



Pergamon

Tetrahedron Letters 41 (2000) 599–602

TETRAHEDRON
LETTERS

Concerning the ‘Wanzlick equilibrium’

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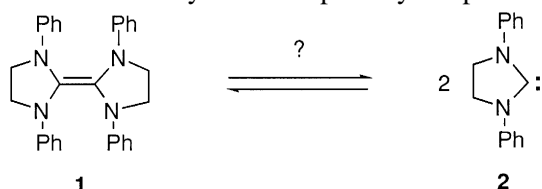
Received 20 October 1999; accepted 18 November 1999

Abstract

A negative crossover experiment performed in the 1960s which ruled out Wanzlick’s tetraaminoethylene–diaminocarbene equilibrium gave erroneous results, according to a recent claim by Denk. In response, this system has been reinvestigated. When potassium hydride is present to preclude electrophilic catalysis, no crossing over occurs and starting tetraaminoethylenes are recovered unchanged. The original conclusion regarding the proposed equilibrium is thus reaffirmed. © 2000 Elsevier Science Ltd. All rights reserved.

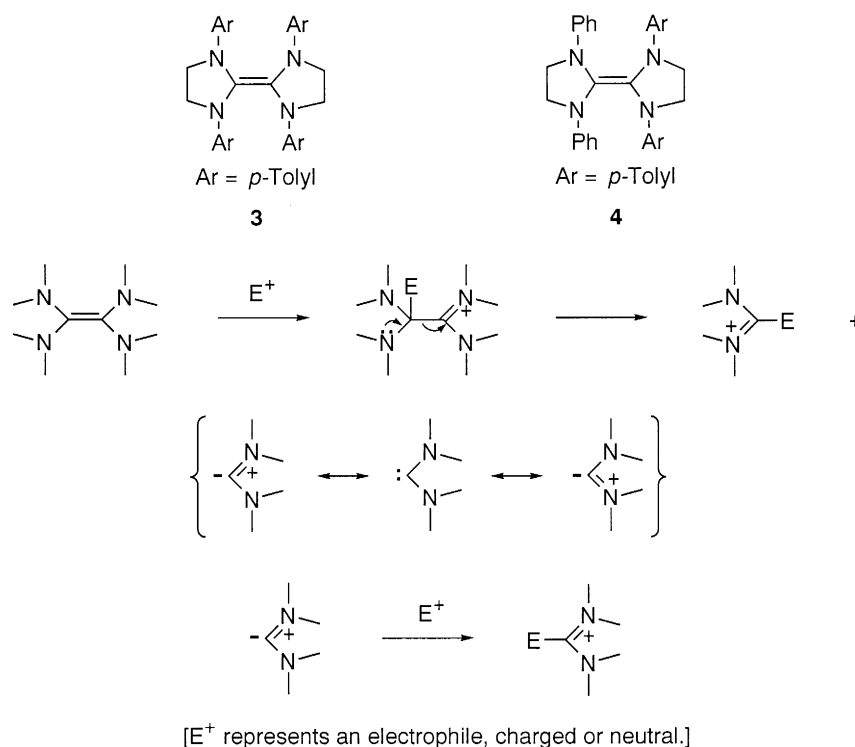
Keywords: carbenes; equilibrium; exchange reactions; catalysis.

In 1960 Wanzlick synthesized tetraaminoethylene **1**¹ and explored its interesting chemistry extensively throughout the following decade. He postulated early on that **1** dissociates readily and reversibly into its diaminocarbene ‘halves’ (**2**). This conclusion was based on a Rast molecular weight determination and the fact that reactions of **1** with a wide variety of electrophiles yield products formally derived from **2**.²



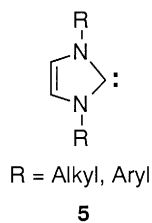
In 1964 Lemal et al. carried out a crossover experiment that showed that this equilibrium does not exist to a detectable extent under conditions more vigorous than those of Wanzlick’s reactions.³ Specifically, when an equimolar mixture of **1** and its *p*-tolyl analog **3** was heated at 140°C in xylene for 2 h, starting materials were recovered, uncontaminated with any of the independently synthesized crossover product **4**. The following year, Winberg et al. performed a similar experiment on *N*-alkyl analogs of **1** at 175°C and again found no crossing over.⁴ Lemal’s group proposed that electrophiles cleave tetraaminoethylenes via the pathway shown in Scheme 1.³

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Scheme 1.

Since Arduengo's striking discovery in 1991 that a diaminocarbene can be a stable, isolable molecule that shows no tendency to dimerize,⁵ a large number of diaminocarbenes have been isolated. Though some are only stable kinetically, carbenes of the type **5** are thermodynamically stable against dimerization.⁶ In light of these findings, Denk has recently reinvestigated the work of Lemal and Winberg with carefully purified tetraaminoethylenes.⁷ He has observed crossing over in each of the systems examined in the 1960s, and he interprets the results as strong evidence for the equilibrium Wanzlick proposed.



A trace impurity, however nefarious, could not prevent the occurrence of a unimolecular dissociation, and therefore could not prevent crossover. On the other hand, it could catalyze crossing over, for example by cleaving a tetraaminoethylene as in Scheme 1. When a unimolecular dissociation is in question, then, a negative crossover experiment makes a compelling statement, but a positive one is suspect unless catalysis can be convincingly ruled out.

We have therefore reexamined the question of crossover with the tetraaminoethylenes used in the 1964 experiment. Samples of **1** and **3** were dissolved in benzene-*d*₆ in a glove box and transferred to NMR tubes which were then flame-sealed under nitrogen. The reaction mixtures could be monitored most effectively by observing the methylene proton singlets at δ 3.37 for **3**, 3.29 for **1** and 3.34, 3.32 ppm for

4.⁸ After 6 h at 100°C we found considerable crossover product (19%, 38% of the way to a statistical mixture). Under these conditions with THF-d₈ as solvent, Denk observed complete equilibration.

In order to forestall electrophilic catalysis,⁹ we repeated the experiment several times with the addition of some potassium hydride.¹⁰ Now starting materials remained at their initial concentrations within experimental error (by integration against an internal standard) after 8 h at 140°C in toluene-d₈, and no trace of **4** was found.^{11,12} In another experiment, no crossover product could be detected after 22 h at 140°C in benzene-d₆, and >90% of the starting tetraaminoethylenes remained unchanged.¹³ The conclusion reached 35 years ago that the ‘Wanzlick dimer’ does not dissociate at a significant rate at temperatures as high as 140°C is thus reaffirmed. The striking contrast in stability (relative to their dimers) between carbenes like **2** and those of type **5**, which enjoy delocalization, is reaffirmed as well.¹⁴

From the absence of crossover product after 22 h at 140°C, it follows that the rate constant for dissociation of the ‘Wanzlick dimer’ **1** must be less than $1 \times 10^{-6} \text{ s}^{-1}$; thus $\Delta G^\ddagger > 35 \text{ kcal/mol}$ at this temperature. Since the ΔS^\ddagger for dissociation is probably positive, ΔH^\ddagger should be greater yet. The bond enthalpy of the central bond of **1** is expected to be significantly less than ΔH^\ddagger , however, based on Alder’s work with bis(*N*-piperidyl)carbene.¹⁵ He has estimated that ΔG^\ddagger for the exoergic dimerization of this carbene is at least 24 kcal/mol at room temperature. Allowance must be made for the negative entropy contribution to this value and for the likelihood that bis(*N*-piperidyl)carbene is present as a lithium complex in solution.¹⁶ Nonetheless, Alder’s finding implies a substantial activation enthalpy for the dimerization of the free carbene, and that energetic price must be added to the bond enthalpy to get ΔH^\ddagger for dissociation of the carbene dimer. A comparable price may be required for dissociation of the ‘Wanzlick dimer’ **1**.

Dimers **1** and **3** used in the present study were made by heating *N,N'*-diarylethylenediamines with triethyl orthoformate.¹⁷ In the original work, the dimers were prepared from imidazolium salts using the strong, hindered base triphenylcarbinol oxide.³ Perhaps that difference in origin explains why the early crossover experiment was not subverted by electrophilic catalysis.

Acknowledgements

The authors thank the donors of the Petroleum Research Fund administered by the American Chemical Society for support of this research (ACS-PRF#31542-AC4). Preliminary experiments were carried out under the National Science Foundation, grant no. CHE-9530352.

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11. The hydride had no influence on the tetraaminoethylene NMR spectra.
12. Again no **4** could be detected when the experiment was carried out at 160°C for 5.5 h, but there was considerable loss of starting material at this temperature.
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