The Thermal (6+4)π Co-cycloaddition of *N*-Alkoxycarbonylazepines: Crystal Structure Analysis of a Derived Monomethiodide

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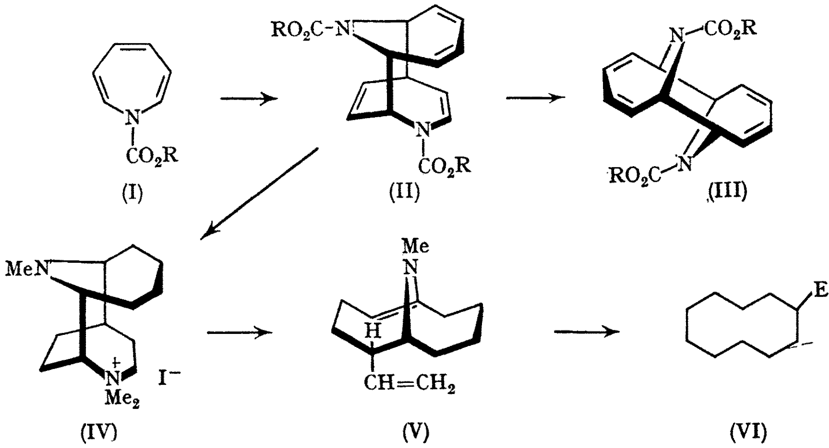
PAQUETTE AND BARRETT[1] reported that *N*-ethoxycarbonylazepine displays a marked proclivity for unprecedented two-stage dimerization, since when it has been found that this unusual thermal self-condensation is a general reaction for a number of *N*-alkoxycarbonylazepines. Thus, when an 8π heterocycle (I) is heated at 125° to 130° for short periods, it gives a dimeric white solid (II), which when briefly heated at 200° gives a new crystalline dimer (III). The structure of (III) was determined from spectroscopic data, chemical intercorrelation,[2,3] and an *X*-ray analysis of its di-*N*-methyl congener.[4] However, the indicated structure of (II) was assigned tentatively on the basis of preliminary chemical and theoretical evidence.[1] We now report evidence for the correctness of the (6 + 4)π *exo*-formulation for these dimers (II) and (III).

Initially, the several unsymmetrical dimers (II) were hydrogenated, reduced with lithium aluminum hydride, and selectively quaternized with methyl iodide to give the same monomethiodide (IV). Double Hofmann degradation of (IV) led to the formation of the vinyl enamine (V) which, by virtue of a series of sequential catalytic hydrogenations and Hofmann degradations, was ultimately converted to ethylcyclodecane (VI).† The isolation of this hydrocarbon (VI) is conclusive proof that the dimerization at moderate temperatures is the result of a (6 + 4)π cycloaddition.



The stereochemistry of dimer (II) was derive dfrom a three-dimension X-ray analysis of the methodide (IV): $C_{15}H_{29}N_2^+\ I^-$, $M = 364{\cdot}3$, monoclinic, $a = 7{\cdot}42(4)$, $b = 16{\cdot}38(4)$, $c = 13{\cdot}26(3)$ Å, $\beta = 90° 20' (20')$, $D_m = 1{\cdot}48(2)$ g.cm.$^{-3}$, $Z = 4$, $D_c = 1{\cdot}51$ g.cm.$^{-3}$; Mo-K_α radiation ($\lambda = 0{\cdot}7107$ Å), precession camera at 4°. Systematic absences, $h0l$, when $h + l = 2n + 1$, and $0k0$, when $k = 2n + 1$, determine the space group as $P2_1/n(C_{2h}^5$, no. 14). The structure was determined from 831 independent structure amplitudes estimated visually from equi-inclination Weissenberg photographs (Cu-K_α) taken at 4°. At present, the R-factor is 0·15 on all observed reflexions. A view of the molecule is shown in the Figure. This result establishes the stereochemistry of the unsymmetrical dimer as shown in (II).

FIGURE. *Stereoscopic view of the perhydromethiodide* (IV) *looking along the b-axis.*

Now that the structural features of the dimer (II) have been revealed, it is clear that orbital symmetry correlations[5] play a significant role in the initial co-cycloaddition of two such azepine molecules. Although a limited number of other (6 + 4)π cycloadditions have recently been discovered,[6] the present example represents the first instance wherein the same molecule functions as both the 6π and 4π components.

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† All new compounds gave satisfactory analytical data and displayed the proper spectral characteristics.

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