

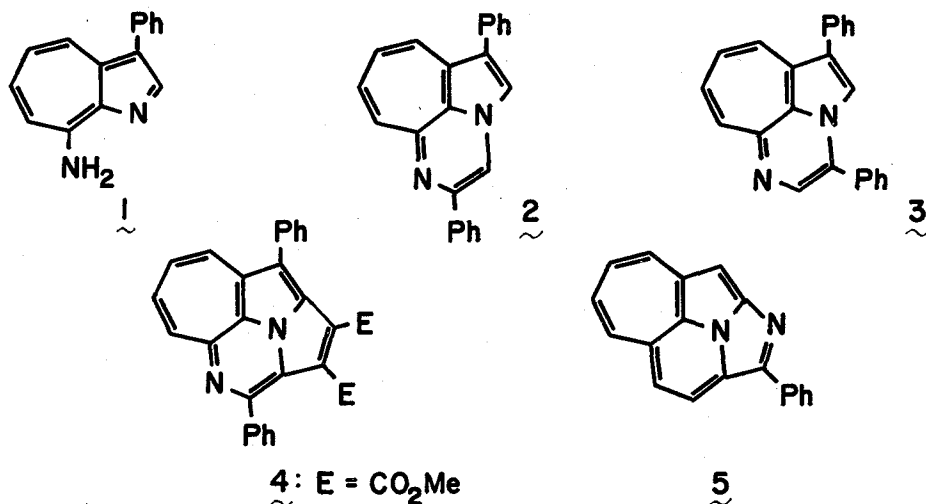
SYNTHESIS AND CYCLOADDITION REACTION OF 2a,5-DIAZACYCLO-
HEPT [cd] INDENES: FORMATION OF CYCLOHEPT [ef] -6-AZA-
CYCL [3.2.2] AZINE SYSTEM

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Abstract-Reaction of 8-amino-3-phenyl-1-azaazulene with phenacyl bromide gave 1,4- and 1,3-diphenyl-2a,5-diazacyclohept [cd] indenenes. Cycloaddition of the former with dimethyl acetylenedicarboxylate gave cyclohept [ef] -6-azacycl [3.2.2] azine derivative.

A number of cycl [3.2.2] azine derivatives have been investigated because of the interest regarding of their chemical and physical properties.¹⁻³ In particular, condensed cyclazines were now attractive attentions. Recently, some [ef]-condensed cycl [3.2.2] azine⁴ and 2-azacycl [3.2.2] azine derivatives⁵ were synthesized. In this paper, I wish to report on the synthesis of 2a,5-diaza-cyclohept [cd] indenenes and its cycloaddition, which afforded novel condensed 6-azacycl [3.2.2] azine⁶ derivative. Treatment of 8-amino-3-phenyl-1-azaazulene⁷ (1) with phenacyl bromide in aq. 1-butanol in the presence of K₂CO₃ under reflux for 2 h gave 1,4-diphenyl-2a,5-diazacyclohept [cd] indene (2) [85%, violet needles, mp 125-127 °C, MS m/z 320 (M⁺), ¹H NMR (60 MHz) δ = 5.17 (1H, ddd, J=11, 7.5, and 2 Hz, H-7), 5.72 (1H, ddd, J=11, 7.5, and 1 Hz, H-8), 5.95 (1H, dd, J=11 and 2 Hz, H-9), 6.27 (1H, dd, J=11 and 1 Hz, H-6), 6.75 (1H, s, H-2), 6.87 (1H, s, H-3), 7.10-8.00 (10H, m, phenyl × 2)] and 1,3-diphenyl-2a,5-diazacyclohept [cd] indene (3) [4%, brownish violet prisms, mp 166-168 °C, MS m/z 320 (M⁺), ¹H NMR (60 MHz) δ = 5.43 (1H, ddd, J=11, 7.5, and 2 Hz, H-7), 5.93 (1H, ddd, J=11, 7.5 and 1 Hz, H-8), 6.15 (1H, dd, J=11 and 2 Hz, H-9), 6.37 (1H, dd, J=11 and 1 Hz, H-6), 6.83 (1H, s, H-2), 7.20-7.75 (9H, m, H-5, m,p-phenyl, and phenyl), 7.90-8.15 (2H, m, o-phenyl)]. In the ¹H NMR spectra of 2 and 3, protons of seven membered ring resonate rather higher field and have large differences of coupling constants (J₇₋₈ ~ J₈₋₉ ~ J₉₋₁₀, Δ 3.5 Hz) which imply bond-alternation. The results suggest that 2 and 3 have a character of butadiene-bridged azaindolizine.



Reaction of \sim 2 with dimethyl acetylenedicarboxylate in acetonitrile under reflux for 1 h afforded a cyclazine \sim 4 [42%, mp 224-225 °C, MS m/z 460 (M⁺), ¹H NMR (250 MHz) δ = 3.64 (3H, s, OMe), 3.67 (3H, s, OMe), 6.63 (dd, J=11.3 and 8.8 Hz, H-7), 7.03 (dd, J=11.6 and 8.8 Hz, H-8), 7.45-7.70 (10H, m, H-6, 9, m,p-phenyl, and phenyl), 7.90-7.95 (2H, m, o-phenyl)].⁸ Higher field resonances (0.85~1.2 ppm) and large differences of coupling constants (ca. 2 Hz) of the seven membered ring protons of \sim 4 were seen in its ¹H NMR spectra in comparison with those of \sim 5.⁵ The results suggest that bond-alternation of seven membered ring of \sim 4 is larger than that of \sim 5.

REFERENCES

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6. Some 6-azacycl[3.2.2]azines were synthesized. M. A. Jessep and D. Leaver, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1319; W. Flitsch, J. Koszinowski, and P. Witthake, *Chem. Ber.*, 1979, 112, 2465.
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8. Small amount of unstable yellow compound, which would be a dihydro derivative of \sim 4, was produced, but could not be purified and structure was not elucidated.

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