethyl ether was refrigerated as well. Dimethyl ether was

purified as a gas by passing it through drying columns containing Drierite, P₂O₅, and activated alumina. It was then condensed into a flame-dried graduated cylinder at –78 °C and used immediately. Chlorosilanes were purified by distillation from magnesium chips and were checked for purity by gas–liquid chromatography (GLC) before use. *n*-Butyllithium in hexane was purchased from the Alfa/Ventron Division of Thiokol Corp. and was used as received. All alkyllithium reagents were standardized by using the method of Kofron and Baclawski.²³

Analytical GLC was performed on a Hewlett-Packard Model 5754 gas chromatograph equipped with a thermal conductivity detector. Preparative GLC was performed on either a Hewlett-Packard/F&M Model 700, Hewlett-Packard/F&M Model 720, or GowMac Model 550P gas chromatograph. GLC columns were constructed from 1/4-in. o.d. copper tubing and were packed with coated diatomaceous silica supports. The silica supports were acid washed and were treated with dimethyldichlorosilane and methanol before being coated with either General Electric Co. SE-30 dimethylsilicone rubber gum or General Electric Co. QF-1 fluorosilicone oil.

Infrared spectra were recorded with a Perkin-Elmer Model 457A or a Perkin-Elmer Model 283B grating infrared spectrophotometer. Proton magnetic resonance spectra were recorded with a Varian Associates T-60 or a Hitachi Perkin-Elmer R-24B spectrometer, operating at 60 MHz. High-field proton magnetic resonance spectra were recorded with a JEOL FX-90Q spectrometer, operating at 90 MHz, or a Bruker WM-250 or WM-270 spectrometer, operating at 250 and 270 MHz, respectively. Chemical shifts are reported in δ units, parts per million downfield from internal tetramethylsilane.

Refractive indices were recorded with a Zeiss-Abbé type refractometer, thermostated either at 20 or 25 °C. Melting points were determined on analytically pure samples with a Büchi Capillary Melting Point Apparatus and are uncorrected.

In Situ Reaction Procedure. The standard apparatus for the reactions of *gem*-(difluoroallyl)lithium generated in situ by lithium–halogen exchange consisted of a three-necked, 200-mL Morton flask equipped with an overhead mechanical stirrer, a pressure-equalizing addition funnel capped with a rubber septum, and a Claisen adapter with low-temperature thermometer and a gas-inlet adapter leading to an inert gas line (argon or prepurified nitrogen).

The apparatus was cooled and maintained at low temperatures by placing it in a wide-mouthed Dewar flask partially filled with liquid nitrogen. By raising or lowering the flask on a laboratory jack, the reaction apparatus can be either immersed in liquid nitrogen or held just above the surface of the liquid to adjust the temperature. Low temperatures were measured with pentane thermometers (W. H. Kessler Co., Inc., +30 °C to –200 °C) with only the bulb immersed in the solution. Pentane total immersion thermometers read –70 °C (bulb immersed) vs. –78 °C (total immersion) in a dry ice–acetone bath, so the temperatures reported in this paper are probably 8–10 °C high for these low-temperature reactions.

Preparation of BrCF₂CH₂CH₂Br. A high-pressure stainless-steel reaction vessel of 1.4-L capacity was conditioned by performing the procedure described below with one-tenth the amount of CF₂Br₂ described. Immediately after conditioning, it was charged with 198.7 g (0.95 mol) of CF₂Br₂ and 1.13 g (4.7 mmol, 0.005 molar equiv) of benzoyl peroxide. The bomb was assembled, mounted on a rocker, and attached to a gas line. The apparatus was charged with 120 psi of ethylene (1.4 L at 8.0 atm, compressibility factor = 0.9451 at 125 psi and 21 °C,²⁴ 0.49 mol of ethylene), heated to 80 °C and allowed to react for 18 h. During this time, some of the ethylene was consumed. The bomb was allowed to cool and disassembled, and the material was emptied from the bomb and weighed (143.7 g).

This product mixture was trap-to-trap distilled (0.15 torr, 50 °C) to remove all volatiles from the brown solid residue left by the decomposition of benzoyl peroxide. The clear distillate was again trap-to-trap distilled (atmospheric pressure, 30 °C) into a flask cooled in dry ice/isopropyl alcohol slush. This was done to collect unreacted CF₂Br₂, and the distillate weighed 74.2 g. The pot residue from this procedure was analyzed by GLC (15% SE-30 on Chromosorb W, 75 °C) and showed two peaks, one for residual CF₂Br₂ and one for the expected product, BrCF₂CH₂CH₂Br. No high boiling components were seen, even at elevated column temperatures. The pot residue was distilled at reduced pressure. At 160 torr, a further 27.9 g of CF₂Br₂ distilled at 25 °C and was collected in a receiver cooled in a dry ice/isopropyl alcohol slush. The pressure was reduced further and the expected product, BrCF₂CH₂CH₂Br, *n*_D²⁵ 1.4463 (lit.⁵ *n*_D²⁵ 1.4450), was collected at 61–67 °C, 97 torr (lit.⁵ bp 62 °C (86 torr)). The yield was 36.7 g (154 mmol, 78%).

(23) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.

(22) (a) Reference 10b, Chapter 9, Section 3. (b) Schlosser, M. *Tetrahedron* **1978**, *34*, 3. (c) Walsh, C. T. *Adv. Enzymol.*, in press.

(24) Walters, R. J.; Tract, J. H.; Weinburger, E. B.; Rodgers, J. K. *Chem. Eng. Prog.* **1954**, *50*, 511.

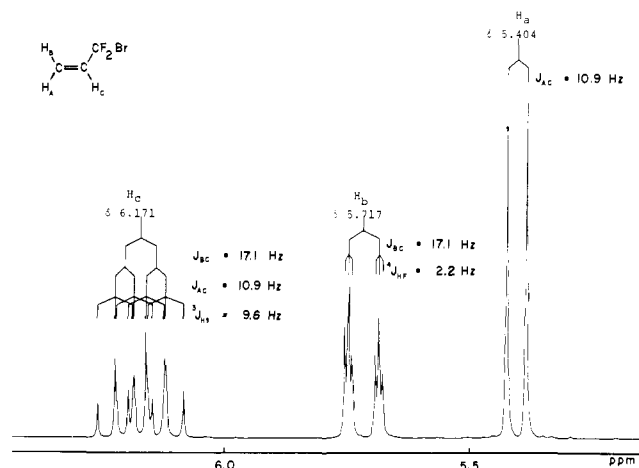


Figure 1. High-field proton NMR spectrum of 3,3-difluoro-3-bromopropene.

NMR (90 MHz, $\text{CDCl}_3/\text{CHCl}_3$) δ 2.90 [t, $^3J(\text{H}-\text{H}) = 7.82$ Hz, $^3J(\text{H}-\text{F}) = 12.5$ Hz, 2 H, $\text{BrCF}_2\text{-CH}_2\text{-CH}_2$], 3.47 [t, $^3J(\text{H}-\text{H}) = 7.82$ Hz, 2 H, $\text{CH}_2\text{-CH}_2\text{Br}$]

The yield in this reaction is based on the estimated amount of dibromodifluoromethane that reacted. This estimate was arrived at by subtracting from the total amount of CF_2Br_2 which was used the amount of recovered CF_2Br_2 as well as the amount of CF_2Br_2 lost in handling operations, especially the venting of excess pressure from the bomb after the reaction is complete. The latter quantity was estimated by taking the difference between the amount of material placed in the bomb and the amount of material removed from the bomb.

Preparation of 3,3-Difluoro-3-bromopropene. To a 500-mL round-bottomed flask containing a magnetic stirring bar was added 202.3 g (3.61 mol) of reagent grade pellets of KOH and 75 mL of distilled water. The KOH pellets dissolved partially to give a saturated aqueous solution at room temperature. To this was added 64 g (0.27 mol) of $\text{BrCF}_2\text{CH}_2\text{CH}_2\text{Br}$, and the flask was attached to a distillation apparatus consisting of a 30-cm Vigreux column, a water-cooled distillation head, and a receiver cooled in a dry ice/isopropyl alcohol slush. An oil bath, with a magnetic stirring bar, a resistive heating coil connected to a variable transformer, and a thermometer, was placed around the reaction flask. A magnetic stirrer was placed under the oil bath to drive both the stirring bar in the bath and the one in the reaction flask.

When the temperature of the oil bath reached 120 °C, a colorless liquid began to distill at temperatures ranging from 25 to 95 °C. At the upper end of the temperature range, the distillate was cloudy and mixed with water. The temperature of the oil bath was increased slowly to 160 °C to force over all of the product. After the distillation was completed, the cooled receiver flask was allowed to warm to room temperature. The dried product (Molecular Sieves, 4A) was redistilled through a 30-cm column packed with $3/16$ -in. glass helices. The fraction distilling from 40–45 °C was collected in a cooled (–78 °C) receiver. NMR analysis of this product showed it to be a 20/1 mixture of $\text{CH}_2=\text{CH-CF}_2\text{Br}/\text{CF}_2=\text{CH-CH}_2\text{Br}$. The yield was 93% (39.1 g, 0.25 mol). NMR spectral data are given in Figure 1.

Reactions of *gem*-(Difluoroallyl)lithium with Chlorosilanes at –95 °C. A reaction with triethylchlorosilane is described in detail. Into the standard reaction apparatus containing 80 mL of THF was introduced 1.69 g (10.8 mmol) of 3,3-difluoro-3-bromopropene and 2.80 mL (16.6 mmol) of Et_3SiCl (Petrarch), followed by 20 mL of diethyl ether and 20 mL of pentane. The reaction mixture was cooled to –95 °C and 7.0 mL (15.1 mmol) of a 2.2 M solution of *n*-butyllithium in hexane was added slowly, dropwise. After the addition was completed, the reaction mixture was stirred at –95 °C for 90 min and then allowed to warm slowly to room temperature. The reaction mixture was worked up in what shall henceforth be called, "the usual manner". Approximately 20 mL of distilled water was added to dissolve the lithium salts. The organic phase was drawn off with use of a separatory funnel, and the aqueous phase was extracted with pentane. The organic phases were combined, dried over anhydrous MgSO_4 , and concentrated with use of a rotary evaporator. The expected product, $\text{Et}_3\text{SiCF}_2\text{CH}=\text{CH}_2$, n^{25}_D 1.4217, was isolated and analyzed by GLC (15% SE 30 Chromosorb P, 135 °C). The yield was 51%.

$^1\text{H NMR}$ ($\text{CCl}_4/\text{C}_6\text{H}_6$) δ 0.15–1.4 (m, 15 H, Et_3Si) and 5.1–6.6 (m, 3 H, $\text{CH}=\text{CH}_2$); IR (thin film) $\nu(\text{C}=\text{C})$ 1645 (w) cm^{-1} .

Anal. Calcd for $\text{C}_9\text{H}_{18}\text{F}_2\text{Si}$: C, 56.21; H, 9.43. Found: C, 56.15; H, 9.42.

The following in situ reactions were carried out in a similar manner.

(1) *gem*-(Difluoroallyl)lithium (from 19.0 mmol of $\text{CH}_2=\text{CHCF}_2\text{Br}$ and 15 mmol of *n*-butyllithium) reacted with 30.0 mmol of PhMe_2SiCl (Petrarch) to give $\text{PhMe}_2\text{SiCF}_2\text{CH}=\text{CH}_2$ in 71% yield. The proton NMR spectrum was in good agreement with that reported earlier.¹

(2) *gem*-(Difluoroallyl)lithium (from 10.9 mmol of $\text{CH}_2=\text{CHCF}_2\text{Br}$ and 10.8 mmol of $\text{C}_2\text{H}_5\text{Li}$ in Et_2O) reacted with 20 mmol of Me_3SiCl to give $\text{Me}_3\text{SiCF}_2\text{CH}=\text{CH}_2$ ¹ in 27% yield.

$^1\text{H NMR}$ ($\text{CCl}_4/\text{C}_6\text{H}_6$) δ 0.12 (s, 9 H, Me_3Si) and 5.0–6.3 (m, 3 H, $\text{CH}=\text{CH}_2$).

When *n*-butyllithium was used to generate *gem*-(difluoroallyl)lithium instead of ethyllithium the yield of $\text{Me}_3\text{SiCF}_2\text{CH}=\text{CH}_2$ was higher (89% by GLC), but the product proved to be difficult to separate by distillation from the *n*-butyl bromide formed in the lithium/halogen exchange reaction.

(3) *gem*-(Difluoroallyl)lithium (from 20.6 mmol of $\text{CH}_2=\text{CHCF}_2\text{Br}$ and 20.3 mmol of *n*-butyllithium) reacted with 10.3 mmol of Me_2SiCl_2 to give $\text{Me}_2\text{Si}(\text{CF}_2\text{CH}=\text{CH}_2)_2$, n^{25}_D 1.4016, in 74% yield. In this reaction the *n*-butyllithium was added in two portions: initially 10 mmol, then, after the reaction mixture had been stirred at –97 °C for 25 min, another 10.3 mmol.

NMR ($\text{CCl}_4/\text{C}_6\text{H}_6$) δ 0.33 (s, 6 H, Me_2Si) and 5.1–6.3 (m, 6 H, $\text{CH}=\text{CH}_2$); IR (thin film) $\nu(\text{C}=\text{C})$ 1640 (w) cm^{-1} .

Anal. Calcd for $\text{C}_8\text{H}_{12}\text{F}_4\text{Si}$: C, 45.27; H, 5.70. Found: C, 45.32; H, 5.63.

Reactions of *gem*-(Difluoroallyl)lithium with Aldehydes and Ketones.

The reaction with pentanal is described to illustrate the procedure used.

The standard reaction apparatus was charged with 80 mL of THF, 1.72 g (10.9 mmol) of $\text{CH}_2=\text{CHCF}_2\text{Br}$, 2.35 mol (22.1 mmol) of pentanal (*n*- $\text{C}_4\text{H}_9\text{CHO}$), 20 mL of diethyl ether, and 20 mL of pentane. The solution was cooled to –95 °C and 5.3 mL (12 mmol) of a 2.3 M solution of *n*-butyllithium in hexane was added dropwise. After the addition had been completed, the reaction mixtures were stirred at –95 °C for 90 min and then was allowed to warm slowly to room temperature. The reaction mixture was treated with saturated aqueous NH_4Cl . The organic layer was separated and the usual workup (as above) followed. GLC analysis of the organic liquid residue (15% SE 30 on Chromosorb P, 100 °C) and collection of the product (at 135 °C) showed that *n*- $\text{C}_4\text{H}_9\text{CH}(\text{OH})\text{-CF}_2\text{CH}=\text{CH}_2$, n^{25}_D 1.4271, had been formed in 87% yield.

NMR ($\text{CCl}_4/\text{C}_6\text{H}_6$) δ 0.66–1.85, (m, 10 H, *n*- C_4H_9 and OH), 3.22–3.98 (m, 1 H, $\text{CH}(\text{OH})$), and 5.28–6.45 (m, 3 H, $\text{CH}=\text{CH}_2$); IR (film) $\nu(\text{C}=\text{C})$ 1647 (w) cm^{-1} .

Anal. Calcd for $\text{C}_8\text{H}_{14}\text{F}_2\text{O}$: C, 58.52; H, 8.59. Found: C, 58.78; H, 8.72.

Similar reactions gave the following products.

(1) $\text{Me}_2\text{C}(\text{OH})\text{CF}_2\text{CH}=\text{CH}_2$, n^{25}_D 1.3950, from 30 mmol of $\text{CH}_2=\text{CHCF}_2\text{Br}$, 42 mmol of anhydrous acetone, and 25 mmol of *n*-butyllithium, in 41% yield.

$^1\text{H NMR}$ ($\text{CCl}_4/\text{C}_6\text{H}_6$) δ 1.17 (s, 6 H, Me_2C), 1.57 (s, 1 H, OH), and 5.23–6.54 (m, 3 H, $\text{CH}=\text{CH}_2$).

Anal. Calcd for $\text{C}_6\text{H}_{10}\text{F}_2\text{O}$: C, 52.93; H, 7.40. Found: C, 52.76; H, 7.52.

(2) $\text{Et}_2\text{C}(\text{OH})\text{CF}_2\text{CH}=\text{CH}_2$, from 3 mmol of $\text{CH}_2=\text{CHCF}_2\text{Br}$, 6 mmol of Et_2CO , and 3 mmol of *n*-butyllithium, in 70% yield. The spectroscopic properties of this product were in good agreement with those reported earlier.¹

(3) $\text{c-C}_6\text{H}_{10}(\text{OH})\text{CF}_2\text{CH}=\text{CH}_2$, mp 27.0–27.5 °C (GLC sample), from 11.5 mmol of $\text{CH}_2=\text{CHCF}_2\text{Br}$, 20.3 mmol of cyclohexanone, and 13 mmol of *n*-butyllithium, in 59% yield.

$^1\text{H NMR}$ ($\text{CCl}_4/\text{C}_6\text{H}_6$) δ 0.89–1.97 (m with 2 broad s at δ 1.22 and 1.52, 11 H, cyclohexyl H and OH), 5.21–6.44 (m, 3 H, $\text{CH}=\text{CH}_2$).

Anal. Calcd for $\text{C}_9\text{H}_{14}\text{F}_2\text{O}$: C, 61.35; H, 8.01. Found: C, 61.44; H, 8.09.

(4) $\text{Ph}(\text{CH}_3)\text{C}(\text{OH})\text{CF}_2\text{CH}=\text{CH}_2$, n^{25}_D 1.4955, from 10.8 mmol of $\text{CH}_2=\text{CHCF}_2\text{Br}$, 21.7 mmol of acetophenone, and 12 mmol of *n*-butyllithium, in 73% yield.

$^1\text{H NMR}$ ($\text{CCl}_4/\text{Me}_4\text{Si}$) δ 1.7 (s, 3 H, CH_3), 2.3 (s, 1 H, OH), 5.2–6.4 (m, 3 H, $\text{CH}=\text{CH}_2$), and 7.4 (s, 5 H, Ph).

Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{F}_2\text{O}$: C, 66.66; H, 6.10. Found: C, 66.44; H, 6.12.

(5) $(\text{CH}_3)_3\text{CCH}(\text{OH})\text{CF}_2\text{CH}=\text{CH}_2$, n^{25}_D 1.4116, from 9.1 mmol of $\text{CH}_2=\text{CHCF}_2\text{Br}$, 18.0 mmol of $(\text{CH}_3)_3\text{CCHO}$, and 10 mmol of *n*-butyllithium, in 95% yield.

$^1\text{H NMR}$ ($\text{CCl}_4/\text{C}_6\text{H}_6$) δ 0.88 (s, 9 H, CH_3), 1.60–1.86 (m, 1 H, $\text{CH}(\text{OH})$), 3.05–3.67 (m, 1 H, OH), and 5.22–6.55 (m, 3 H, $\text{CH}=\text{CH}_2$).

Anal. Calcd for $\text{C}_8\text{H}_{14}\text{F}_2\text{O}$: C, 58.52; H, 8.54. Found: C, 58.42; H, 8.72.

(6) $\text{CH}_2=\text{CHCH}(\text{OH})\text{CF}_2\text{CH}=\text{CH}_2$, n^{20}_D 1.4118, from 10.8 mmol of $\text{CH}_2=\text{CHCF}_2\text{Br}$, 30.0 mmol of $\text{CH}_2=\text{CHCHO}$, and 10 mmol of *n*-butyllithium, 20% yield.

$^1\text{H NMR}$ ($\text{CCl}_4/\text{C}_6\text{H}_6$) δ 2.10 (s, 1 H, OH), 4.27 (m, 1 H, $-\text{CH}(\text{OH})$), and 5.10–6.55 (m, 6 H, $\text{CH}=\text{CH}_2$).

Anal. Calcd for $\text{C}_6\text{H}_8\text{F}_2\text{O}$: C, 53.73; H, 6.01. Found: C, 53.66; H, 6.25.

Also formed was $\text{CH}_2=\text{CHCH}(\text{OH})\text{C}_4\text{H}_9$, n^{20}_D , 1.4333 (lit.²⁵ n^{20}_D 1.4337), in 51% yield.

$^1\text{H NMR}$ ($\text{CCl}_4/\text{C}_6\text{H}_6$) δ 0.63–1.57 (m, 9 H, C_4H_9), 1.70 (s, 1 H, OH), 3.97 (m, 1 H, $-\text{CH}(\text{OH})$), and 4.73–6.06 (m, 3 H, $\text{CH}=\text{CH}_2$).

(7) $\text{PhCH}(\text{OH})\text{CF}_2\text{CH}=\text{CH}_2$, n^{25}_D 1.5008, from 6 mmol of $\text{CH}_2=\text{C}(\text{HCF}_2)\text{Br}$, 12 mmol of benzaldehyde, and 7 mmol of *n*-butyllithium in 15% yield.

$^1\text{H NMR}$ (CDCl_3) δ 2.4 (s, 1 H, OH), 4.9 (t, $J = 8$ Hz, 1 H, CHCF_2), 5.25–6.3 (m, 3 H, $\text{CH}=\text{CH}_2$), and 7.4 (m, 5 H, Ph).

Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{F}_2\text{O}$: C, 65.2; H, 5.43. Found: C, 64.9; H, 5.62.

In another experiment, $\text{PhCH}(\text{OH})\text{C}_4\text{H}_9$ also was identified (78%) and isolated; n^{20}_D 1.5083 (lit.²⁶ n^{20}_D 1.5078).

$^1\text{H NMR}$ ($\text{CCl}_4/\text{Me}_4\text{Si}$) δ 0.9–1.9 (m, 10 H, C_4H_9 and OH), 4.6 (t, $^3J(\text{H}-\text{H}) = 7$ Hz, 1 H, PhCH), and 7.2 (s, 5 H, Ph).

Reactions of *gem*-(Difluoroallyl)lithium with Esters. The reaction of *gem*-(difluoroallyl)lithium with methyl chloroacetate is typical.

The standard apparatus was charged with 80 mL of THF, 1.68 g (10.7 mmol) of $\text{CH}_2=\text{CHCF}_2\text{Br}$, 3.02 g (27.8 mmol) of methyl chloroacetate, 20 mL of diethyl ether, and 20 mL of pentane. This mixture was cooled to -95°C and 4.5 mL (10 mmol) of 2.3 M *n*-butyllithium in hexane was added dropwise, very slowly. Upon completion of the addition the reaction mixture was stirred at -95°C for 90 min and subsequently was allowed to warm slowly to room temperature. Hydrolysis with saturated aqueous NH_4Cl and work up as in the other experiments followed. GLC analysis of the organic residue (15% QF-1 on Chromosorb W, 100°C) showed the presence of $\text{ClCH}_2\text{C}(\text{O})\text{CF}_2\text{CH}=\text{CH}_2$, n^{20}_D 1.4122, in 95% yield.

$^1\text{H NMR}$ ($\text{CCl}_4/\text{C}_6\text{H}_6$) δ 4.10 (s, 2 H, ClCH_2) and 5.50–5.82 (m, 3 H, $\text{CH}=\text{CH}_2$); IR (thin film) $\nu(\text{C}=\text{O})$ 1752 cm^{-1} .

(25) Grayson, J. T.; Greenlee, K. W.; Derfer, J. M.; Boord, C. E. *J. Org. Chem.* 1955, 20, 275.

(26) Ipatieff, V. N.; Haensel, V. *J. Am. Chem. Soc.* 1942, 64, 520.

Anal. Calcd for $\text{C}_5\text{H}_5\text{ClF}_2\text{O}$: C, 38.86; H, 3.26. Found: C, 39.21; H, 3.50.

The following were prepared by this procedure.

(1) $(\text{CH}_3)_2\text{CHC}(\text{O})\text{CF}_2\text{CH}=\text{CH}_2$, n^{25}_D 1.3792, from 11.5 mmol of $\text{CH}_2=\text{CHCF}_2\text{Br}$, 30.1 mmol of $(\text{CH}_3)_2\text{CHCO}_2\text{CH}_3$, and 10 mmol of *n*-butyllithium, in 62% yield.

$^1\text{H NMR}$ ($\text{CCl}_4/\text{C}_6\text{H}_6$) δ 1.21 (d, $^3J(\text{H}-\text{H}) = 7$ Hz, 6 H, CH_3), 3.13 (sept, $^3J(\text{H}-\text{H}) = 7$ Hz, 1 H, Me_2CH), and 5.38–6.27 (m, 3 H, $\text{CH}=\text{CH}_2$); IR (thin film) $\nu(\text{C}=\text{O})$ 1740 cm^{-1} .

Anal. Calcd for $\text{C}_7\text{H}_{10}\text{F}_2\text{O}$: C, 56.75; H, 6.80. Found: C, 56.75; H, 6.90.

(2) $(\text{CH}_3)_3\text{CC}(\text{O})\text{CF}_2\text{CH}=\text{CH}_2$, n^{25}_D 1.3902, from 16.0 mmol of $\text{CH}_2=\text{CHCF}_2\text{Br}$, 20.3 mmol of $(\text{CH}_3)_3\text{CCO}_2\text{CH}_3$, and 15 mmol of *n*-butyllithium, in 49% yield.

$^1\text{H NMR}$ ($\text{CCl}_4/\text{C}_6\text{H}_6$) δ 1.30 (t, $^5J(\text{H}-\text{F}) = 0.8$ Hz, 9 H, CH_3) and 5.36–6.13 (m, 3 H, $\text{CH}=\text{CH}_2$); IR (thin film) $\nu(\text{C}=\text{O})$ 1730 cm^{-1} .

Anal. Calcd for $\text{C}_8\text{H}_{12}\text{F}_2\text{O}$: C, 59.25; H, 7.46. Found: C, 59.26; H, 7.49.

Reaction of Methyl Chloroacetate with 2 Molar Equiv of *gem*-(Difluoroallyl)lithium. Using the usual procedure, 4.1 mL of 2.4 M *n*-BuLi (9.8 mmol) in hexane was added dropwise, very slowly, to a solution of 4.50 g (28.7 mmol) of $\text{CH}_2=\text{CHCF}_2\text{Br}$ in 80 mL of THF, 20 mL of diethyl ether, and 20 mL of pentane. The resulting mixture was stirred at -95°C for 60 min and then 4.5 mL (11 mmol) of *n*-BuLi solution was added. After the reaction mixture had been stirred for another 60 min, 2.5 mL (20 mmol) of Me_3SiCl was added at -95°C and then the mixture was stirred and allowed to warm slowly to room temperature. After trap-to-trap distillation (70°C , 0.10 mmHg) into a liquid nitrogen cooled receiver and concentration of the volatiles at reduced pressure, GLC analysis of the liquid residue showed the presence of a major product which was identified as $\text{ClCH}_2\text{C}(\text{OMe})(\text{OSiMe}_3)\text{CF}_2\text{CH}=\text{CH}_2$ (36% yield), n^{20}_D 1.4222.

$^1\text{H NMR}$ ($\text{CCl}_4/\text{C}_6\text{H}_6$) δ 0.16 (s, 9 H, SiMe_3), 3.41 (s, 3 H, OMe), 3.67 (s, 2 H, ClCH_2), and 5.30–6.10 (m, 3 H, $\text{CH}=\text{CH}_2$).

Anal. Calcd for $\text{C}_9\text{H}_{17}\text{ClF}_2\text{O}_2\text{Si}$: C, 41.77; H, 6.62. Found: C, 42.02; H, 6.65.

Acknowledgment. This work was supported in part by the U.S. Office of Naval Research.

Comparison of Radiationless Decay Processes in Osmium and Platinum Porphyrins

Glauco Pontorini,^{†1} Nick Serpone,[‡] Michael A. Bergkamp,[†] and Thomas L. Netzel^{*†}

Contribution from the Departments of Chemistry, Brookhaven National Laboratory, Upton, New York 11973, and C.P.L.F.P. Centre, Concordia University, Montreal, Canada H3G-1M8. Received October 12, 1982

Abstract: Two osmium porphyrin complexes, $\text{Os}(\text{OEP})\text{L}_2$ [OEP = octaethylporphyrin, L = py(pyridine) or NO], and PtOEP were investigated by picosecond laser spectroscopy with use of a double-beam, mode-locked Nd:glass system delivering 6-ps (fwhm) pulses at 527 nm with 1–2 mJ/pulse. Time-resolved excited-state spectra were recorded from the time of photoexcitation to 5 ns after photoexcitation. The initial excited state, S_1 , decayed in ≤ 9 ps for the two osmium complexes and in ≤ 15 ps for the platinum porphyrin. A second excited state, T_1 , lived for 1, 9, and >50 ns respectively for $\text{Os}(\text{OEP})(\text{py})_2$, $\text{Os}(\text{OEP})(\text{NO})_2$, and PtOEP . The ΔA spectra of the T_1 states of the osmium complexes were similar to those of previously reported (d_{π}, π^*) states for $\text{Os}(\text{OEP})(\text{py})_2$ and (π, π^*) states for $\text{Os}(\text{OEP})(\text{NO})_2$. This finding supports prior assignments of these states on the basis of expected axial and equatorial back-bonding of the osmium's d electrons. Additionally, a long-lived ($\tau > 5$ ns) photochemical product (probably a result of ligand loss) was found in the case of $\text{Os}(\text{OEP})(\text{py})_2$.

Recent attempts to understand bonding and back-bonding relationships within biologically important iron porphyrins have been supported by studies of the related osmium porphyrins.² Osmium(II) porphyrins have d_{xy} and d_{π} ($d_{\pi} = d_{xz}, d_{yz}$) orbitals of nearly the same energy as those of iron(II) porphyrins, but the $\text{Os}(\text{II})$ orbitals extend further into space, thus the π -back-bonding

effects will be more pronounced for osmium than for iron porphyrins. The $\text{Fe}(\text{porphyrin})\text{L}_2$ complexes are all labile in solution but $\text{Os}(\text{porphyrin})\text{L}_2$ complexes are kinetically inert making reliable spectral and other physical data much easier to obtain for

(1) Visiting Research Associate from the Department of Chemistry, Concordia University.

(2) Buchler, J. W.; Kokisch, W.; Smith, P. D. *Struct. Bonding (Berlin)* 1978, 34, 79.

[†] Brookhaven National Laboratory.
[‡] Concordia University.