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

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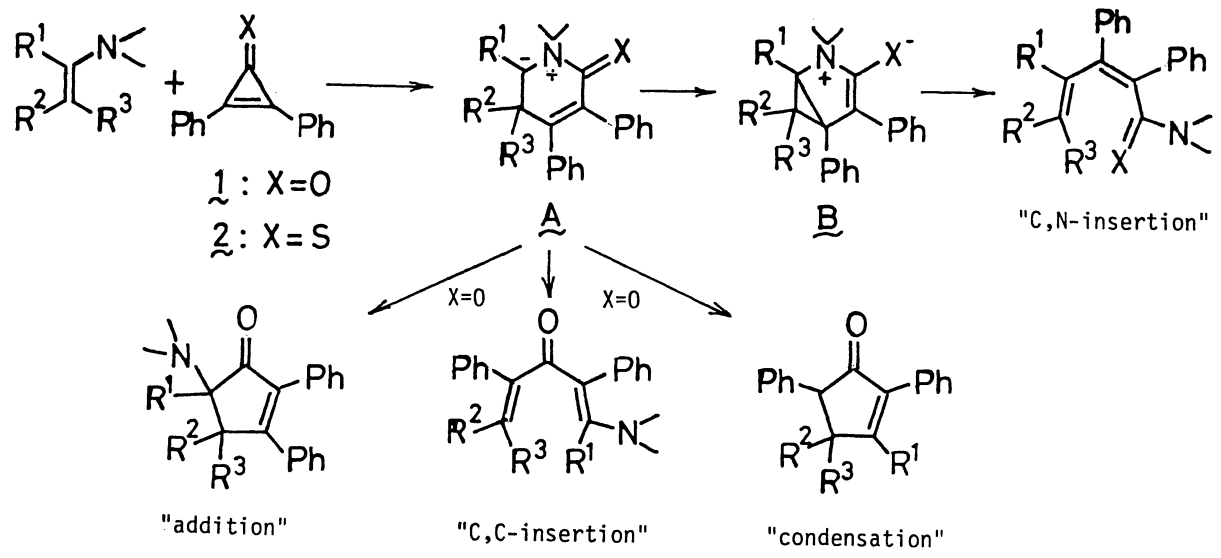
An enamine, 1-(1-pyrrolidinyl)acenaphthylene, reacts with diphenylcyclopropenone to give δ-aminocyclopentenone derivative together with a trace amount of acecyclone. In the reaction of the enamine with diphenylcyclopropenethione, however, γ-aminocyclopentenethione derivative is formed as the major product 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.[1-7] In some reactions with 1 these are accompanied by δ-aminocyclopentenones, β-aminoenones and cyclopentenones arising from "addition", "C,C-insertion" and "condensation", respectively (Scheme 1).

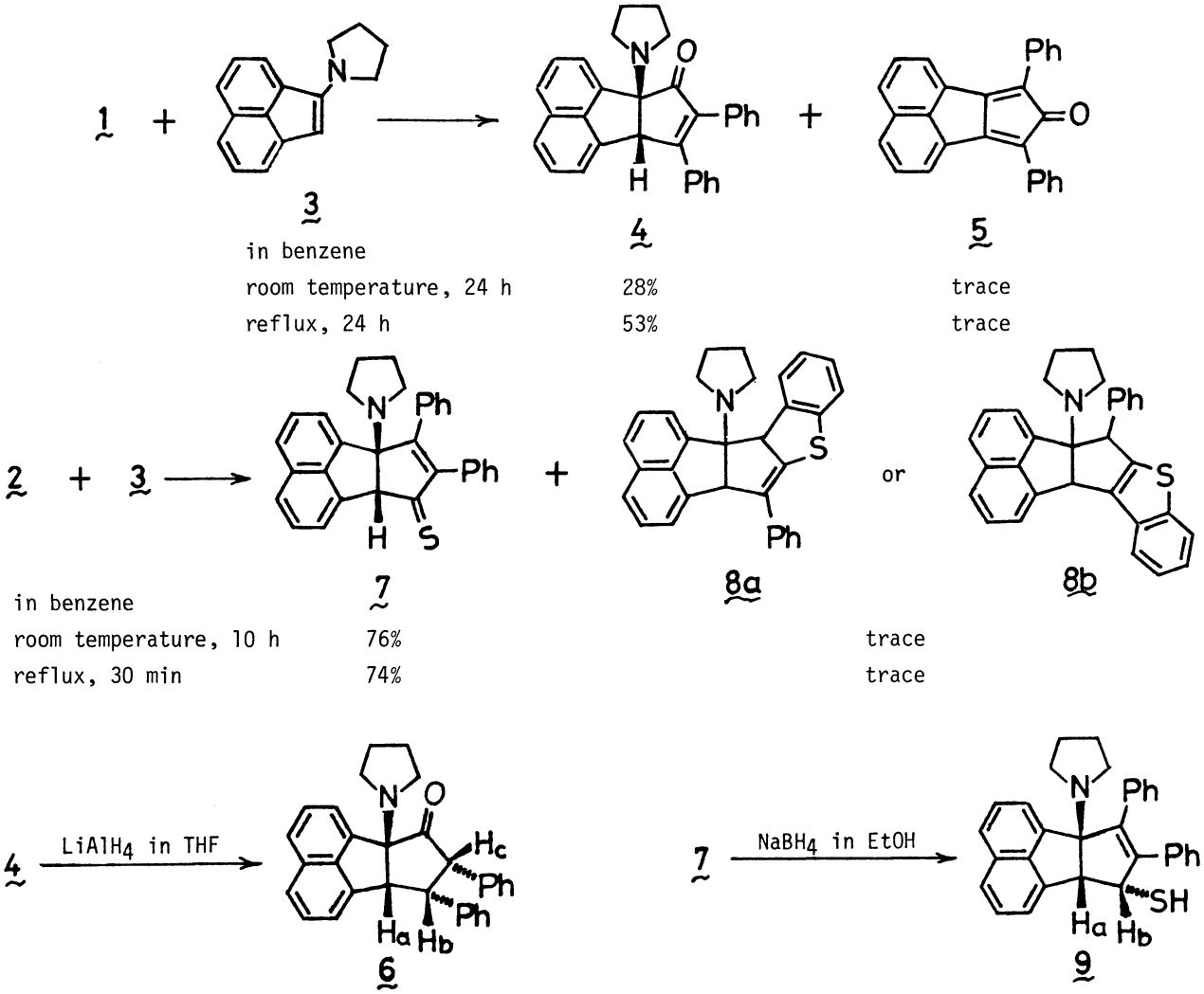


Scheme 1

In this paper we wish to report a dramatic change in the course of the reaction of an enamine, 1-(1-pyrrolidinyl)acenaphthylene (3)[8], with 1 and 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°C (dec), yellow prisms] was obtained as the major product together with a trace amount of acecyclone 5 [mp 293-294°C (lit.[9] mp 289-290°C] which was identical with an authentic sample prepared from acenaphthenequinone and dibenzyl ketone.[9] On the basis of spectral data[10] and of the chemical conversion, the major product 4 was assigned as δ-aminocyclopentenone derivative

which corresponds to a compound arising from "addition" in Scheme 1. Reduction of 4 with $LiAlH_4$ in THF at room temperature for 7 h afforded a 98% yield of α-aminocyclopentanone derivative 6 [mp 226-227°C (dec), colorless prisms] whose structure was confirmed on the basis of spectral data.[11]



Scheme 2

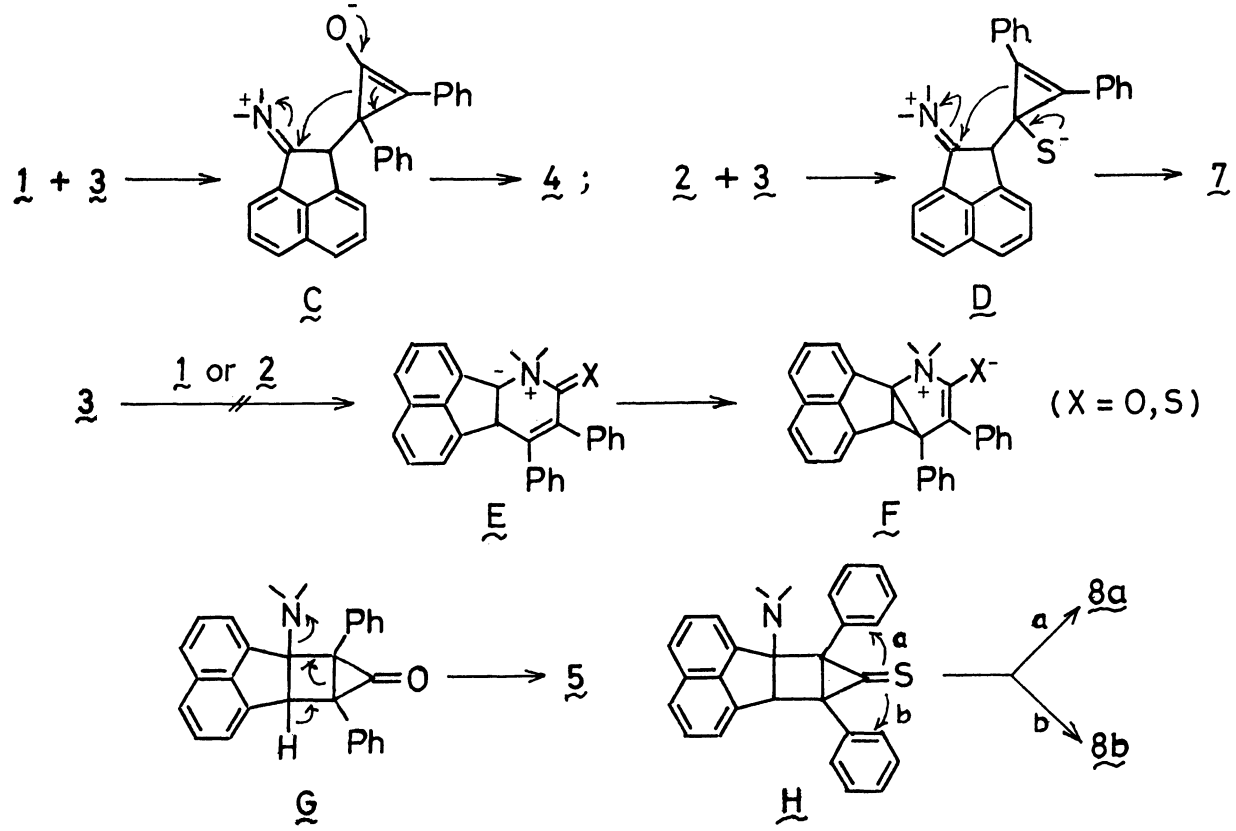
On the other hand, 2 proved to be more reactive toward 3 than 1, and reacted with 3 to give a mixture of two 1:1 adducts 7 [mp 153-158°C (dec), green leaflets] and 8 [mp 219-221°C (dec), pale yellow crystals].[12] Reduction of the major product 7 with $NaBH_4$ in EtOH at room temperature for 3 h afforded 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 ^1H NMR spectrum exhibited signals ascribable to two vicinal methine protons and a thiol proton.[13] It is thus evident that 7 is γ-aminocyclopentenethione derivative. No γ-aminocyclopentenethiones have so far been formed in the reactions of enamines with 2.

Contrary to 7, the minor 1:1 adduct 8 was negative for the color-test reaction with silver perchlorate[14]; this implies that there is no thiocarbonyl group in 8. On the basis of spectral data[12] and of the mode of formation described later, 8 was tentatively assumed to be a benzothiophene derivative, either 8a or 8b.

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 δ-aminocyclopentenones were obtained as major products together with "C,N-insertion" products,[15] generally enamines react with 1 and 2 to give "C,N-insertion" products via ylides A and betaines B (Scheme 1), and examples of stable betaines B have been reported.[5-7] 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 β-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



Scheme 3

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 7. 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 G 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 H (path a or b), and subsequent ring expansion and hydrogen shift furnish 8a or 8b.[16]

References

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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 $CDCl_3$ using TMS as an internal standard, and ^1H NMR data of pyrrolidinyl and aromatic protons were omitted here. 4: IR 1700 cm^{-1} (C=O); ^1H NMR δ 5.40 (1H, s, ≡CH); ^{13}C NMR δ 23.4, 48.4 (each t, CH_2), 52.0 (d, tert. C), 80.7 (s, quat. C), 167.4 (C=C), 203.6 (C=O); UV λmax nm (log ε) 222 (4.83), 290 (4.12), 305 (4.06); MS m/e 427 (M^+).
11. 6: IR 1745 cm^{-1} (C=O); ^1H NMR δ 3.70 (1H, d, H_a, J=15 Hz), 4.30 (1H, dd, H_b, J=15, 8 Hz), 4.66 (1H, d, H_c, J=8 Hz); ^{13}C NMR δ 23.3, 48.4 (each t, CH_2), 49.0, 50.5, 53.8 (each d, tert. C), 83.2 (s, quat. C), 210.9 (C=O); UV λmax nm (log ε) 221 (4.66), 283 (3.73), 293 (3.80), 308 (3.60), 316 (3.52), 323 (3.36); MS m/e 429 (M^+).
12. 7: ^1H NMR δ 5.52 (1H, s, ≡CH); ^{13}C NMR δ 23.6, 48.1 (each t, CH_2), 55.2 (d, tert. C), 88.7 (s, quat. C), 166.5 (C=C), 242.9 (C=S); MS m/e 443 (M^+). Picrate of 7: mp 208-209°C (dec). 8: ^1H NMR δ 4.88, 5.62 (each 1H, s, CH); MS m/e 443 (M^+).
13. 9: IR 2500 cm^{-1} (weak, SH); ^1H NMR δ 4.10 (1H, broad, SH, exchanged with D_2O), 4.62 (1H, d, H_a, J=10 Hz), 5.08 (1H, d, H_b, J=10 Hz); ^{13}C NMR δ 23.9, 47.6 (each t, CH_2), 48.4, 50.6 (each d, tert. C), 88.8 (s, quat. C); UV λmax nm (log ε) 230 (4.23), 283 (4.07), 294 (4.13), 350 (3.45); MS m/e 445 (M^+).
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16. An adduct arising from a similar type reaction was obtained in the reaction of benzothiazolium 3-phenacylide with 2. The result will be reported elsewhere.

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