

A NEW SYNTHESIS OF 3H-CYCL[3.2.2]AZINO[1,2-*e*]CYCL[3.3.2]-  
AZIN-3-ONE DERIVATIVE

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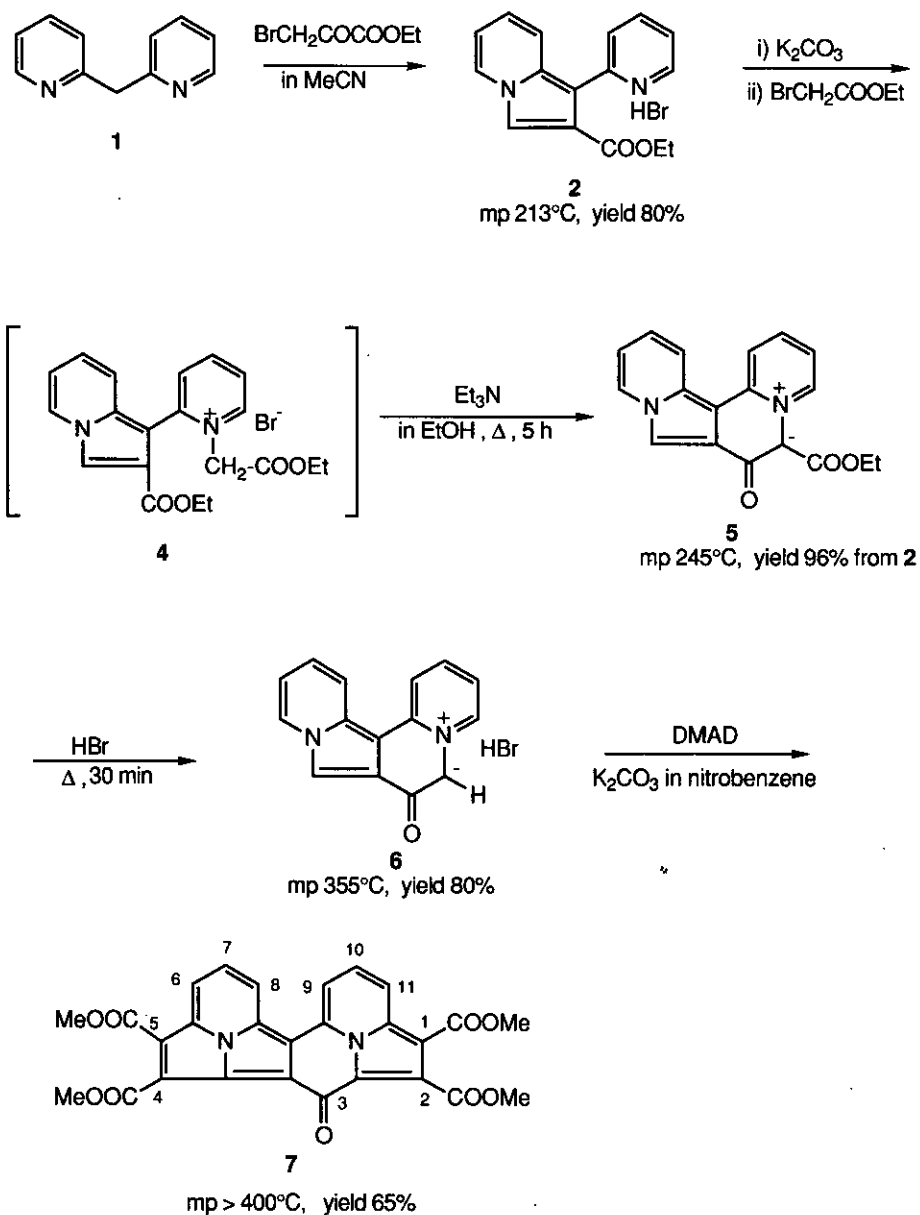
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**Abstract** - Treatment of indolizinoquinolizinium salt (6) with dimethyl acetylenedicarboxylate in the presence of K<sub>2</sub>CO<sub>3</sub> in refluxing nitrobenzene gave a nitrogen-bridged annulenoannulene, 3H-cycl[3.2.2]azino[1,2-*e*]cycl[3.3.2]azinone derivative (7).

In view of the interest in heterocyclic annulenes<sup>1-5</sup> we have previously reported a new nitrogen-bridged annulene heterocyclic system, cyclazine (cycl[3.2.2]azines,<sup>6</sup> cycl[3.2.2]azinophanes,<sup>7</sup> cycl[3.3.2]azinones,<sup>8</sup> cycl[3.3.3]azines<sup>5</sup>). In this communication we wish to report a novel synthesis of 3H-cycl[3.2.2]azinocycl[3.3.2]azin-3-one derivative (7) by the cyclization of the key intermediate, indolizinoquinolizinium salt (6) with dimethyl acetylenedicarboxylate (DMAD).

The starting bispyridylmethane (1) used in the present work was prepared according to Newkome's method.<sup>9</sup> The reaction of 1 with ethyl bromopyruvate at room temperature for a week gave pyridylindolizine hydrobromide (2) in good yield. Treatment of the hydrobromide (2) with K<sub>2</sub>CO<sub>3</sub> afforded the free base, pyridylindolizine (3) and then the crude free base (3) was allowed to react with ethyl

## Scheme 1



bromoacetate in acetonitrile at room temperature for a week. The crude salt (4) resulted above was refluxed with triethylamine in EtOH to produce the cyclic ylide (5) in 96% yield from 2. Heating of 5 in refluxing 47% hydrobromic acid for 30 min gave the salt (6) through decarboxylation. After many attempts to obtain cyclazino-cyclazinone (7), the synthesis of the desired compound (7) was achieved on employing the procedure of Farquhar.<sup>10</sup> Reaction of 6 with DMAD in the presence of K<sub>2</sub>CO<sub>3</sub> in refluxing nitrobenzene for 1 h gave 1,2,4,5-tetrakis carbomethoxy-3H-cycl[3.2.2]azino[1,2-*e*]cycl[3.3.2]azin-3-one (7)<sup>11</sup> in moderate yield. The structure of 7 was supported by a satisfactory elemental analysis, the presence of carbonyl absorptions in the ir spectrum, and the signals of four doublets (C<sub>6,8,9,11</sub>-H) in the <sup>1</sup>H-nmr spectrum. Of particular interest is that the six-membered ring proton signals of 7 in trifluoroacetic acid are shifted *ca.* 1 ppm to lower field than those of 7 in DMSO-*d*<sub>6</sub>. Such lower field shift is characteristic of cyclazinone system.<sup>8</sup> Further discussion of the spectra will be presented in a future publication.

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11. For **7**, mp > 400°C (65%); ir(KBr)  $\nu_{\max}$  1740(CO), 1710(CO), 1630(CO)  $\text{cm}^{-1}$ ; uv(EtOH)  $\lambda_{\max}$  215, 243, 318, 468, 503 nm;  $^1\text{H-nmr}$ (DMSO- $d_6$ )  $\delta$  3.89(3H, s, OCH<sub>3</sub>), 3.95(3H, s, OCH<sub>3</sub>), 3.96(3H, s, OCH<sub>3</sub>), 4.04(3H, s, OCH<sub>3</sub>), 6.77-7.59(2H, m), 7.83-9.12(4H, m);  $^1\text{H-nmr}$ (CF<sub>3</sub>COOD)  $\delta$  4.33(3H, s, OCH<sub>3</sub>), 4.35(3H, s, OCH<sub>3</sub>), 4.39(3H, s, OCH<sub>3</sub>), 4.43(3H, s, OCH<sub>3</sub>), 8.70(1H, t,  $J=8$  Hz), 8.98(1H, t,  $J=8$  Hz), 9.13(1H, d,  $J=8$  Hz), 9.42(1H, d,  $J=8$  Hz), 9.48(1H, d,  $J=8$  Hz), 9.75(1H, d,  $J=8$  Hz). *Anal.* Calcd for C<sub>27</sub>H<sub>18</sub>N<sub>2</sub>O<sub>9</sub>: C, 63.04; H, 3.53; N, 5.45. Found: C, 62.99; H, 3.76; N, 5.60.

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