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.

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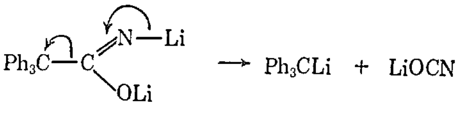
A Novel Decarboxamidation of Certain Primary Carboxamides by Means of *n*-Butyllithium[1]

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)

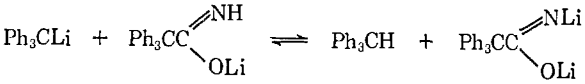


$$Ph_3C{-}C(=N{-}Li)OLi \longrightarrow Ph_3CLi + LiOCN \qquad (1)$$

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).



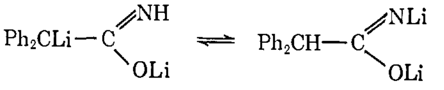
$$Ph_3CLi + Ph_3CC(=NH)OLi \rightleftharpoons Ph_3CH + Ph_3CC(=NLi)OLi \qquad (2)$$

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



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

7a 7b

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.).

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[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 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 (pK = 33) is expected to be much more basic than the monoanion of 1 (p$K \sim 25$).

[6] The color is characteristic of 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.

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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

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[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).

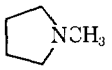
[2] A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 5126 (1956).

[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.

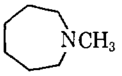
[4] G. Binsch, *Topics Stereochem.*, 3, 97 (1968). For an alternative procedure, see L. B. Holzman, Ph.D. Dissertation, Yale University, 1968.

experimentally differentiating between nitrogen inversion and rotation about N–X bonds in many of these systems,[5] it has become increasingly important to have specific and independent information about both processes. We wish to report the first dnmr examples of nitrogen inversion in which angle and steric constraints have been removed and nitrogen is bonded only to saturated carbon atoms.

In order to dissociate the inversion process from single-bond rotations, open-chain systems were excluded from this study.[6] To avoid ambiguities with ring reversal,[7] six-membered rings were not used. We therefore selected N-methylpyrrolidine (I) and N-methylhomopiperidine (II) for our investigations.



I



II

Pseudorotation of the ring is the only conceivably competitive process. Particularly for five-membered rings, but also for seven-membered rings,[8] this process is of such low energy that it should not be and has not been observed on the nmr time scale.[9]

When nitrogen inversion is rapid, the α protons of I or II in Freon 22 ($CHClF_2$) are magnetically equivalent on the average and give rise to a second-order triplet, which becomes a sharp singlet when the resonance frequency of the β protons is irradiated.[10] As the temperature is lowered, the α-proton resonances reversibly broaden and ultimately produce two well-separated groupings, corresponding to the protons *cis* and *trans* to methyl. The coalescence temperature for N-methylpyrrolidine (I) is about $-100°$ ($\nu_{AB} = 1.08$ ppm), and for N-methylhomopiperidine (II) it is about $-125°$ ($\nu_{AB} = 0.49$ ppm). From these data, the free energies of activation were found to be about 8 kcal/mol for I and 7 kcal/mol for II.[11] These values correspond to the barrier to nitrogen inversion unconstrained by small valence angles or lone-pair bearing substituents.

A number of compounds were examined as controls. The spectra of pyrrolidine (III) and of homopiperidine (IV) in $CHClF_2$ were unchanged down to $-150°$. Atomic inversion is not expected to perturb the spectra of these compounds in this temperature range, both because the proton on nitrogen is exchanging fast[12] and because secondary amines invert more rapidly than tertiary amines.[13] If the spectral changes of I and II had been due to pseudorotation, III and IV should have exhibited similar changes. The absence of such changes is therefore consistent with a rapid pseudorotation process. The spectrum of tetrahydrofuran, in agreement with this conclusion, is also unchanged above $-150°$.

Ring reversal has previously been studied in N-methylpiperidine-3,3,5,5-d_4 (V).[14] The coalescence temperature for this process was found to be about $-30°$. Since the internal C–N–C angle for V should be bracketed by those of I and II,[15] the activation energy for the pure nitrogen inversion should also be bracketed by those for I and II. We observed no further changes in the methyl or the α-proton resonances for V down to $-150°$. The absence of spectral changes could result either from conformational biasing (although the ratio is only 10:1) or from chemical shift differences that are too small for observation. Alternatively, the atomic inversion process may have been appreciably altered by the operation in the same molecule of the ring reversal.[16]

We are continuing our studies in the five- and the seven-membered series in order more fully to delineate the nature of pure nitrogen inversion as a function of substituent.

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(5) (a) D. L. Griffith and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 4089 (1965); (b) M. Raban and G. W. J. Kenney, Jr., *Tetrahedron Lett.*, 1295 (1969).

(6) M. Raban, F. B. Jones, Jr., and G. W. J. Kenney, Jr., *ibid.*, 5055 (1968).

(7) J. B. Lambert and W. L. Oliver, Jr., *ibid.*, 6187 (1968). We prefer the term "ring reversal" to "ring inversion" in order to avoid confusion with the phrase "nitrogen inversion." In the latter context, "inversion" is adequately descriptive, but in the former it is somewhat of a misnomer, since ideally the term should refer only to configuration and not to conformation.

(8) J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961).

(9) This statement would not be correct for geminally disubstituted or certain unsaturated seven-membered rings.[4] The exclusion of the pseudorotation alternative, although almost certain for I, thus cannot be considered rigorous for II (however, *vide infra*).

(10) All nmr spectra were taken on the Bruker HFX-10 90-MHz spectrometer, which was purchased by an equipment grant from the National Science Foundation.

(11) A complete line-shape analysis is in progress.

(12) G. A. Yousif and J. D. Roberts, *J. Am. Chem. Soc.*, **90**, 6428 (1968).

(13) G. W. Koeppl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, *ibid.*, **89**, 3396 (1967).

(14) J. B. Lambert, R. G. Keske, R. E. Carhart, and A. P. Jovanovich, *ibid.*, **89**, 3761 (1967).

(15) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1965, p 198.

(16) Evidence for concurrent and cooperative processes has been presented by J. J. Delpeuch, Y. Martinet, and B. Petit, *J. Am. Chem. Soc.*, **91**, 2158 (1969).

(17) Alfred P. Sloan Foundation Fellow, 1968–1970.

(18) National Science Foundation Trainee, 1966–1967; National Institutes of Health Fellow, 1968–1970 (Fl GM-39,218).

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Bredt's Rule. IV.[1] Bicyclo[3.2.2]non-1-ene and Bicyclo[3.2.2]non-1(7)-ene, Examples of Bridged *trans*-Cycloheptenes

In previous papers we have outlined criteria for the qualitative estimation of the strain of bridgehead olefins.[1,2] Briefly, we have postulated that bicyclic olefins with bridgehead double bonds endocyclic in rings of at least eight members should be stable enough to permit their isolation and purification at normal temperatures, and that reaction intermediates with bridgehead double bonds should be possible if the double bond is endocyclic in a ring of at least seven members.[3] We have put this postulate to the test by synthesizing, isolating, and characterizing three bicyclic olefins, **1**,[2,4] **2**, and **3**,[5] which have bridgehead double bonds endocyclic in eight-membered rings. Two additional ex-

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(1) Part III: J. R. Wiseman and W. A. Pletcher, *J. Amer. Chem. Soc.*, in press.

(2) J. R, Wiseman, *ibid.*, **89**, 5966 (1967).

(3) In at least three cases the existence of intermediates with bridgehead double bonds endocyclic in six-membered rings has been claimed: (a) S. Beckman and O. S. Ling, *Ber.*, **94**, 1899 (1961); (b) P. C. Guha, *ibid.*, **72B**, 1359 (1939); (c) S. F. Campbell, R. Stephens, and J. C. Tatlow, *Tetrahedron*, 21, 2997 (1965).

(4) J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, **89**, 5965 (1967).

(5) J. R. Wiseman, H.-F. Chan, and C. Ahola, *ibid.*, **91**, 2812 (1969).