# REACTIONS OF 2-AMINO-1-AZAAZULENES WITH DIPHENYLCYCLOPROPENONE

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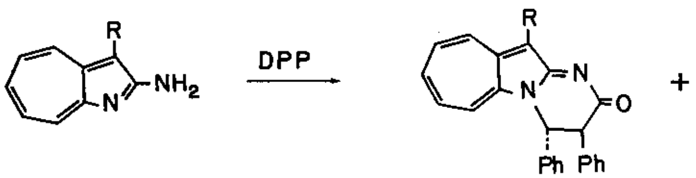
Abstract - Reaction of 2-amino-1-azaazulene with diphenylcyclopropenone gave 1,2-diphenyl-1,2,3,10b-tetrahydro-4,10b-diazabenz[a]azulen-3-one, which rearranged to N-(1-azaazulen-2-yl)-α-cis-stylbenecarboxamide and N-(1-azaazulen-2-yl)-α-trans-stylbenecarboxamide by heating. Some structures of these products were determined by the X-ray structure analyses. The reaction mechanism is discussed.

Diphenylcyclopropenone (DPP) is used in organic syntheses for its interesting structure and reactivities.[1] Cycloaddition reactions of DPP with heterocycles are particularly interesting for the construction of novel heterocycles.[2] It is also known that 1-azaazulenes undergo interesting cycloaddition reactions with dimethyl acetylenedicarboxylate (DMAD).[3] Despite the expectation of a novel cycloaddition reaction, the reaction of 1-azaazulenes with DPP was hitherto unknown. Therefore, we studied the reaction of 2-amino-1-azaazulenes with DPP, and found an interesting cycloaddition and rearrangement reaction.

Treatment of 2-amino-1-azaazulene (1a) with DPP in refluxing xylene for 1 h gave 1,2-diphenyl-1,2,3,10b-tetrahydro-4,10b-diazabenz[a]azulen-3-one

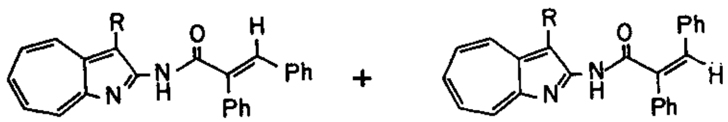
(2a), N-(1-azaazulen-2-yl)-α-cis-stylbenecarboxamide (3a) and N-(1-azaazulen-2-yl)-α-trans-stylbenecarboxamide (4a) in 3%, 28%, and 7% yields, respectively. When the reaction was performed under milder conditions such as in refluxing acetonitrile for 1 h, 2a was obtained in 83% yield. Therefore, 3a and 4a are considered to be ring-opening compounds of 2a. Indeed, heating 2a in tert-butylbenzene under reflux for 6 h afforded 3a and 4a in 55% and 16% yields, respectively. A cis/trans-isomerization between 3a and 4a was considered. Thus, treatment of 3a in refluxing tert-butylbenzene for 24 h was performed and the tautomeric mixture of 3a (77%) and 4a (22%) was obtained.

The structures of these compounds were deduced on the basis of their spectral data as well as elemental analyses,[4-7] and the structures of 2a and 3a were confirmed by X-ray structural analyses.[8,9] The two phenyl groups of 2a are situated trans. The fact agrees with the observation



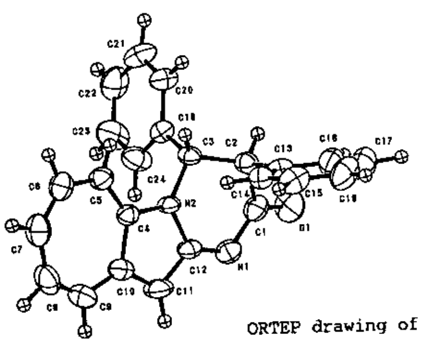

1a: R=H
1b: R=$CO_2Et$

2a: R=H
2b: R=$CO_2Et$

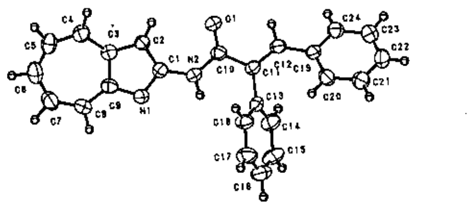



3a: R=H
3b: R=$CO_2Et$

4a: R=H
4b: R=$CO_2Et$



ORTEP drawing of 2a.



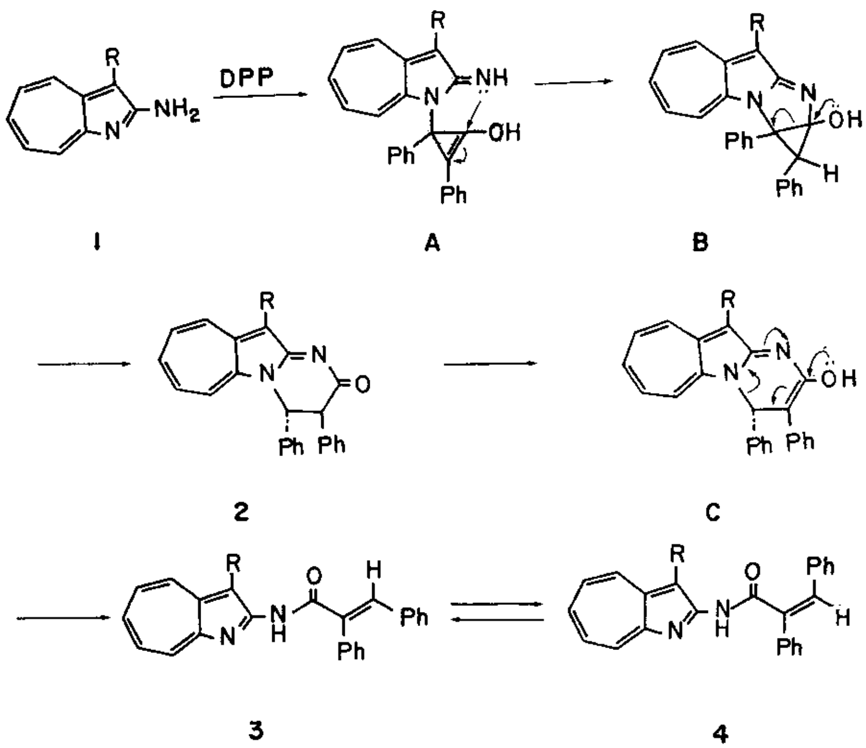
ORTEP drawing of 3a.

that in the nmr spectrum of 2a the two methine protons ($H_3$ and $H_4$) resonate at $\delta$ 4.11 and 5.81 as two singlets.

In a similar manner, the reaction of 1b with DPP in refluxing acetonitrile for 6 h gave 3b and 4b in 40% and 20% yield, respectively.[4]

One reasonable mechanism is shown in the Scheme 1. From the consideration that 2-amino-1-azaazulenes preferentially reacted at N-1 nitrogen with DMAD,[3] first a Michael-type attack of N-1 nitrogen of 1-azaazulene to DPP would occure and forms A; this step is similar to that of the reaction of DPP with ammonia.[10] Cyclization of A gives B, and successive ring-opening furnishes 2. Enolization of 2 and successive ring-cleavage gives 3.

Further studies of the reactions of DPP with 1-azaazulenes such as 2-(substituted amino)-1-azaazulenes and 2-hydrazino-1-azaazulenes are now in progress.




Scheme 1

## REFERENCES

1. K. Matsumoto, Yuki Gosei Kagaku Kyokai Shi, 1972, 30, 1035.
2. J. W. Lown and K. Matsumoto, Can. J. Chem., 1971, 49, 1165; ibid., 1971, 49, 3119.
3. N. Abe and T. Takehiro, Bull. Chem. Soc. Jpn., 1988, 61, 1225; N. Abe, Heterocycles, 1987, 26, 51; N. Abe and T. Ueno, Bull. Chem. Soc. Jpn., 1990, 63, 2121; T. Kurihara, A. Kerim, S. Ishikawa, T. Nozoe, and N. Abe, Bull. Chem. Soc. Jpn., 1993, 66, 1229.
4. All new compounds gave satisfactory elemental analyses and spectral data.
5. 2a: Orange prisms, mp 206-208 ℃, $^1$H nmr δ =4.11 (1H, s), 5.81 (1H, s), 6.67 (1H, s), 7.00-7.35 (14H, m), and 7.76 (1H, d, J=10.6 Hz), ir 1658 $cm^{-1}$ (C=O).
6. 3a: Orange needles, mp 183-184 ℃, $^1$H nmr δ =7.00-7.07 (2H, m), 7.12-7.25 (3H, m), 7.35-7.41 (2H, m), 7.48-7.55 (3H, m), 7.56-7.72 (3H, m), 8.01 (11H, s), 8.08 (1H, s), 8.26 (1H, dd, J=9.8 and 2.4 Hz), 8.42 (1H, d, J=9.8 Hz), and 8.61 (1H, br s), ir 3400 (NH) and 1684 $cm^{-1}$ (C=O).
7. 4a: Orange needles, mp 190-191 ℃, $^1$H nmr δ =7.01 (1H, s), 7.20-7.47 (11H, m), 7.55-7.80 (3H, m), 7.98 (1H, s), 8.22 (1H, d, J=10.4 Hz), and 8.42 (1H, d, J=10.4 Hz), ir 3400 (NH) and 1682 $cm^{-1}$ (C=O).
8. Crystal data of 2a: M.W.=350.42, monoclinic, space group $P2_1/c$, Z=4, a=8.733(6), b=17.020(4), c=12.521(3) Å, β =105.16(2)°, V=1796(1) $Å^3$, Dcalcd=1.296 $g/cm^3$, R=0.049, Rw=0.052, for total 4541 reflections.
9. Crystal data of 3a: M.W.=350.42, triclinic, space group $P\bar{1}$, Z=2, a=11.228(3), b=14.500(4), c=6.202(1) Å, α =102.08(2)°, β =92.41(2)°, γ =111.08(2)°, V=913.6(4) $Å^3$, Dcalcd=1.274 $g/cm^3$, R=0.047, Rw=0.050, for total 4386 reflections.
10. F. Toda, T. Mitote, and K. Akagi, Chem. Commun., 1969, 228.

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