THE NUCLEOPHILIC REACTION OF TRICARBONYL(2-5-η-1H-AZEPINE)IRON. NOVEL PREPARATION AND THERMAL 1,5-HYDROGEN MIGRATION OF 3-(2,4,6-CYCLOHEPTATRIENYL)-3H-AZEPINE

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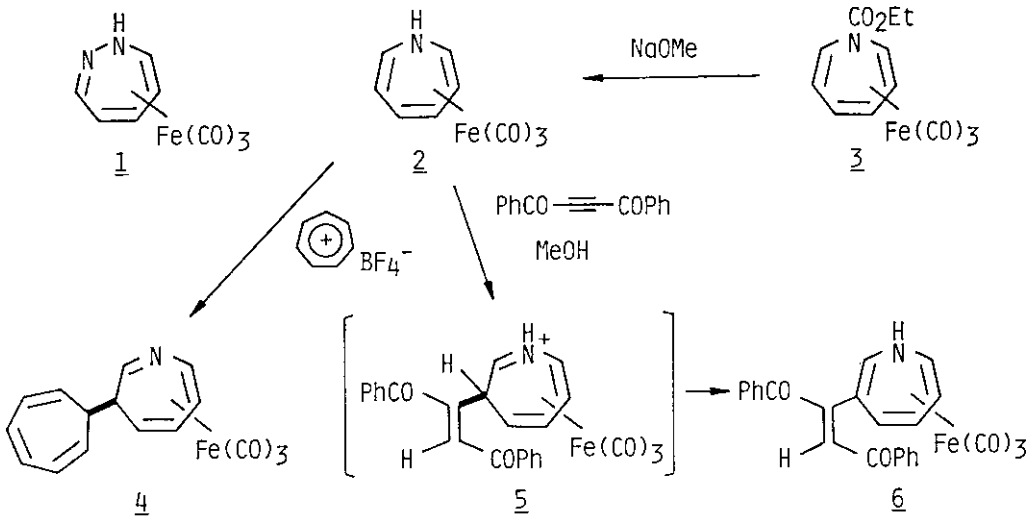
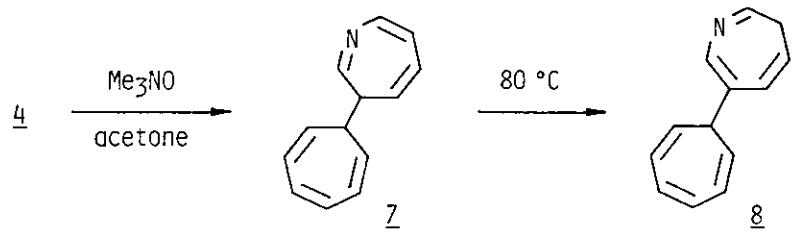
Abstract — The nucleophilic reaction of tricarbonyl(2-5-η-1H-azepine)iron with tropylium cation and several electrophiles was studied. The decomplexation giving 3-(2,4,6-cycloheptatrienyl)-3H-azepine and its novel 1,5-hydrogen migration in the azepine ring are discussed.

Previously, we have studied the reaction of tricarbonyl(4-7-η-1H-1,2-diazepine)iron (1)[1] with activated acetylenes or with 2-halotropones to provide convenient methods for the preparation of novel 1-vinyl-1H-1,2-diazepines and three isomers of 1-troponyl-1H-1,2-diazepine in good yields.[2] Although tricarbonyl(2-5-η-1H-azepine)iron (2), which is isoelectronic with 1, has been prepared[3] and its structure has been elucidated by X-ray crystallography,[4] no synthetic utility has been explored. Recently, a convenient synthetic method of 3H-azepines via the Dewar azepines of 1-methoxycarbonyl-3H-azepines has been reported.[5] Our interest in the synthesis and chemical properties of 1H- and 3H-azepine derivatives prompted us to investigate the nucleophilic reaction of 2 with tropylium cation and several electrophiles. We report here the results of nucleophilic reaction of 2 and, the preparation and thermal 1,5-hydrogen migration of 3-(2,4,6-cycloheptatrienyl)-3H-azepine (7). The complex 2, which is unstable to air,[3] was prepared in situ by the reaction of 3 (5 mmol) with NaOMe (5 mmol) in methanol (20 ml) at 40 °C for 1.5 h.[3] To this solution was added Et_3NHCl (5 mmol) and then tropylium tetrafluoroborate (10 mmol) and the mixture was stirred for 4 h at 40 °C. The reaction mixture was chromatographed on silica gel, which is deactivated by pretreatment with aqueous NH_4OH, to give 4 (mp 94-95 °C) in 46% yield:[6] ^{1}H-NMR ($CDCl_3$), δ=1.76 (1H, ddd, J=5.9, 5.8, 5.5 Hz), 2.77 (1H, ddd, J=6.0, 5.2, 2.9 Hz), 3.16 (1H, ddd, J=6.2, 4.0, 3.3 Hz), 4.17 (1H, ddd, J=5.9, 4.0, 1.9 Hz), 5.05 (1H, dd, J=9.6, 5.8 Hz), 5.25-5.48 (2H,



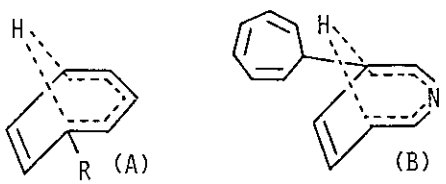
m), 5.54 (1H, dd, J=9.5, 5.5 Hz), 6.00-6.40 (2H, m), 6.45-6.80 (2H, m), 7.97 (1H, dd, J=5.2, 1.9 Hz); ^{13}C-NMR ($CDCl_3$), δ=209.2 (3C, s), 162.1 (d), 130.8 (d), 130.4 (d), 124.7 (d), 124.5 (d), 124.4 (d), 123.3 (d), 93.6 (d), 88.4 (d), 63.8 (d), 63.4 (d), 50.4 (d), 47.3 (d). The stereochemical arrangement of 4 was deduced by comparison of the chemical shift and the coupling constant of a signal of 3H on the azepine ring with those of 7H on the 7-substituted cycloheptatriene complex.[7] The enamine-type reaction of 2 to give 4 has a resemblance to that of 3 with electrophiles.[8]

On the other hand, the reaction of 2 with dibenzoylacetylene under similar conditions underwent the enamine-type addition, and the subsequent deprotonation to give 1H-azepine complex 6 (mp 115-116 °C) in 31 % yield. The complex 6 will be more stable than the corresponding 3H-azepine complex because of a conjugative effect of the dibenzoylethylene moiety. For 6:[6] ^{1}H-NMR (d_6-DMSO), δ=4.54 (1H, ddd, J=6.8, 4.4, 0.7 Hz), 4.78 (1H, broad d, J=7.8 Hz), 5.09 (1H, ddd, J=7.8, 4.4, 1.3 Hz), 5.27 (1H, broad dd, J=6.8, 6.6 Hz), 5.97 (1H, broad d, J=6.4 Hz), 7.22-7.62 (7H, m), 7.70-7.86 (2H, m), 7.88-8.06 (2H, m), 8.57 (1H, broad dd, J=6.6, 6.4 Hz); ^{13}C-NMR (d_6-DMSO), δ=212.5 (3C, s), 197.3 (s), 186.0 (s), 157.4 (s), 138.0 (s), 136.7 (s), 135.3 (d), 132.3 (d), 132.0 (d), 128.2 (4C, d), 127.7 (2C, d), 127.5 (2C, d), 109.2 (s), 107.2 (d), 86.3 (d), 76.1 (d), 73.9 (d), 60.0 (d). The stereochemical situation of the benzoyl groups of 6 was deduced as depicted based on the mechanistic aspect of the nucleophilic addition to activated acetylenes in protic media.[2a] The nucleophilicity of 2 seems to be weak. The reaction of 2 with dimethyl



acetylenedicarboxylate, benzoyl chloride, or tosyl chloride gave no distinct product, and only tarry materials were obtained.

On the decomplexation with trimethylamine oxide,[9] 4 was converted to 3-(2,4,6-cycloheptatrienyl)-3H-azepine (7) in 73% yield:[6] pale yellow oil; ^{1}H-NMR ($CDCl_3$), δ=2.35 (1H, broad ddd, J=8.2, 5.5, 5.4 Hz), 3.01 (1H, dddd, J=8.2, 5.5, 2.2, 1.3 Hz), 5.33 (1H, dd, J=9.6, 5.4 Hz), 5.45 (1H, dd, J=10.3, 5.5 Hz), 5.64 (1H, broad dd, J=9.5, 5.5 Hz), 6.15-6.57 (3H, m), 6.59-7.00 (4H, m), 7.91 (1H, ddd, J=2.2, 1.3, 1.1 Hz); ^{13}C-NMR ($CDCl_3$), δ=156.8 (d), 136.3 (d), 130.9 (d), 130.6 (2C, d), 130.4 (d), 127.8 (d), 125.6 (d), 125.3 (d), 124.4 (d), 123.3 (d), 62.3 (d), 43.6 (d). The azepine 7 is stable but it underwent a facile 1,5-hydrogen migration in benzene under reflux for 3.5 h to give 6-(2,4,6-cycloheptatrienyl)-3H-azepine (8) in 97% yield after purification through chromatography on alumina:[6] pale yellow oil; ^{1}H-NMR ($CDCl_3$), δ=2.43 (2H, broad dd, J=6.6, 5.2 Hz), 2.63 (1H, broad t, J=5.5 Hz), 5.16 (1H, dt, J=8.4, 6.6 Hz), 5.43 (2H, dd, J=8.8, 5.5 Hz), 6.05-6.48 (4H, m), 6.48-6.75 (3H, m); ^{13}C-NMR ($CDCl_3$), δ=153.9 (s), 135.3 (d), 130.6 (2C, d), 127.5 (d), 124.4 (2C, d), 124.0 (2C, d), 113.9 (d), 111.0 (d), 46.7 (d), 34.3 (t). This hydrogen shift is probably a sigmatropic in character because it took place in the absence of base.[10] Furthermore, a sample of 7 in benzene containing 2 fold excess of MeOD was heated for 4 h in a sealed tube at 80 °C to result in no incorporation of deuterium into 8 (obtained in 98% yield), thus ruling out any proton shift either autocatalyzed or mediated by adventitious trace of water. The facile hydrogen shift in the azepine ring, not in the cycloheptatriene ring, would be due to the change in orbital energies rather than the structural geometry in the ring. The transition state (A) for hydrogen shift in cycloheptatriene has been calculated,[11] and it has a planar pentadienyl unit and the CH=CH group which is virtually out of conjugation. The important orbital interaction in



(A) is that between HOMO of the pentadienyl radical and the 1s orbital of the hydrogen atom.[11] The plausible transition state for the present reaction in the azepine would have a geometry (B), which contains the azapentadienyl unit. It is of interest to note that the CH=CH in cyclohepta-triene is replaced by (O-CO) and N=N, the rapid hydrogen migration in the pentadi-enyl unit has been observed.[12] In the present case, the energy of azapentadienyl HOMO is expected to be much lowered by electronegative nitrogen as compared to that of pentadienyl HOMO, thus stabilizing the transition state (B). The selective hydrogen shift in azepine 7 to give more stable isomer 8 thus seems to accord with a simple orbital interaction.

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