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GENERATION AND FATE OF T-BUTYLPOTASSIUM IN SOLUTION

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The study of carbanions in the past has been hampered by the fact that reagents most likely to contain anions, organopotassium and -cesium compounds, are insoluble in most solvents tried or react violently.

In the course of some studies on the generation of carbanions via the diimide route (1)

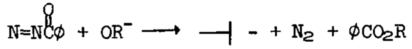
1 $$R{-}N{=}N^- \longrightarrow R^- + N_2$$

we have investigated the utility of 2,5,8,15,18,21-hexaoxatricyclo-(20.4.0.0^{9,14}) hexacosane, crown ether (2), an excellent ligand which renders many potassium salts soluble in non-polar media.

Herein, we report two examples where organopotassium compounds have been generated in solution via the diimide route, in the presence of crown ether and the resulting chemistry investigated. These examples involve the decomposition of phenylazoformate salts, 2, and the

2 $$\phi N{=}NCO_2^- \longrightarrow \phi^- + N_2 + CO_2$$

alcoxide cleavage of benzoyl-t-butyldiimide, 1, 3.



$$N{=}N\overset{O}{\overset{\|}{C}}\phi + OR^- \longrightarrow -\!\!\!\mid^- + N_2 + \phi CO_2R$$

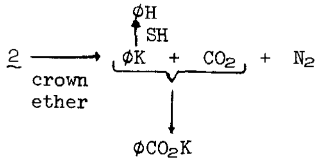
1

Phenylazoformate salts, originally reported by Thiele (3), have been used to generate phenyldiimide (4). Dry potassium phenylazoformate, 2, decomposed rapidly at 180° in vacuum to give mainly biphenyl and benzamide. The salt is insoluble in all non-polar media tried, however, in the presence of crown ether (2) it readily dissolves in THF. In contrast to the dry decomposition, when a solution of 2 and crown ether, both 0.1 M in THF, was heated at the reflux temperature for 20 minutes gas was evolved and the other products consisted of benzene and potassium benzoate. The benzene/potassium benzoate ratio increased substantially when helium was swept through the reacting solution compared to the closed system. When this reaction took place in the presence of amyl acetate a small yield of acetophenone, 0.5%, was isolated. These results clearly indicate that *at least part of the decomposition of 2 proceeds via phenylpotassium*. In separate experiments it was shown that though phenylpotassium is soluble in a mixture of crown ether and THF it rapidly abstracts protons from the medium. Evidently, the role of crown ether in the decomposition of 2 is to remove potassium ion from the vicinity of the carbanion such that reactions typical of carbanions take place.

4

$$\begin{array}{llllll} \underset{2}{\phi N_2CO_2K} & \xrightarrow[\text{crown ether}]{\text{THF}} & \phi H & + \phi CO_2K & + CO_2 + N_2 & \\ & & 50\% & 20\% & & \text{closed system} \\ & & 60\% & 10\% & & \text{He ebullition} \end{array}$$

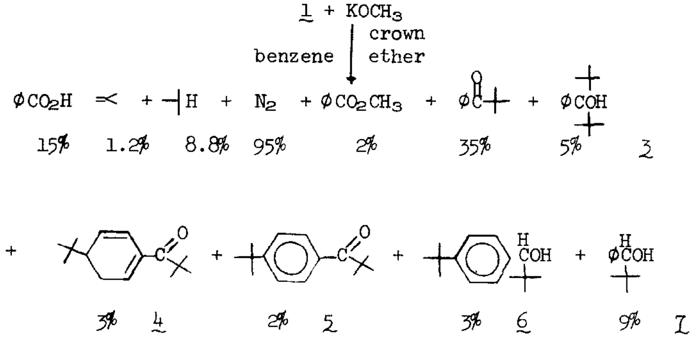
5



$$2 \xrightarrow[\text{crown ether}]{} \phi K + CO_2 + N_2;\quad \phi K \xrightarrow{SH} \phi H;\quad \phi K + CO_2 \longrightarrow \phi CO_2K$$

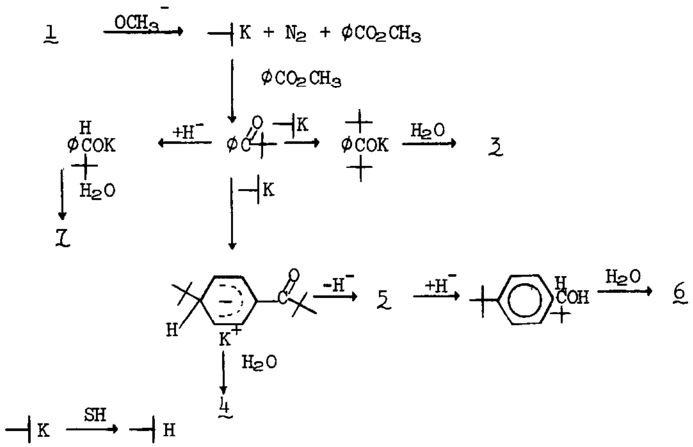
Potassium methoxide with one equivalent of crown ether dissolves readily in benzene, 0.1 M. The slow addition of one equivalent of benzoyl-*t*-butyldiimide to this solution results in the immediate evolution of nitrogen together with a mixture of ketones and alcoxides which are all soluble in the reaction medium, Chart 1. Hydrolysis and work-up yielded the compounds listed under 6, (5). This distribution of products is very similar to that obtained from the reaction of *t*-butyllithium and methylbenzoate (6).

6



There is no doubt that most of the products from reaction, 6, come from carbanion processes, i.e., initial formation of 2,2-dimethylpropiophenone followed by a series of typical carbonyl additions and hydride transfer processes outlined in Chart 1. Of special note is the considerable amount of product from ring alkylation due to steric hindrance at the carbonyl groups (7).

Chart 1



Compared to the system just described, the corresponding heterogeneous fragmentation of 1 by methoxide (1) proceeds more slowly, in lower yield, gives a smaller proportion of carbanion products (mainly ester and 2,2-dimethyl-propiophenone) together with more radical products.

From these results it appears that solvated t-butylpotassium is far more reactive in carbonyl addition reactions (70%) than in abstracting protons from the medium (10%). Unsolvated t-butylpotassium gives similar amounts of products from proton abstraction (20%) and carbonyl addition (19%).

Altogether we have found that the chelation action of crown ether renders organopotassium compounds soluble in non-polar media and makes it possible to study the chemistry of the most reactive carbanions in solution (8). These carbanions should be regarded as unperturbed by the counter ion.

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5. Analyses, nmr, ir and mass spectral data for all new compounds are in accord with the assigned structures.
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7. The benzoic acid comes from the radical fragmentation path, see Ref. 1.
8. Further examples of solvated carbanions will be published in a full paper.