Studies on Heterocyclic Analogs of Azulene. VII.[1] Regioselective Cycloadditions of Cycloheptimidazole to Electron-deficient Olefins

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Synopsis. Cycloheptimidazole reacted with electron-deficient olefins (*e.g.*, ethyl acrylate or acrylonitrile) to give the regioselective [6+2] cycloadducts, which were readily dehydrogenated to give 2a,3-dihydro-1,2a-diazacyclopent[*cd*]-azulenes.

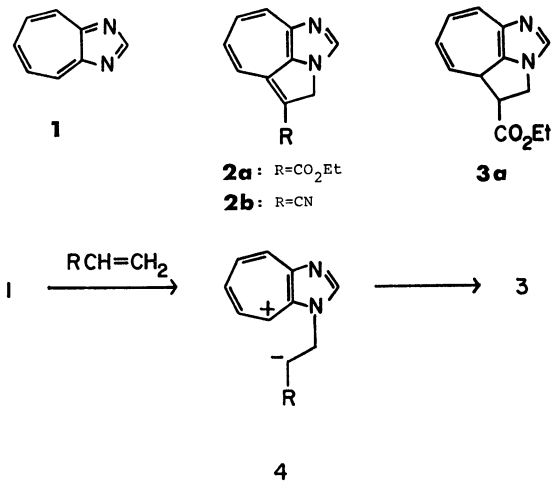
We have recently reported[2] that the reaction of aza analogs of azulene with dimethyl acetylenedicarboxylate affords cycloadducts, the formation of which is accounted for in terms of an intramolecular cyclization of an extended dipolar species.[3] This paper is concerned with the regioselective cycloadditions of cycloheptimidazole with electron-deficient olefins.

When a mixture of cycloheptimidazole (**1**) and ethyl acrylate was heated under reflux for 20 h, two products, ethyl 2a,3-dihydro-1,2a-diazacyclopent[*cd*]azulene-4-carboxylate (**2a**) (24%) and ethyl 2a,3,4,4a-tetrahydro-1,2a-diazacyclopent[*cd*]azulene-4-carboxylate (**3a**) (48%), were isolated as red needles and an unstable pale yellow oil, respectively. The ^{1}H-NMR spectrum of the former (**2a**) shows two 1H doublets at δ 6.89 (H-8) and 7.23 (H-5) (J=11 Hz) and two 1H double doublets at δ 6.12 (H-7) and 6.51 (H-6) (J=11 and 9 Hz) assignable to seven-membered ring protons, and a 2H doublet at δ 5.07 (J=1.5 Hz, H-3) which shows a long-range coupling with the H-2 proton resonating at δ 7.62 (t, J=1.5 Hz), in addition to signals for an ethyl group. An absorption at 1675 cm^{-1} in its IR spectrum indicates the presence of a conjugated ester carbonyl. These observations allow the ester group to be assigned at C-4. The latter compound was found to be rather unstable and changed into **2a** on storage in air or by dehydrogenation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone supporting the structure of **3a**. IR spectrum of picrate of **3a** shows an absorption of unconjugated ester carbonyl at 1720 cm^{-1}, and ^{1}H-NMR spectrum of the picrate accords with the structure in spite of its quite complex feature.

Since the presence of a dehydrogenation catalyst such as palladium–charcoal may stimulate[4] the formation of **2a**, the reaction was repeated in the presence of palladium–charcoal. As expected, **2a** was obtained in higher yield and **3a** was not isolated at all.

Acrylonitrile similarly reacts with **1** in the absence of palladium–charcoal to yield **2b** as red prisms (15%), according to the manner of the regioselective [6+2] cycloaddition reaction. This reaction was sluggish than that of ethyl acrylate, *i.e.*, 73% of the starting material **1** was recovered even after reflux for 48 h.

In these reaction, the electrophilic olefin attacks the ring nitrogen to give a dipolar species (**4**) followed by the intramolecular cyclization reaction. These results further lend support the mechanism we advanced previously for the reaction of **1** with dimethyl acetylenedicarboxylate.[2]



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Experimental

Melting points were uncorrected. IR spectra were recorded for Nujol mulls. ^{1}H-NMR spectra were recorded with JEOL FX-100 (100 MHz) or Hitachi R-24B (60 MHz) spectrometers. UV spectra were measured for ethanol solutions. Kiesel gel 60 was used for chromatography unless otherwise stated. Yields are based on consumed starting material.

Reaction of 1 with Ethyl Acrylate. (*a*): A mixture of **1** (1.00 g) and ethyl acrylate (4.00 g) was heated under reflux for 20 h. Reaction mixture was evaporated under reduced pressure, and the residue was chromatographed. Elution with chloroform gave **2a** (0.176 g, 24%), red needles (from petroleum ether), mp 80—82 °C, UV_{max} 223 nm (log ε 4.36), 253^{sh} (4.18), 359 (4.13), 375 (4.08), 424 (3.57), 448 (3.61), 477 (3.55), 513 (3.35), 555^{sh} (2.95). IR 1675 cm^{-1} (ester C=O). ^{1}H-NMR ($CDCl_3$) δ=1.32 (3H, t, J=7 Hz, CH_3), 4.22 (2H, q, J=7 Hz, OCH_2), 5.07 (2H, d, J=1.5 Hz, H-3), 6.12 (1H, dd, J=11 and 9 Hz, H-6), 6.51 (1H, dd, J=11 and 9 Hz, H-7), 6.89 (1H, d, J=11 Hz, H-8), 7.23 (1H, d, J=11 Hz, H-5), 7.62 (1H, t, J=1.5 Hz, H-2). Found: C, 68.39; H, 5.58; N, 12.08%. Calcd for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30; N, 12.27%. Picrate of **2a**, red needles (from ethanol), mp 195—197 °C (dec.). IR 1680 cm^{-1} (ester C=O). Found: C, 49.85; H, 3.40; N, 15.04%. Calcd for $C_{19}H_{15}N_5O_9$: C, 49.89; H, 3.31; N, 15.31%. Elution with ethyl acetate gave **3a** as a pale yellow oil (0.349 g, 48%). Picrate of **3a**, orange needles (from ethanol), mp 166—167 °C. IR 1720 cm^{-1} (ester C=O). ^{1}H-NMR (DMSO-d_6) δ=1.27 (3H, t, J=7 Hz, CH_3), 4.18 (2H, q, J=7 Hz, OCH_2), 4.2—4.7 (4H, m, H-3, 4, and 4a), 5.5—6.8 (5H, m, H-2, 5, 6, 7, and 8), and 9.00 (1H, s, OH), and phenyl proton of picric acid appeared at δ 8.55 (2H, s). Found: C, 49.75; H, 3.97; N, 15.00%. Calcd for $C_{19}H_{17}N_5O_9$: C, 49.67; H, 3.73; N, 15.25%. Further elution gave the starting material **1** (0.579 g). (*b*): A mixture of **1** (0.30 g), ethyl acrylate (4.00 g), and 5% palladium–charcoal (0.10 g) was heated under reflux for 20 h. The mixture was cooled and filtered. The filtrate was evaporated under reduced pressure and the residue was similarly chro-

matographed as above to afford **2a** (0.129 g, 41%) and the starting material **1** (0.120 g).

*Reaction of **1** with Acrylonitrile.* A mixture of **1** (0.60 g) and acrylonitrile (4.00 g) was heated under reflux for 48 h. The mixture was evaporated under reduced pressure, and the residue was chromatographed. Elution with chloroform gave **2b** (0.034 g, 15%), red prisms (from cyclohexane), mp 149—150 °C, UV_{max} 223 nm (log ε 4.16), 256^{sh} (4.04), 354 (3.93), 370^{sh} (3.85), 424 (3.34), 452 (3.33), 483 (3.25), 520 (3.06), 560^{sh} (2.74). IR 2200 cm^{-1} (C≡N). ^{1}H-NMR ($CDCl_3$) δ=5.07 (2H, d, J=1 Hz, H-3), 6.12 (1H, dd, J=11 and 8 Hz, H-6), 6.44 (1H, dd, J=11 and 8 Hz, H-7), 6.66 (1H, d, J=11 Hz, H-5), 6.90 (1H, d, J=11 Hz, H-8), 7.64 (1H, t, J=1 Hz, H-2). Found: C, 73.05; H, 3.85; N, 23.02%. Calcd for $C_{11}H_7N_3$: C, 72.91; H, 3.89; N, 23.19%. Elution of ethyl acetate gave the starting material **1** (0.438 g).

*Oxidation of **3a**.* A mixture of **3a** (0.050 g) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.055 g) in benzene (20 ml) was heated under reflux for 24 h, then chromatographed on alumina. **2a** (0.035 g, 71%) was eluted with chloroform.

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