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Preparation and ^{13}C NMR Spectroscopy of ^{13}C-1 Labelled 2,2-Diaryl-1-fluoro-1-lithioalkenes

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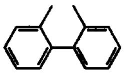
Abstract: Two ^{13}C-1 labelled 2,2-diaryl 1-fluoro-1-lithioalkenes have been synthesised. and the first ^{13}C NMR spectra of fluorocarbenoids have been obtained. © 1997 Elsevier Science Ltd.

Simple 1-fluoro-1-lithioalkenes lacking either a fluorine or trifluoromethyl group *cis*- to the lithium are difficult to study, presumably due to the strong lithium-fluorine interaction which leads to very ready Li-F scission.[1,2,3] We have recently published the preparation and first ^{19}F NMR examination of two 2,2-diaryl-1-fluoro-1-lithioalkenes **1** and **2** prepared from the corresponding 1-bromo-compounds **5** and **6** as shown in equation (1).[3] This showed that ^{19}F NMR was a valuable tool for the examination of fluorocarbenoids. Unfortunately 2,2-dialkyl-1-lithioalkenes were not sufficiently stable as to be susceptible to NMR studies, even at -120°C. We were surprised at the ^{19}F chemical shifts of **1** and **2** compared with **5**, **6** and a variety of geminal F-C-X compounds we had to hand, and felt that a ^{13}C NMR study of **1** and **2** would help to throw light on their nature. *Additionally there are no ^{13}C NMR data on such fluorocarbenoids in the literature.*

$$\underset{\textbf{5, 6, 7, 8}}{Ar_2\overset{2}{C}=\overset{1}{C}BrF} \xrightarrow[-105°C]{BuLi} \underset{\textbf{1, 2, 3, 4}}{Ar_2C=CLiF} \qquad (1)$$

1, 5 : $Ar_2 = Ph_2$; C-1 = ^{12}C; **3, 7** : $Ar_2 = Ph_2$; C-1 = ^{13}C
2, 6 : Ar_2 = BP*; C-1 = ^{12}C; **4, 8** : Ar_2 = BP*; C-1 = ^{13}C

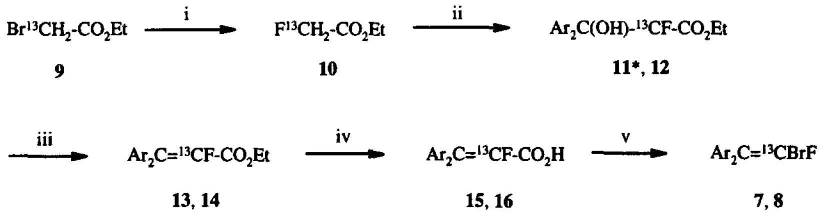
*BP =


Equation 1

The ^{13}C NMR of organyllithiums has been used as an indication of their state of association in solution at any particular temperature and solvent.[4,5] Thus at -100°C, vinyllithium is mainly tetrameric, but is dimeric in the presence of TMEDA.[4] The ^{13}C NMR spectra of a variety of geminal lithium-bromo- and lithium-chloro-compounds (carbenoids) were also studied and found to be most probably monomeric.[5]

We attempted to study the ^{13}C NMR spectra of **1** and **2** but could not obtain analysable signals due to multiple splitting leading to broad bands. To obtain a good signal, ^{13}C-1 labelled species, **7** and **8**, were required as precursors to the labelled carbenoids **3** and **4**.

We had previously produced **5** and **6** by an approach involving a Horner-Wadsworth-Emmons reaction of ethyl (diethoxyphosphoryl)fluoroacetate.[6,7] However labelled precursors such as ethyl (diethoxyphosphoryl)fluoroacetate[7] or tribromofluoromethane[8] are difficult to access. We therefore designed another synthesis (Scheme 1) starting with readily available ^{13}C-2 ethyl bromoacetate and using the lithium enolate of ^{13}C-2 ethyl fluoroacetate as the key intermediate[9].



* Substitution of **11**, **13**, **15** corresponds to **7**; **12**, **14**, **16** corresponds to **8**.
(i) KF, 18-crown-6, 140°C, 2h. (96%); (ii) Ar_2CO, HMDS-Li, THF, HMPA, -110°C (**11**, 38%, **12**, 47%); (iii) TsOH, toluene, reflux, 48h. (**13**, 98%, **14**, 81%); (iv) NaOH, dioxane, r.t., 24h. (**15**, 89%, **16**, 99%); (v) excess Br_2, $CHCl_3$, reflux, 32h. then Na_2SO_3, H_2O, r.t., 48h. for **7** (98%) and Br_2, $CHCl_3$, r.t., 12h. then $NaHCO_3$, acetone, reflux, 16h. for **8** (74%).

Scheme 1

The conversion of **9** to **10** was highly efficient making **10** readily available. The production of **11** and **12** proceeded in moderate yields but their conversions to **13** and **14** were satisfactory as was the production of **15** and **16**. The bromo-decarboxylation of **16** to **8** *via* the isolated dibromoacid was straightforward with an overall yield of 71%. The equivalent acid could not be isolated in the reaction of **15**, which on the other hand gave directly a mixture of **7** and its brominated derivative on reflux with excess of bromine. This mixture was debrominated with sodium sulfite without isolation to yield **7** in an overall yield of 95% from **15**. To our knowledge this is the first time that **10** has been used synthetically and also the first time that a ^{13}C-F grouping has been produced by any other way than direct fluorination.

Carbenoids **3** and **4** were produced from **7** and **8** respectively by reaction with butyllithium at -105°C in a mixture of THF-d_8 and THF (1:4) directly in an NMR tube. At -120°C the ^{13}C-1 signals were observed as simple doublets of quartets (Figure 1). Table 1 shows the relevant data.

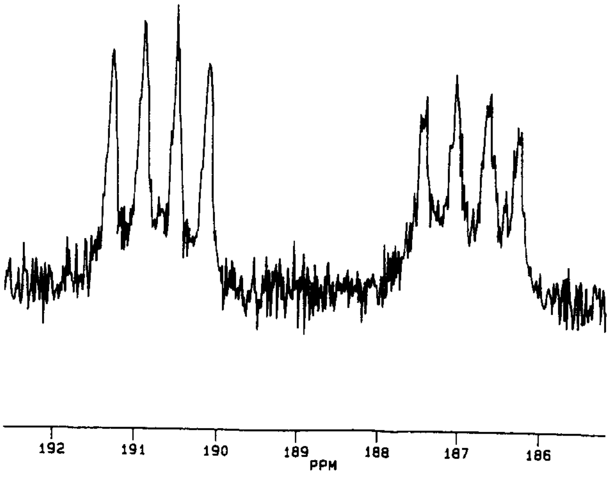


Figure 1. The ^{13}C NMR signal of C-1 of **4**

Compound	δ (ppm)	$J_{^{13}C^{19}F}$ (Hz)	$J_{^{13}C^{7}Li}$ (Hz)
3	235.4	319	40
4	188.8	386	38

Table 1 Chemical shifts and coupling constants of C-1 of **3** and **4**

The signals observed are due to couplings between ^{13}C-^{19}F (spin number, 0.5) and ^{13}C-^{7}Li (spin number, 1.5). *Hence the lithium atom is coordinated to only one carbanionic carbon and therefore the alkenylfluorocarbenoids are not associated at -120°C in THF*, in line with previous observations on bromo- and chlorocarbenoids.[5]

The labelled carbenoid carbon of **3** gave a signal at 235.4 ppm and of **4** at 188.8 ppm compared with 134.6 ppm for **7** and 133.9 ppm for **8**, the bromo precursors. Thus substitution of lithium for bromine led to *downfield* shifts of *ca* 100 and 55 ppm respectively, despite the proven[3] carbanionic character of the carbenoids. This correlates with findings on bromo- and chloro-carbenoids derived from sp^3 carbon atoms.

Very recently a model has been proposed to account for the fact that when charge is plotted against chemical shift then CH_3^+, $C_7H_7^+$, C_6H_6, $C_5H_5^-$ and CH_3^- all fall on a straight line.[10] The model also explains the remarkable downfield shifts found with carbenes.[11,12] It remains to explain the effects on the sp^2 carbenoid carbons of our series.

Acknowledgements

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