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SYNTHESIS AND CYCLOADDITION REACTION OF 2a,5-DIAZACYCLOHEPT[cd]INDENES: FORMATION OF CYCLOHEPT[ef]-6-AZACYCL[3.2.2]AZINE SYSTEM

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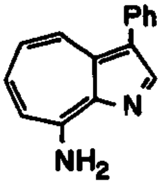
Abstract-Reaction of 8-amino-3-phenyl-1-azaazulene with phenacyl bromide gave 1,4- and 1,3-diphenyl-2a,5-diazacyclohept[cd]indenes. Cycloaddition of the former with dimethyl acetylenedicarboxylate gave cyclohept[ef]-6-azacycl[3.2.2]azine derivative.

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]-condenced cycl[3.2.2]azine[4] and 2-azacycl[3.2.2]azine derivatives[5] were synthesized. In this paper, I wish to report on the synthesis of 2a,5-diaza-cyclohept[cd]indenes and its cycloaddition, which afforded novel condenced 6-azacycl[3.2.2]azine[6] derivative. Treatment of 8-amino-3-phenyl-1-azaazulene[7] (1) with phenacyl bromide in aq. 1-butanol in the presence of K_2CO_3 under reflux for 2 h gave 1,4-diphenyl-2a,5-diazacyclohept[cd]indene (2) [85%, violet needles, mp 125-127 ℃, MS m/z 320(M^+), ^{1}H 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, phehyl × 2)] and 1,3-diphenyl-2a,5-diazacyclohept[cd]-indene (3) [4%, brownish violet prisms, mp 166-168 ℃, MS m/z 320 (M^+), ^{1}H 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 2Hz, 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 ^{1}H NMR spectra of 2 and 3, protons of seven membered ring resonate rather higher field and have large differences of coupling constants ($J_{7-8} \sim J_{8-9} \sim J_{9-10}$, $\triangle$ 3.5 Hz) which imply bond-alternation. The results suggest that 2 and 3 have a character of butadiene-bridged azaindolizine.



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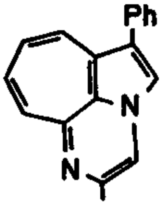
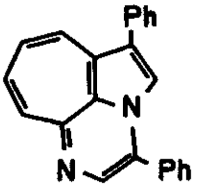


2



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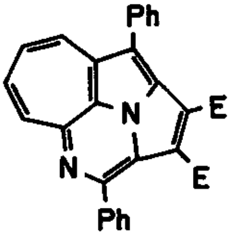
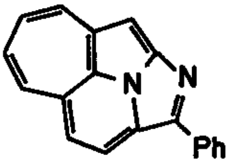


4: E = CO_2Me



5

Reaction of 2 with dimethyl acetylenedicarboxylate in acetonitrile under reflux for 1 h afforded a cyclazine 4 [42%, mp 224-225 ℃, 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 4 were seen in its ^1H NMR spectra in comparison with those of 5.[5] The results suggest that bond-alternation of seven membered ring of 4 is larger than that of 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 4, was produced, but could not be purified and structure was not elucidated.

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