## KETENAMINALS AS 1,3-DINUCLEOPHILES IN THE SYNTHESIS OF CONDENSED

1,4-DIAZINES AND 1,2,4-TRIAZINES

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Enamines and ketenaminals (KA) are commonly used in Diels-Alder reactions with reversed electronic requirements in transformations of 1,2,4-triazines and other azadienes by the action of electron-rich olefins [1].

We report some features of the chemical behavior of KA containing an NH<sub>2</sub> group, which are also capable of acting as C,N-dinucleophiles. The action of KA (1) on 3-morpholino-l-ethyl-1,2,4-triazinium tetrafluoroborate in ethanol does not give [4 + 2] cycloaddition but rather nucleophilic C,N-diaddition, leading to 1,4,4a-7a-tetrahydropyrrolo[3,2-e]-1,2,4-triazine (III). The cyclization of KA (I) with l-methylquinoxalinium iodide (IV) in ethanol in the presence of Et<sub>3</sub>N or Et<sub>2</sub>NH also leads to fusion of a pyrrole ring and the generation of pyrrolo[2,3-b]quinoxaline (V).



The orientation of the pyrrole ring in (III) and (V) was unequivocally established by selective spin decoupling of the angular protons with the NH protons.

The yield of (III) was 76%, mp 140-142°C (dec.). PMR spectrum in DMSO-d<sub>6</sub> ( $\delta$ , ppm, J, Hz): 1.05 t (CH<sub>3</sub>), 2.09 s (COCH<sub>3</sub>), 3.00 m (CH<sub>2</sub>), 3.40 m (NCH<sub>2</sub>), 3.65 m (OCH<sub>2</sub>), 5.01 d.d (H<sup>4</sup>a, <sup>3</sup>J<sub>4</sub>a,<sub>7a</sub> = 9.5, <sup>3</sup>J<sub>4</sub>a,<sub>a</sub> = 3.1), 5.52 d.d (H<sup>7a</sup>, <sup>3</sup>J<sub>4</sub>a,<sub>7a</sub> = 9.5, <sup>3</sup>J<sub>7a,7</sub> = 1.5), 7.58 m and 7.92 m (C<sub>6</sub>H<sub>5</sub>), 8.85 br. d (H<sup>7</sup>, <sup>3</sup>J<sub>7,7a</sub> = 1.5), 9.24 br. d (H<sup>4</sup>, <sup>3</sup>J<sub>4</sub>,<sub>4a</sub> = 3.1), 10.08 br. s (NH<sup>+</sup>), 13.78 br.s (NHCO).

The yield of (V) was 42%, mp 145-147°C (dec.). PMR spectrum in DMSO-d<sub>6</sub> ( $\delta$ , ppm, J, Hz): 2.16 s (COCH<sub>3</sub>), 2.74 s (NCH<sub>3</sub>), 4.19 d (H<sup>3a</sup>, <sup>3</sup>J<sub>3a,9a</sub> = 6.4), 5.54 br.d.d (H<sup>9a</sup>, <sup>3</sup>J<sub>9a,3a</sub> = 6.4, <sup>3</sup>J<sub>9a,9</sub> = 4.1), 6.01 br.d (H<sup>9</sup>, <sup>3</sup>J<sub>9,9a</sub> = 4.1), 6.62 s (COC<sub>6</sub>H<sub>5</sub>), 7.3-8.1 m (other arom.), 8.48 br.s (H<sup>1</sup>), 13.14 br.s (NHCO).

KA (I) with mp 163-164°C was obtained by the action of methanol on PhCONH(NH<sub>2</sub>)C=CAc<sub>2</sub> [2] in the presence of  $Co(OAc)_2 \cdot 4H_2O$ .

## LITERATURE CITED

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