Acknowledgments. We are grateful to the National Institutes of Health (MH-08912) for its support and Badische Anilin und Sodafabrik, A.G., for gifts of cyclooctatetraene.

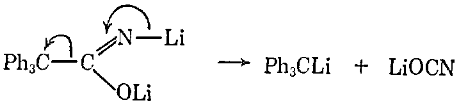
Thomas J. Katz, J. J. Cheung
Department of Chemistry, Columbia University
New York, New York 10027
Received October 1, 1969

A Novel Decarboxamidation of Certain Primary Carboxamides by Means of n-Butyllithium[1]

Sir:

We wish to report that certain primary carboxamides undergo decarboxamidation when treated with n-butyllithium. Thus 2,2,2-triphenylacetamide (**1**) in tetrahydrofuran (THF) solution was treated with 1.2 equiv of n-butyllithium in hexane. The red solution was refluxed for 6 hr to give, after work-up, a 65% yield of triphenylmethane (**2**) and 21% of recovered **1**. Starting material was quantitatively recovered when less than 1 equiv of the organolithium reagent was used.

Apparently the reaction proceeds by diionization at the carboxamide function[2] to give a species such as **3**, which undergoes carbon–carbon bond cleavage (eq 1)

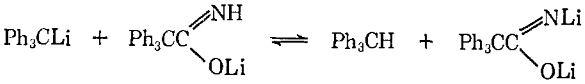


$$\mathrm{Ph_3C{-}C({=}N{-}Li)(OLi)} \longrightarrow \mathrm{Ph_3CLi} + \mathrm{LiOCN} \qquad (1)$$

3 **4**

to give trityllithium (**4**)[3] and lithium cyanate. Lithium cyanate was detected in the reaction mixture as follows. Upon work-up, the water-soluble fraction was freeze-dried to produce a solid residue. All of the bands in the ir spectrum of the residue accorded with those of an authentic mixture of lithium cyanate and lithium hydroxide, and in particular each spectrum exhibited a strong band at 4.46 μ, ascribed to cyanate.[4]

If dianion **3** is required for cleavage, it is interesting that good yields of **2** are obtained with only 1.2 equiv of n-butyllithium. In this case the reaction mixture would be expected to contain mostly monoanion **5**, along with only 20 mol % of dianion **3**. Decomposition of **3** (see eq 1) would produce trityllithium (**4**). Apparently dianion **3** and monoanion **4** are of comparable basicity,[5] and **4** can abstract a proton from monoanion **5** (eq 2).



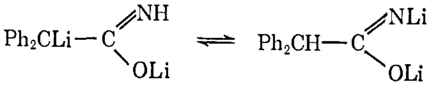
$$\mathrm{Ph_3CLi} + \mathrm{Ph_3CC({=}NH)(OLi)} \rightleftharpoons \mathrm{Ph_3CH} + \mathrm{Ph_3CC({=}NLi)(OLi)} \qquad (2)$$

4 **5** **2** **3**

The additional dianion **3** so produced then decomposes (eq 1), and so on.

Interestingly, even 2,2-diphenylacetamide (**6**) underwent a similar decomposition. Thus, treatment of **6** in THF with 1.2 equiv of n-butyllithium gave a yellow[6] solution which was refluxed 2.5 hr to give diphenylmethane in 86% yield. Again, starting material was quantitatively recovered when less than 1 equiv of n-butyllithium was used.

Although the predominant dianion in this case, **7a**, is probably that resulting from loss of the methinyl hydrogen, **7a** apparently is in equilibrium with dianion **7b** which results from diionization at the carboxamide function (see eq 3).[7] Dianion **7b** is considered to



$$\mathrm{Ph_2CLi{-}C({=}NH)(OLi)} \rightleftharpoons \mathrm{Ph_2CH{-}C({=}NLi)(OLi)} \qquad (3)$$

7a **7b**

undergo decomposition in a manner analogous to **3**.

Treatment of lithium cyanate with lithium diphenylmethide under typical reaction conditions gave only recovered starting material. The irreversibility of the overall reaction may be due to the insolubility of lithium cyanate in the medium.

Although decarboxylation of acids has often been effected through the anion, the analogous reaction of primary carboxamides has not been reported. The decompositions reported in the present paper appear to be the first examples of decarboxamidation[8] effected through ionization. This novel type of reaction should be useful in synthesis. Further studies are in progress on the scope, mechanism, and synthetic utility of this reaction.

Acknowledgment. We thank the National Science Foundation for the award of a Science Faculty Fellowship (to H. A. S.).

---

[1] Supported by the National Science Foundation.

[2] Trianions previously prepared from phenyl- and diphenylacetamide with n-butyllithium [see E. M. Kaiser, R. L. Vaulx, and C. R. Hauser, *J. Org. Chem.*, 32, 3640 (1967)] involved diionization at the carboxamide function.

[3] The red color observed in the reaction mixture is characteristic of $\mathrm{Ph_3CLi}$ in THF.

[4] See L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1958, p 267.

[5] Some support for this assumption is given by the fact that the monoanion of **2** ($\mathrm{p}K = 33$) is expected to be much more basic than the monoanion of **1** ($\mathrm{p}K \sim 25$).

[6] The color is characteristic of $\mathrm{Ph_2CHLi}$ in THF.

[7] Support for existence of an appreciable quantity of **7b** at equilibrium is afforded by previous results (see Kaiser, *et al.*, ref 2), confirmed in the present study, that treatment of the dilithio salt of **6** with excess deuterium oxide incorporates only 0.7 methinyl deuterium atom per molecule.

[8] Loss of the carboxamide group as urea has been reported for certain α,β-acetylenic carboxamides upon treatment with amide ion [J. C. Craig and M. Moyle, *J. Chem. Soc.*, 4402 (1963)]; however, this cleavage is nucleophilic acyl substitution by amide ion.

Homer A. Smith, C. R. Hauser
The Paul M. Gross Chemical Laboratory, Duke University
Durham, North Carolina 27706
Received October 23, 1969

Nitrogen Inversion without Retarding Factors[1]

Sir:

Angle strain[2] and electronegative substituents[3] have been widely utilized to bring the rate of nitrogen inversion within the range of dynamic nuclear magnetic resonance (dnmr) methods.[4] Because of the difficulty in

---

[1] This work was supported by the National Science Foundation (Grant GP-9257) and by the Petroleum Research Fund, administered by the American Chemical Society (PRF 2970-A4,5).

[2] A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, 78, 5126 (1956).

[3] J. M. Lehn, B. Munsch, P. Millie, and A. Veillard, *Theoret. Chim. Acta*, 13, 313 (1969); D. L. Griffith and B. L. Olson, *Chem. Commun.*, 1682 (1968). The more important factor may actually be the presence of lone pairs on these substituents.

[4] G. Binsch, *Topics Stereochem.*, 3, 97 (1968). For an alternative procedure, see L. B. Holzman, Ph.D. Dissertation, Yale University, 1968.