high-frequency IR bands reported by Baird et al.[19] (which are in agreement with ours), however, the IR spectrum of 7 has not been reported. Photolysis of 6 under the same conditions but at λ = 250 nm, where COS absorbs, yielded the same products, but the time required to achieve complete photolysis was shorter.

Flow pyrolysis of 6 at 660 °C under the same conditions as described for 5 also resulted in the formation of COS and ketene 7.

These results indicate that COS elimination from vinylene thioxocarbonates and Wolff rearrangement of the ketocarbene intermediate to ketene is probably a general process in both photolysis and pyrolysis, thus paralleling the behavior of α-diazo ketones. The advantages of using these precursors are that they are easily prepared[20,21] and can be stored in large quantities (in contrast to α-diazoacetaldehyde and o-diazophenol) and, under matrix-isolation conditions, it appears that 5 and 6 undergo complete conversion to COS + ketene, without interfering side reactions. Thus vinylene thioxocarbonates are ideal precursors for the synthesis and characterization of novel ketenes and, since the primary fragment is very likely a ketocarbene, photolysis and thermolysis of these compounds constitute a new methodology for mechanistic studies of the Wolff rearrangement.

No transient spectra which could be attributed to oxirene or benzoxirene were detected upon photolysis of 5 or 6. This result was not unexpected since oxirene was not detected in the 8 K photolysis of α-diazoacetaldehyde[8] and, in fact, is predicted to be kinetically only marginally stable.[9] Also, the solution-phase photolysis of various ^{13}C-labeled annelated α-diazo ketones[22] did not yield scrambled products, presumably because the hypothetical oxirene intermediate is further destabilized by a prohibitively high ring-strain energy. As mentioned above, however, the conformation of thioxocarbonates is favorable to the generation of oxirenes, especially under matrix conditions, and we intend to examine the photolysis of variously substituted source compounds in our efforts to isolate a stable oxirene. ESR experiments are currently under way to ascertain whether ketocarbenes are formed in photolysis.

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gem-Difluoroallyllithium: Improved Synthesis Brings Improved Applicability

Summary: The action of *n*-butyllithium in hexane on $CF_2BrCH=CH_2$/$CF_2=CHCH_2Br$ (5:2 to 20:1 mixture) in 5:1:1 THF/Et_2O/pentane at -95 °C generates *gem*-difluoroallyllithium which may be trapped, generally in good yield, by an in situ procedure using triorganochlorosilanes

($R_3SiCF_2CH=CH_2$) and aldehydes and ketones ($RR'C(OH)CF_2CH=CH_2$).

Sir: *gem*-Difluoroallyllithium (I) is of interest as a reagent which allows the introduction of a functional fluorinated substituent into organic and organometallic compounds. We have generated this reagent at low temperature by the transmetalation procedure (eq 1).[1]   The reagent is not

$$Me_3SnCH_2CH=CF_2 + n\text{-}C_4H_9Li \xrightarrow[THF]{-95\ °C}$$
$$Li[CF_2CHCH_2] + n\text{-}C_4H_9SnMe_3 \quad (1)$$
$$I$$
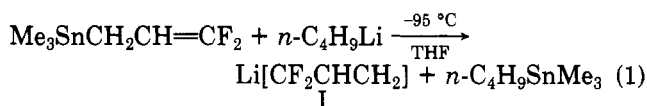
stable in solution even at -95 °C and cannot be preformed prior to its reaction with the desired substrate. Its reactions with chlorosilanes were carried out by the in situ procedure: slow addition of *n*-C₄H₉Li solution to a mixture of $Me_3SnCH_2CH=CF_2$ and the chlorosilane, so that the reagent is trapped as it is formed. The addition of Li[CF₂CHCH₂] to the C=O of 3-pentanone by the in situ procedure was not successful since the rate of *n*-butyllithium addition to the ketone is faster than its rate of displacement of the difluoroallyl substituent from tin. Addition of Li[CF₂CHCH₂] to the C=O bond of 3-pentanone to give ($C_2H_5)_2C(OH)CF_2CH=CH_2$ (75% yield) was achieved by the method of alternate, incremental additions.[1] However, this procedure is tedious and cumbersome and not well adapted to larger scale application.

In view of these difficulties with Li[CF₂CHCH₂]/carbonyl reactions and also because of the difficult, multistep preparative route to $Me_3SnCH_2CH=CF_2$, the Li[CF₂CHCH₂] precursor,[1] we sought an alternative method of generating *gem*-difluoroallyllithium.

The benzoyl peroxide induced addition of dibromodifluoromethane to ethylene in an autoclave at 80 °C was reported by Tarrant and Lovelace[2] to give CF₂BrCH₂CH₂Br. The single example of this reaction which was described[2] involved a runaway exotherm with consequent loss of most of the contents of the autoclave through the rupture disk, but we have used this reaction repeatedly without mishap. In a typical example, the yield of CF₂BrCH₂CH₂Br was 76%, based on unrecovered CF₂Br₂, which had been used in excess. Treatment of CF₂BrCH₂CH₂Br with aqueous KOH at 115-130 °C gave a 5:2 mixture (by NMR) of $CF_2BrCH=CH_2$ and $CF_2=CHCH_2Br$ in 74% yield. Slow distillation of this product mixture gave a distillate with an isomer ratio which had been increased to ca. 20:1. Either isomer mixture serves well as a precursor for *gem*-difluoroallyllithium (eq 2).[3] In

$$CF_2BrCH=CH_2 + n\text{-}C_4H_9Li \xrightarrow{-95\ °C}$$
$$Li[CF_2CHCH_2] + n\text{-}C_4H_9Li \quad (2)$$
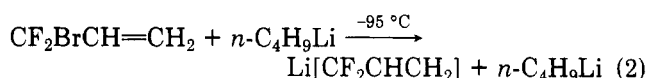
situ reactions with chlorosilanes gave moderate to good yields of 1,1-difluoroallylsilanes. In one such reaction, when 15 mmol of *n*-butyllithium in hexane was added slowly to a mixture of 19 mmol of 20:1 $CF_2BrCH=CH_2$/$CF_2=CHCH_2Br$ and 30 mmol of PhMe₂SiCl in 5:1:1 (by volume) THF/Et_2O/pentane at -95 °C (under nitrogen, with stirring for 60 min at -95 °C), $PhMe_2SiCF_2CH=CH_2$[1] was produced in 71% yield. Also prepared in this manner were $Et_3SiCF_2CH=CH_2$ (51%), *n*-$Pr_3SiCF_2CH=CH_2$ (50%), and $Me_3SiCF_2CH=CH_2$ (89%). In the case of the

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(3) In writing eq 2 we have assumed that it is CF₂BrCH=CH₂, not its isomer, which leads to Li[CF₂CHCH₂], in analogy to RLi/polyhalomethane vs. RLi/allylic halide reactions. This question, however, will be investigated in future experiments.

latter, separation from the *n*-butyl bromide formed in the Li/Br exchange reaction could not be effected by distillation. However, ethyllithium may be used in place of *n*-butyllithium to form Li[CF_2CHCH_2], and the ethyl bromide formed in the exchange is much more volatile and does not interfere in product isolation.

The real utility of this new procedure for Li[CF_2CHCH_2] lies in its applicability to [CF_2CHCH_2]$^-$ and ketone difluoroallylation. In the Me_3SnCH_2CH=CF_2/*n*-C_4H_9Li route to Li[CF_2CHCH_2] it is a matter of nucleophilic displacement of [CF_2CHCH_2]$^-$ from tin by *n*-butyllithium. This polar process is relatively slow at low temperature and cannot compete with the more rapid addition of the lithium reagent to the C=O bond. On the other hand, the lithium/halogen exchange reaction, especially when polyhalomethanes are involved, is an electron-transfer process[4] and, as such, is rapid even at low temperature in ether solvents. Therefore, one might expect that the CF_2BrCH=CH_2/*n*-C_4H_9Li reaction would proceed at a rate comparable to or even faster than *n*-butyllithium addition to the carbonyl compound. Such was found to be the case. In situ reactions in which *n*-butyllithium in hexane was added slowly to a mixture of CF_2BrCH=CH_2/CF_2=$CHCH_2Br$ and the aldehyde or ketone in 5:1:1 THF/Et_2O/pentane solvent at -95 °C (under nitrogen, with stirring for 90 min), with subsequent slow warming to room temperature and hydrolysis, gave alcohols of type RR'C(OH)CF_2CH=CH_2 in good yield (by GLC). Thus prepared were $Me_2C(OH)CF_2CH$=CH_2 (41%), $Et_2C(OH)CF_2CH$=CH_2 (70%), c-$C_6H_{10}(OH)CF_2CH$=CH_2 (59%), $PhMeC(OH)CF_2CH$=CH_2 (73%), *n*-$C_4H_9CH(OH)CF_2CH$=CH_2 (87%), and $Me_3CCH(OH)CF_2CH$=CH_2 (95%).[5]

One object of our study of the reactions of *gem*-difluoroallyllithium with carbonyl compounds was to see if its α/γ regioselectivity in C=O additions was the same as or different from that of *gem*-dichloroallyllithium, a reagent which we had prepared and investigated in an earlier study.[6] As in the case of Li[CCl_2CHCH_2], the reactions of *gem*-difluoroallyllithium with aliphatic ketones

resulted in C=C bond formation at the halogenated terminus of the reagent. However, in contrast to the results obtained in reactions of *gem*-dichloroallyllithium with aliphatic aldehydes and with acetophenone (mixtures of alcohols RR'C(OH)CCl_2CH=CH_2 and RR'C(OH)-CH_2CH=CCl_2, in which the former predominated), such reactions of *gem*-difluoroallyllithium gave only a single product of type RR'C(OH)CF_2CH=CH_2. Further work will be aimed at a more detailed comparison of the reactions of Li[CF_2CHCH_2] and Li[CCl_2CHCH_2] using a wider selection of carbonyl substrates.

The Me_3SnCH_2CH=CF_2/*n*-C_4H_9Li in situ procedure for *gem*-difluoroallyllithium also failed to give the desired result in the attempted difluoroallylation of dimethyldichlorosilane to $Me_2Si(CF_2CH$=$CH_2)_2$. Apparently the substitution of the first chlorine by *n*-butyllithium is faster than its transmetalation with the tin precursor, and Me_2(*n*-C_4H_9)$SiCF_2CH$=CH_2 was the product which was isolated.[1] In contrast, the rate of the CF_2BrCH=CH_2/*n*-C_4H_9Li reaction is faster than that of *n*-butyllithium with dimethyldichlorosilane under the conditions of our experiment, and $Me_2Si(CF_2CH$=$CH_2)_2$ was obtained in 73% yield.

Using this new and improved route for its generation, we are investigating further aspects of the chemistry of *gem*-difluoroallyllithium.

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