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CYCLOADDITION REACTION OF MESOIONIC 3a,6a-DIAZAPENTALENES WITH DIMETHYL ACETYLENEDICARBOXYLATE

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Mesoionic 3a,6a-diazapentalenes (1) and (6) react with two equimolar amounts of dimethyl acetylenedicarboxylate to give the rearranged 1:2 adducts (5) and (9), respectively whose structures are assigned on the basis of spectral data as well as mechanistic considerations.

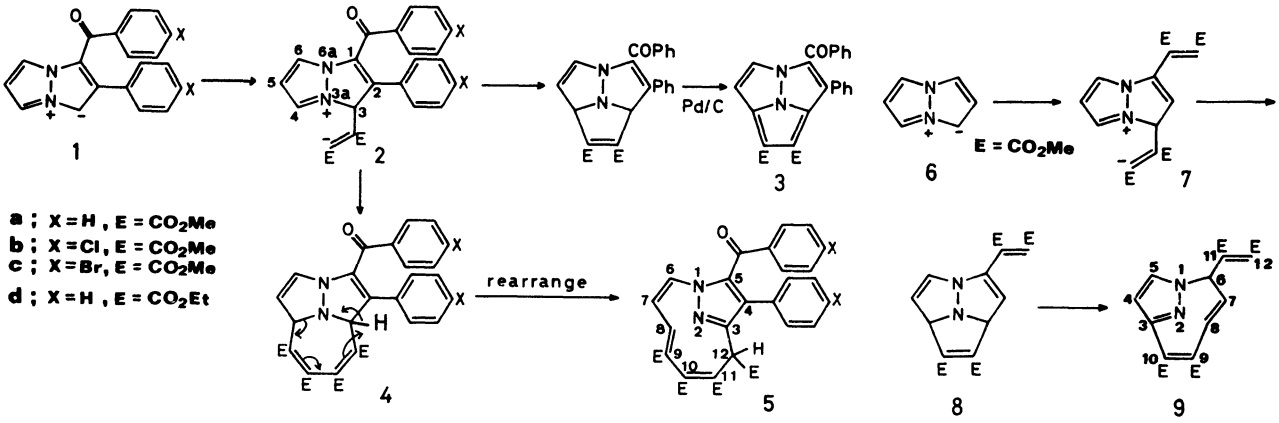
The chemistry of mesoionic heteropentalenes has attracted considerable attention in recent years because of their interesting chemical properties.[1] Most of these have been known to undergo cycloaddition with electron deficient acetylenes and olefins to give a novel type of compounds.[2] For example, Boekelheide and Fedoruk[3] reported the formation of a 2a-azacycl[2.2.2]azine (3) by reaction of 1-benzoyl-2-phenyl-3a,6a-diazapentalene (1-benzoyl-2-phenylpyrazolo[1,2a]pyrazole) (1a) with dimethyl acetylenedicarboxylate (DMAD) in the presence of palladium-charcoal. In contrast to this, an attempted cycloaddition of the parent 3a,6a-diazapentalene has been reported to be unsuccesful.[4] In the course of our studies on N-bridged heterocycles, we reinvestigated their reactions in the absence of Pd-C and found a formation of 1:2 adducts. This is the subject of the present report.

The stable 1-benzoyl-2-phenyl-3a,6a-diazapentalene (1a)[5] reacted with two equimolar amounts of DMAD in benzene at room temperature to give the rearranged 1:2 adduct (5a) as an orange solid in 65 % yield. Analytical and mass spectral data established the composition of this product. 5a: mp 152-153°C; IR(KBr) cm^{-1} 1734, 1703, 1650 (C=O); ^{1}H-NMR($CDCl_3$) δ 3.40, 3.60, 3.73, 3.78(each s, 12H, CO_2CH_3), 4.77 (d, 1H, 8-H, J=2.5 Hz), 5.37(s, 1H, 12-H), 5.78(dd, 1H, 7-H, J=2.5 and 10 Hz), 7.09 (d, 1H, 6-H, J=10 Hz), 7.05-8.06(m, 10H, aromatic H); ^{13}C-NMR($CDCl_3$) δ 51.33, 52.63 52.87(each q, CH_3), 61.56(d, C-12), 94.78(d, C-8), 117.93(d, C-7), 121-146(aromatic and quaternary carbons), 161.38, 163.41, 166.66(each s, ester C=O), 189.24(s, benzoyl C=O).[6] The 1:2 adducts of the type (4) have been described in the reactions of related heteropentalenes.[7,8] Thus, the rearranged adduct (5a) can be pictured as arising by way of electrophilic attack of the acetylenic ester at position 3 of 1a[9] to form the 1,5-dipolar species (2a) which combines with another molecule of the ester giving the primary adduct (4a), followed by rearrangement to produce 5a. (Scheme). The driving force of this rearrangement is possibly due to the aromatic stabilization of pyrazole ring, although there remains uncertainty as to the reason why no rearrangement is observed in the similar reaction of a triazapentalene.[7]

An analogous type of the zwitterions to 2a have been proposed in the reactions of a variety of heterocycles with the acetylenic esters.[10]

Interaction of the highly unstable parent 3a,6a-diazapentalene (6)[11] with excess DMAD in dichloromethane afforded a somewhat different, rearranged 1:2 adduct (9) as orange needles; mp 127-128°C; 30 %; m/e 390 (M^+); IR(KBr) cm^{-1} 1738, 1700 (C=O); ^{1}H-NMR($CDCl_3$) δ 3.58, 3.68, 3.72, 3.73(each s, 12H, CO_2CH_3), 5.09(dd, 1H, 7-H, J=7, 9 Hz), 5.20(s, 1H, 12-H), 6.60(d, 1H, 6-H, J=9 Hz), 6.64(d, 1H, 4-H, J= 4 Hz), 6.78(d, 1H, 8-H, J=7 Hz), 7.35(d, 1H, 5-H, J=4 Hz); ^{13}C-NMR($CDCl_3$) δ 51.46, 52.11, 52.27, 53.24(each q, CH_3), 96.02(d, C-6), 110.14(d, C-7), 118.82(d, C-8), 119.55(s, C-11), 133.76(d, C-12), 134.81(s, C-9, 10), 143.74(s, C-3), 148.12(d, C-4), 155.51(d, C-5), 162.24, 162.73, 163.63, 166.55(each s, ester C=O).[6] Since electrophilic substitution of 6 takes place at 1,3 positions exclusively,[11] formation of the product can be accomodated by a mechanism started by electrophilic attack of DMAD at 1,3 positions of 6, followed by cyclization and rearrangement as shown in the Scheme. It remains to be explained why a 1:3 adduct which corresponds to 5 was not formed in this case.

Reactions of the derivatives (1b, c) with DMAD, and 1a with diethyl acetylenedicarboxylate produced the corresponding rearranged 1:2 adducts (5b-d).



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