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HIGHLY CROWDED ENOLATES FROM REACTION OF DI-*tert*-BUTYLKETENE WITH ALKYLLITHIUM REAGENTS[1]

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Abstract. Di-*tert*-butylketene reacts with alkyllithiums to give enolate intermediates which can be captured by silylation or alkylation.

The reaction of ketenes with alkyllithium reagents has previously been shown to be an effective route for the generation of directed enolates which can be trapped by alkylation or silylation, as in the examples of equations 1 and 2.[2] The reported reactions of di-*tert*-butylketene (**2**) and bis(trimethylsilyl)ketene (**3**) with PhLi or *n*-BuLi, respectively, followed by hydrolysis to give ketones **4**[3] and **5**[4] (equations 3, 4), respectively, suggested that this reaction might also be valuable for the preparation of some highly crowded derivatives.

$$Et_2C{=}C{=}O \xrightarrow[\text{THF}]{n\text{-BuLi}} \underset{\mathbf{1}}{Et_2C{=}C(OLi)\text{-}n\text{-Bu}} \xrightarrow{Me_3SiCl} Et_2C{=}C(OSiMe_3)\text{-}n\text{-Bu} \qquad (1)$$

$$\mathbf{1} + MeI \longrightarrow MeEt_2CC(=O)\text{-}n\text{-Bu} \qquad (2)$$

$$\underset{\mathbf{2}}{t\text{-}Bu_2C{=}C{=}O} \xrightarrow[2)\,H_2O]{1)\,PhLi} \underset{\mathbf{4}}{t\text{-}Bu_2CHC(=O)Ph} \qquad (3)$$

$$\underset{\mathbf{3}}{(Me_3Si)_2C{=}C{=}O} \xrightarrow[2)\,H_2O]{1)\,n\text{-BuLi, THF, 25°C}} \underset{\mathbf{5}}{(Me_3Si)_2CHC(=O)\text{-}n\text{-Bu}} \qquad (4)$$

This prediction has now been confirmed reaction of 2 with t-BuLi followed by hydrolysis has been found to yield 6[5] at 25 °C (equation 5). Reaction does not occur in THF at -70 °C and at 25 °C in this solvent the ratio of 6 to

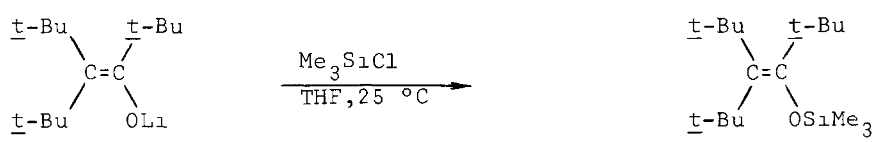
$$\underset{\mathbf{2}}{t\text{-}Bu_2C{=}C{=}O} \xrightarrow[2)\,H_2O]{1)\,t\text{-}BuLi} \underset{\mathbf{6}}{t\text{-}Bu_2CH\overset{O}{\overset{\|}{C}}\text{-}t\text{Bu}} + \underset{\mathbf{7}}{t\text{-}Bu_2CHCH{=}O} \qquad (5)$$

the aldehyde 7 resulting from reduction is 1 to 9. The ketone 8 was also isolated from this reaction mixture in 30% yield and characterized by its spectral properties, this compound evidently arose from reaction of t-BuLi with THF to give ethylene[6a] which is known to add to t-BuLi (equation 6)[6b] However

$$THF + t\text{-}BuLi \longrightarrow CH_2{=}CH_2 \xrightarrow{t\text{-}BuLi} t\text{-}BuCH_2CH_2Li \xrightarrow[2)\,H_2O]{1)\,\mathbf{2}} \underset{\mathbf{8}}{t\text{-}BuCH_2CH_2\overset{O}{\overset{\|}{C}}CH\text{-}t\text{-}Bu_2} \qquad (6)$$

when the reaction of eq 5 was conducted in hexane at 25 °C the formation of 6 was quite efficient, and gave a ratio of 6 to 7 of 5 to 1.

The presumed enolate intermediate 9 from equation 5 does not react with Me_3SiCl in hexane. However when 9 is generated in hexane and the hexane evaporated and replaced with THF, addition of Me_3SiCl gives the enol silyl ether 10[7] as the only product (equation 7)



(7)

9 10

Ether **10** is evidently the only substituted tri-*tert*-butylethylene which has been isolated and characterized.[8] Similarly this procedure represents the first recorded generation of enolate **9**, as previous treatments of **6** with base even under drastic conditions failed to give evidence for the formation of **9**.[9]

Reaction of **2** with MeLi in THF at 0 °C followed by treatment with MeI gives the ketones **11**-**13** (equation 8). This efficient alkylation of the enolate

$$\underset{\mathbf{2}}{\textit{t}\text{-}Bu_2C{=}C{=}O} \xrightarrow[\text{2) MeI}]{\text{1) MeLi}} \underset{\mathbf{11}}{\textit{t}\text{-}Bu_2MeC\overset{O}{\overset{\|}{C}}Me} + \underset{\mathbf{12}}{\textit{t}\text{-}Bu_2MeC\overset{O}{\overset{\|}{C}}Et} + \underset{\mathbf{13}}{\textit{t}\text{-}Bu_2Me\overset{O}{\overset{\|}{C}}\text{-}\textit{i}\text{-}Pr} \qquad (8)$$

t-$Bu_2C{=}C(OLi)Me$ on carbon[10] is in contrast to the result obtained with the potassium enolate of **7**, which we find gives only oxygen alkylation (equation 9).

$$\underset{\mathbf{7}}{\textit{t}\text{-}Bu_2CHCH{=}O} \xrightarrow[\text{THF, 25 °C}]{\text{KH, MeI}} \textit{t}\text{-}Bu_2C{=}CHOMe \qquad (9)$$

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(7) ^{1}H NMR (CCl_4) δ 0.14 (Me_3SiO), 1.12, 1.16, 1.21 (each *t*-Bu). ^{13}C NMR ($CDCl_3$) 4.9 (Me_3Si), 34.3, 36.4, 37.7 (Me of different *t*-Bu), 38.0, 41.2, 42.4 (quaternary C of different *t*-Bu), 138.5 (*t*-Bu_2*C*), 159.8 (*C*O).[11]

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