REACTIONS OF 2-AMINO-1-AZAAZULENES WITH
DIPHENYLCYCLOPROPENONE

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

Diphenylicyclopropenone (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 (1g) with DPP in refluxing xylene for 1
h gave 1,2-diphenyl-1,2,3,10b-tetrahydro-4,10b-diazaben[a]azulen-3-one
(2a), N-(1-azaazulen-2-yl)-α-cis-stylenecarboxamide (3a) and N-(1-azaazulen-2-yl)-α-trans-stylenecarboxamide (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 (7/3%) and 4a (22%) was obtained.

The structures of these compounds were deduced on the basis of their spectral data as well as elemental analyses, and the structures of 2a and 3a were confirmed by X-ray structural analyses. The two phenyl groups of 2a are situated trans. The fact agrees with the observation.
that in the nmr spectrum of 2g the two methine protons (H₁ and H₂)
resonate at 8 4.11 and 5.01 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,⁵ first a Michael-type attack of N-1 nitrogen of 1-azaazulene to DPP
would occur and forms A; this step is similar to that of the reaction of
DPP with ammonia.⁶ 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](image-url)
REFERENCES

4. All new compounds gave satisfactory elemental analyses and spectral data.
5. 2a: Orange prisms, mp 206-208 °C, '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 °C, '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), 9.01 (11H, s), 8.08 (1H, s), 8.26 (1H, d, 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 °C, '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 P2₁/c, Z=4, a=8.733(6), b=17.020(4), c=12.521(3) Å, β =105.16(2)°, V=1796(1) Å³, Dcalc=1.296 g/cm³, R=0.049, Rw=0.052, for total 4541 reflections.
9. Crystal data of 3a: M.W.=350.42, triclinic, space group P-T, Z=2, a=11.228(3), b=14.500(4), c=6.202(1) Å, α =102.08(2)°, b =92.41(2)°, γ =111.00(2)°, V=913.6(4) Å³, Dcalc=1.274 g/cm³, R=0.047, Rw=0.050, for total 4386 reflections.

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