## COMMUNICATIONS

| Temperature<br>(°C) | Ratio of alcohol/ketone for |            |             |             |
|---------------------|-----------------------------|------------|-------------|-------------|
|                     | sec-Butyl                   | sec-Hexyl* | Cyclopentyl | Cycloheptyl |
| + 100               |                             |            |             | 2.5         |
| 75                  |                             | _          |             | 1.7         |
| +50                 |                             | 1.0        | 1.4         | 1.0         |
| + 25                | _                           | 0.63       | 0.95        | 0.83        |
| 0                   | _                           | 0.50       | 0.71        | 0.67        |
| -25                 | 0.48                        | 0.34       | 0.40        |             |
| - 50                | 0.38                        | 0.22       | 0.25        | _           |
| -75                 | 0.20                        | 0.16       | 0.14        |             |
| -100                | 0.15                        |            | 0.06        | _           |
| -125                | 0.11                        | ~          | _           | —           |

TABLE 2. Effect of temperature on the ratios of the yields of alcohol and ketone from the mutual termination of *sec*-alkylperoxy radicals

\*Ratio is (2-hexanol + 3-hexanol)/(2-hexanone + 3-hexanone) though all four products were determined separately.

[Ketone] = 0.35-0.55, instead of unity as required by reaction 3c).

The present results show that at low temperatures the mutual termination of *sec*-alkylperoxy radicals does not proceed through a cyclic transition state, as in the Russell mechanism, but through an alternative state, namely



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## C-Acetylation of Ketones

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The action of 2 equiv. of methyllithium on the monoanion of simple  $\beta$ -keto esters gives the  $\beta$ -diketone in good yield. This represents a facile and new method to achieve the C-acylation of a ketone.

La réaction de 2 équiv. de méthyllithium avec le monoanion de  $\beta$ -céto d'esters simples conduit avec de bons rendements aux  $\beta$ -dicétones. Cette approche représente une méthode nouvelle et facile pour provoquer une *C*-acylation d'une cétone. [Traduit par le journal]

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Recently we have been interested in the generation of the dianions from  $\beta$ -keto esters

(1-3) and in their chemistry (3-6). Usually we form these dianions by treating the corresponding  $\beta$ -keto esters with 1 equiv. of sodium hydride to give a monoanion which on subsequent treat-

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1379

## CAN. J. CHEM. VOL. 52, 1974

ment with 1 equiv. of *n*-butyllithium at  $0^{\circ}$  gives the dianion, for example, eq. 1 for methyl acetoacetate (1).



 $\begin{array}{c} O \\ I \\ I \\ CO_2Me \\ \hline 2 MeLi \\ \hline 0 \\ \hline 0 \\ \hline 0 \\ CO_2Me \\ \hline 2 MeLi \\ \hline 0 \\ \hline$ 

This represents a novel method to formally achieve the C-acetylation of a ketone and avoids any problems of self-condensation inherent in the Claisen reaction or difficulties with O- vs. C-acylation of the  $\beta$ -keto esters (10). Also it was found that treatment of the monoanions of **1** and **2** with 3 equiv. of methyllithium at 0° gave greater than 80% yields of the expected (8,9) tertiary alcohols **3** and **4**. In addition in these



simple cases, it appears that excess methyllithium and higher reaction temperatures are deleterious to the yield of tertiary alcohol. The availability and different reactivities of organolithium compounds (7) represent a drawback to the overall generality of these reactions and hence we are studying the reactivity of the dianions of  $\beta$ -keto esters with other organometallic reagents.

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1380



A slight excess of *n*-butyllithium at  $0^{\circ}$  does not react with these dianions. However, excess *n*-butyllithium at higher temperature does lead to a variety of carbonyl addition products (7).

Hence we were intrigued by the reports of the addition of excess methyllithium to the monoanions of fused 2-carboxymethylcyclohexanones which gave tertiary alcohols in a very clean reaction (eq. 2) (8,9). We have found that



treatment of the monoanion of simple  $\beta$ -keto esters with only 1 equiv. of methyllithium leads to formation of the corresponding dianion in very good yield (2,3). Hence, it would appear that the  $\beta$ -keto ester dianion is an intermediate in the above reaction (eq. 2). This led us to study the reaction of the monoanion of a  $\beta$ -keto ester with exactly 2 equiv. of methyllithium.

The monoanions of two simple  $\beta$ -keto esters, methyl acetoacetate (1) and methyl 2-oxocyclohexanecarboxylate (2), were prepared by treating a solution of the  $\beta$ -keto ester in dry tetrahydrofuran with 1 equiv. of sodium hydride at 0 °C. These monoanions were then treated with 2 equiv. of methyllithium in hexane at 0 °C. After a  $\frac{1}{2}$ -h period the reaction mixture was quenched with acid and worked up. A v.p.c. analysis of the crude oil indicated that a new product had been formed in greater than 90% in each case. From the reaction of methyl acetoacetate (1), pentane-2,4-dione was isolated in 80% yield as its 2,4-dinitrophenylhydrazone derivative (m.p. 207-209 °C). The analogous reaction with methyl 2-oxocyclohexanecarboxylate (2) gave 2-acetylcyclohexanone (b.p. 106-108°/15 mm) in 83% yield.

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