Novel Heterocyclic Systems by Intramolecular Cycloadditions with Unactivated Olefins

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Summary A method is illustrated for the preparation of novel polycyclic systems, such as (**3**) and (**6**), by intramolecular cycloaddition to unactivated double bonds.

THERE is a growing recognition of the value of intramolecular cycloaddition reactions in synthesis.[1] Although polar cycloadditions are well known in chemistry[2] they generally involve intermolecular reactions, and, often, activated olefinic or acetylenic bonds. We now report two examples illustrating the use of polar cycloadditions involving intramolecular cycloaddition to unactivated olefinic bonds.

The betaine (**1**) has been shown to possess dual properties in dipolar cycloadditions, acting as either a four-electron component across the 2,6-positions[3] or a two-electron component across the 2,4-positions.[4] Preparation of the

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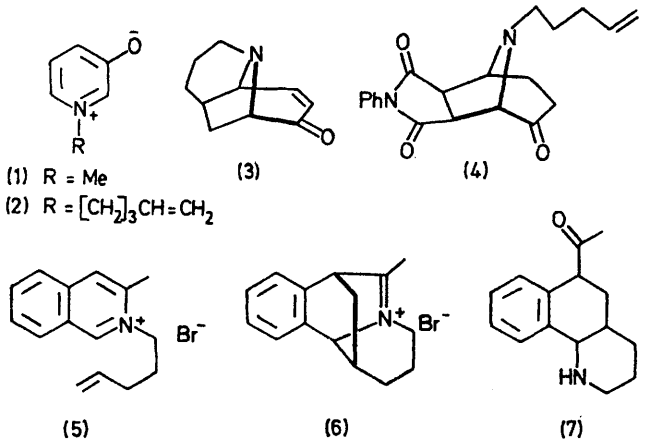
betaine (**2**) was accomplished by quaternisation of 3-hydroxypyridine with 1-bromopent-5-ene, followed by treatment



(1) R = Me
(2) R = $[CH_2]_3CH{=}CH_2$

(3) (4)

(5) (6) (7)

with basic ion exchange resin in acetonitrile. Thermolysis, in acetonitrile at 140 °C for 24 h, gave the cycloadduct (**3**) (32%), ν_{max} 1690 cm^{-1}, m.p. (2,4-dinitrophenylhydrazine derivative) 225—227 °C. This bridged tropanoid derivative was formed regioselectively. The direction of cycloaddition was as predicted by simple frontier molecular orbital calculations.[5] The cycloaddition process was relatively slow in that competition reactions gave normal cycloadducts; *N*-phenylmaleimide reacted with the betaine (**2**) at 80 °C to give the adduct (**4**) only.

Cationic polar cycloadditions have also been illustrated with isoquinolinium ions and electron-rich dienophiles.[6] Although isolated olefins are normally inert towards these substrates, intramolecular participation enhances reactivity. Thus thermolysis of the salt (**5**), m.p. 158—159 °C, produces a single, unstable adduct, assigned structure (**6**) (46%), m.p. 250—252 °C. On treatment with dilute aqueous base, the ketone (**7**), ν_{max} 3330 and 1705 cm^{-1}, was produced.‡

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‡ All compounds gave satisfactory microanalytical and spectral data.

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