## NOVEL REACTIONS OF 1-(1-PYRROLIDINYL)ACENAPHTHYLENE WITH DIPHENYLCYCLOPROPENONE AND DIPHENYLCYCLOPROPENETHIONE

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An enamine, 1-(1-pyrrolidiny1) acenaphthylene, reacts with diphenylcyclopropenone to give  $\delta$ -aminocyclopentenone derivative together with a trace amount of acecyclone. In the reaction of the enamine with diphenylcyclopropenethione, however,  $\gamma$ -aminocyclopentenethione derivative is formed as the major product accompanied by another 1:1 adduct which was tentatively assumed to be a benzothiophene derivative.

It has been shown that reactions of acyclic and cyclic enamines with diphenylcyclopropenone (1) and diphenylcyclopropenethione (2) proceed via ylides A and betaines B to afford amides and thioamides, which were designated as arising from "C,N-insertion", as principal products.<sup>1-7</sup> In some reactions with 1 these are accompanied by  $\delta$ -aminocyclopentenones,  $\beta$ -aminoenones and cyclopentenones arising from "addition", "C,C-insertion" and "condensation", respectively (Scheme 1).



## Scheme 1

In this paper we wish to report a dramatic change in the course of the reaction of an enamine, 1-(1-pyrrolidiny1) acenaphthylene  $(\underline{3})^8$ , with  $\underline{1}$  and  $\underline{2}$ .

When enamine 3 was allowed to react with an equimolar amount of 1 in benzene under nitrogen, a 1:1 adduct 4 [mp 232-234<sup>o</sup>C (dec), yellow prisms] was obtained as the major product together with a trace amount of acecyclone 5 [mp 293-294<sup>o</sup>C (lit.<sup>9</sup> mp 289-290<sup>o</sup>C] which was identical with an authentic sample prepared from acenaphthenequinone and dibenzyl ketone.<sup>9</sup> On the basis of spectral data<sup>10</sup> and of the chemical conversion, the major product 4 was assigned as  $\delta$ -aminocyclopentenone derivative which corresponds to a compound arising from "addition" in Scheme 1. Reduction of  $\underline{4}$  with LiAlH<sub>4</sub> in THF at room temperature for 7 h afforded a 98% yield of  $\alpha$ -aminocyclopentanone derivative 6 [mp 226-227<sup>o</sup>C (dec), colorless prisms] whose structure was confirmed on the basis of spectral data.<sup>11</sup>





On the other hand, 2 proved to be more reactive toward 3 than 1, and reacted with 3 to give a mixture of two 1:1 adducts  $\chi$  [mp 153-158°C (dec), green leaflets] and 8 [mp 219-221°C (dec), pale yellow crystals].<sup>12</sup> Reduction of the major product  $\chi$  with NaBH<sub>4</sub> in EtOH at room temperature for 3 h afforded a dihydro compound 9 [mp 183-184°C (dec), yellow prisms] in 91% yield. Structural elucidation of 9 was accomplished on the basis of spectral data; the <sup>1</sup>H NMR spectrum exhibited signals ascribable to two vicinal methine protons and a thiol proton.<sup>13</sup> It is thus evident that  $\chi$  is  $\gamma$ -aminocyclopentenethione derivative. No  $\gamma$ -aminocyclopentenethiones have so far been formed in the reactions of enamines with 2.

Contrary to  $\underline{Z}$ , the minor 1:1 adduct  $\underline{8}$  was negative for the color-test reaction with silver perchlorate<sup>14</sup>; this implies that there is no thiocarbonyl group in  $\underline{8}$ . On the basis of spectral data<sup>12</sup> and of the mode of formation described later,  $\underline{8}$  was tentatively assumed to be a benzothiophene derivative, either <u>8a</u> or <u>8b</u>. It is noteworthy that a dramatic change of regiochemistry occurs in the course of the reaction of 3 with 1 and 2.

Although in the reactions of certain bicyclic enamines with  $1 \delta$ -aminocyclopentenones were obtained as major products together with "C,N-insertion" products, <sup>15</sup> generally enamines react with 1 and 2 to give "C,N-insertion" products via ylides <u>A</u> and betaines <u>B</u> (Scheme 1), and examples of stable betaines <u>B</u> have been reported. <sup>5-7</sup> In the reactions of 1 and 2 with 3, however, no "C,N-insertion" products were formed.

We now wish to postulate the pathways for novel reactions of 1 and 2 with 3 as outlined in Scheme 3. The reaction of 1 with 3 proceeds via betaine C arising from an attack of the  $\beta$ -carbon atom of 3 on the carbon atom at 1-position of 1, followed by cyclization with concurrent ring opening of the three-membered ring to give the major product 4. Contrary to the reaction of 1 with 3, 3 attacks on





the thiocarbonyl carbon atom of 2 to yield betaine D, and subsequent cyclization of D with ring opening of the three-membered ring gives the major product Z. It is reasonable to exclude the pathway via ylides E and betaines F, since neither "C,N-insertion" products nor betaines F were formed in both reactions (Scheme 2).

The formation of the minor product 5 can be easily interpreted as arising from a ring expansion of [2 + 2] cycloadduct 6 with concurrent elimination of pyrrolidine. On the other hand, the formation of the minor product 8 might be explained as follows. Ring closure between the thiocarbonyl group and either phenyl group occurs in [2 + 2] cycloadduct  $\underline{H}$  (path a or b), and subsequent ring expansion and hydrogen shift furnish 8a or 8b.<sup>16</sup>

References

- 1. M. A. Steinfels and A. S. Dreiding, Helv. Chim. Acta, <u>55</u>, 702 (1972).
- 2. V. Bilinski, M. A. Steinfels, and A. S. Dreiding, ibid., <u>55</u>, 1075 (1972).
- 3. V. Bilinski and A. S. Dreiding, ibid., 55, 1271 (1972).
- 4. M. A. Steinfels, H. W. Krapf, R. Riedl, J. Sauer, and A. S. Dreiding, ibid., 55, 1759 (1972).
- 5. Th. Eicher and S. Böhm, Tetrahedron Lett., 1972, 2603.
- 6. Th. Eicher and S. Böhm, Chem. Ber., <u>107</u>, 2186 (1974).
- 7. Th. Eicher and S. Böhm, ibid., <u>107</u>, 2215 (1974).
- 8. O. Tsuge and H. Watanabe, Bull. Chem. Soc. Jpn., <u>52</u>, 641 (1979).
- 9. W. Dilthey, I. ter Horst, and W. Schommer, J. prakt. Chem., 143, 189 (1935).
- 10. All new compounds in this paper gave satisfactory elemental analyses. IR spectra were taken in KBr disks, and UV spectra were measured in EtOH. NMR spectra were determined in CDC1<sub>3</sub> using TMS as an internal standard, and <sup>1</sup>H NMR data of pyrrolidinyl and aromatic protons were omitted here. 4: IR 1700 cm<sup>-1</sup> (C=0); <sup>1</sup>H NMR  $\delta$  5.40 (1H, s,  $\equiv$ CH); <sup>13</sup>C NMR  $\delta$  23.4, 48.4 (each t, CH<sub>2</sub>), 52.0 (d, tert. <u>C</u>), 80.7 (s, quat. <u>C</u>), 167.4 (<u>C</u>=C), 203.6 (<u>C</u>=0); UV  $\lambda$ max nm (log  $\epsilon$ ) 222 (4.83), 290 (4.12), 305 (4.06); MS m/e 427 (M<sup>+</sup>).
- 11. <u>6</u>: IR 1745 cm<sup>-1</sup> (C=0); <sup>1</sup>H NMR  $\delta$  3.70 (1H, d, H<sub>a</sub>, J=15 Hz), 4.30 (1H, dd, H<sub>b</sub>, J=15, 8 Hz), 4.66 (1H, d, H<sub>c</sub>, J=8 Hz); <sup>13</sup>C NMR  $\delta$  23.3, 48.4 (each t, <u>CH</u><sub>2</sub>), 49.0, 50.5, 53.8 (each d, tert. <u>C</u>), 83.2 (s, quat. <u>C</u>), 210.9 (<u>C</u>=0); UV  $\lambda$ max nm (log  $\epsilon$ ) 221 (4.66), 283 (3.73), 293 (3.80), 308 (3.60), 316 (3.52), 323 (3.36); MS m/e 429 (M<sup>+</sup>).
- 12. <u>7</u>: <sup>1</sup>H NMR & 5.52 (1H, s, ≥C<u>H</u>); <sup>13</sup>C NMR & 23.6, 48.1 (each t, <u>C</u>H<sub>2</sub>), 55.2 (d, tert. <u>C</u>), 88.7 (s, quat. <u>C</u>), 166.5 (<u>C</u>=C), 242.9 (<u>C</u>=S); MS m/e 443 (M<sup>+</sup>). Picrate of 7: mp 208-209<sup>o</sup>C (dec). <u>8</u>: <sup>1</sup>H NMR & 4.88, 5.62 (each 1H, s, C<u>H</u>); MS m/e 443 (M<sup>+</sup>).
- 13. 9: IR 2500 cm<sup>-1</sup> (weak, SH); <sup>1</sup>H NMR  $\delta$  4.10 (1H, broad, S<u>H</u>, exchanged with D<sub>2</sub>O), 4.62 (1H, d, H<sub>a</sub>, J=10 Hz), 5.08 (1H, d, H<sub>b</sub>, J=10 Hz); <sup>13</sup>C NMR  $\delta$  23.9, 47.6 (each t, <u>CH</u><sub>2</sub>), 48.4, 50.6 (each d, tert. <u>C</u>), 88.8 (s, quat. <u>C</u>); UV  $\lambda$ max nm (log  $\epsilon$ ) 230 (4.23), 283 (4.07), 294 (4.13), 350 (3.45); MS m/e 445 (M<sup>+</sup>).
- 14. A. Schönberg, Ber., <u>58</u>, 1793 (1925).
- 15. M. H. Rosen, I. Fengler, and G. Bonet, Tetrahedron Lett., 1973, 949.
- An adduct arising from a similar type reaction was obtained in the reaction of benzothiazolium 3-phenacylide with <u>2</u>. The result will be reported elsewhere.

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