Evidence for an Imine-Carbodiimide 1,2-Cycloaddition Adduct

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Sir:

Several articles have appeared recently which describe 1,2-cycloaddition reactions of unsaturated molecules and heterocumulenes (1,2,3,4). However, no literature reference to a 1,2-cycloaddition of imines and carbodiimides exists. We have observed evidence for such a cycloaddition.

In a study of the thermal decomposition of a mixture of diazetidines **1** and **2** of known composition (5) when the heating period was much longer than needed for complete decomposition of **1** and **2** (5), the three carbodiimides **5**, **6**, and **7** and imines **3** and **4** were obtained (Scheme I). Hinton and Webb have shown that unsym-

SCHEME I

Ar = p-Tolyl
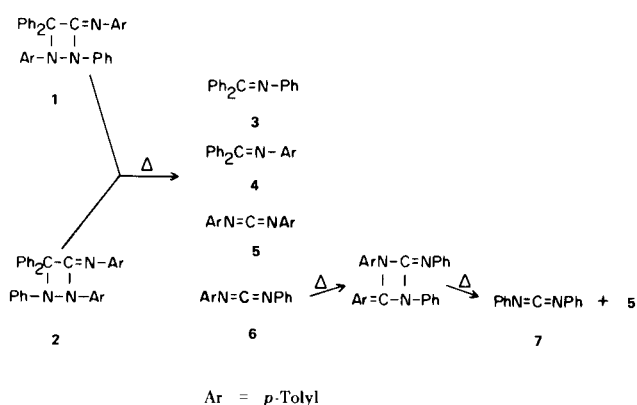
metrical carbodiimides disproportionate through dimeric structures (6). Thus **6** which is a product of the decomposition of **1** is responsible through disproportionation for **7** and **5**, the remaining carbodiimide, can arise from either **2** or **6**.

Imine **4** should have been 65% of the imine fraction - the value obtained from shorter heating periods (5). However, under these conditions **4** proved to be only 57% of the imine fraction. Although this difference could be due to greater thermal stability of **3** compared to **4**, the possibility also exists that a series of reactions as shown in Scheme II is operative. To test this **4** and **7** were heated in a sealed tube for 18 hours at 220°. The contents of

SCHEME II
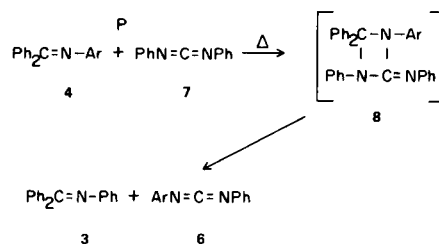
the sealed tube were taken up in benzene and analyzed by vpc on a 4 foot column of 15% SE 30 on Chromat CE. No evidence of a residue was obtained. The ratio of imines, identified from known retention times (5), was determined from peak areas. The resulting mixture contained 68% imine **3** and 32% imine **4**. Although thermal stabilities may be partially responsible for the imine ratio through the reactions illustrated by Scheme I, the concept can not apply to the reaction of **4** and **7**. Therefore, we propose that the reaction is proceeding through the 1,3-diazetidine, **8**, which we were unable to isolate. Again all three carbodiimides (**5**, **6**, and **7**) were obtained because of the disproportionation reaction; however, only adduct **8** can account for the appearance of both imines (7).

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(7) One of the Reviewers was concerned that diphenylcarbodiimide might arise from Ph_2C-C=NPh. This adduct could come from either a cycloaddition of Ph_2C=C=NPh and ArN=NPh or PhN=C=NPh and Ph_2C=NAr. Since ketenimines have not been shown to rearrange, no process exists for the production of Ph_2C=C=NPh. Thus, this adduct could only come from the condensation of the imine and carbodiimide which is the postulation of this communication.