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3H-INDOLES AND ACETYLENECARBOXYLIC ESTERS

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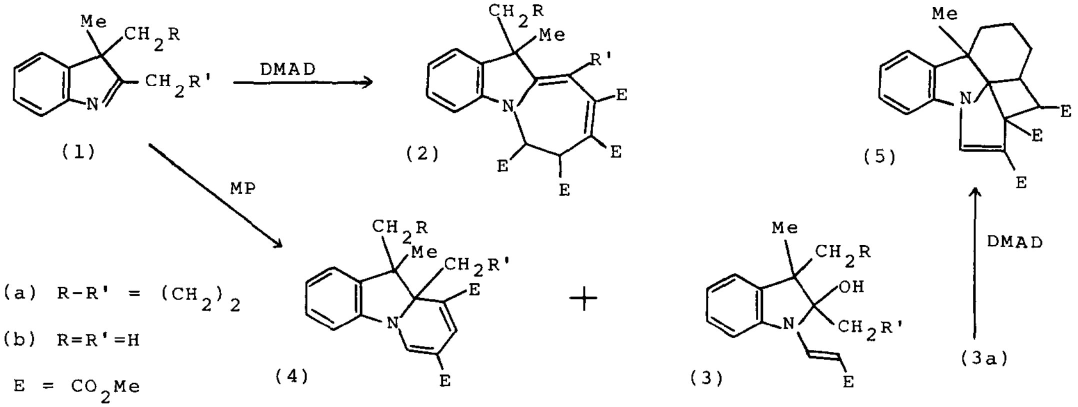
Summary: *The 3H-indoles (1) and dimethyl acetylenedicarboxylate (DMAD) give azepino [1,2-a]indoles (2), and with methyl propiolate, (1) gives stable carbinolamines (3) and pyrido[1,2-a]indoles (4); (3a) and DMAD give a novel 8,9-methanopyrrolo[2,1-k]carbazole (5).*

Reactions between 3H-indoles and acetylenecarboxylic esters have not previously been reported. We now report on the products from the 3H-indoles (1a) and (1b); the structures of these adducts were elucidated by spectroscopy.

In wet methanol (or acetonitrile, or acetic acid), (1a) and DMAD give a yellow (1IND + 2DMAD) adduct (2a) 40%; m.p. 186-188°C; $\lambda_{max.}$ 256 (ε 9000), and 400nm (16000); m/z 469 (100%), 423 (35), and 410 (35)] exhibiting ^{1}H n.m.r. AB resonances at δ_H(90 MHz, $CDCl_3$) 5.67 (1H, d, J 5.7 Hz, H-6) and 5.25 (1H, d, J 5.7 Hz, H-7), and with the corresponding ^{13}C n.m.r. resonances at δ($CDCl_3$) 59.5 (d) and 45.8 (d); this data is very similar to that which was reported[1] as being diagnostic for several (1:2DMAD) adducts with azepine structures.

With methyl propiolate (MP) in wet methanol (or acetonitrile), (1a) reacts quite differently, giving two products isolated by t.l.c.: the major product (40% yield) is a (1IND + 1MP + H_2O) adduct, the carbinolamine (3a) [m.p. 91-92°C; $\lambda_{max.}$ 290 (ε 9500) and 323nm (19000); m/z 287 (100%) and 254 (30); δ_H (90 MHz, $CDCl_3$) 7.92 (1H, d, J 14.0 Hz, olefinic H), 7.3-6.9 (4H, m, aryl H), 5.67 (1H, d, J 14.0 Hz, olefinic H), 3.70 (3H, s, OMe), 3.40 (1H, s, OH, D_2O



exchangeable), 2.2-1.0 (8H, m, 4 x CH_2) and 1.23 (3H, s, CMe); the minor product (8% yield), a (1IND + 2MP) adduct, (4a) [m.p. 104-105°C; $\lambda_{max.}$ 263 (ϵ 24000), 292 (20000), and 433nm (15000): δ_H(90 MHz, $CDCl_3$) 8.12 (1H, d, *J* 1.3 Hz, H-6), 7.81 (1H, d, *J* 1.3 Hz, H-8), 7.3-7.0 (4H, m, aryl H), 3.79 (3H, s, OMe), 3.76 (3H, s, OMe), 3.05-1.0 (8H, m, 4 x CH_2), and 1.36 (3H, s, CMe); *m/z* 353 (10%), and 294 (100%)] was formulated mainly on the basis of n.m.r. resonances which reveal among other features, four methylene groups, two 1,3-coupled olefinic protons, and two δ_C resonances for quaternary sp^3 carbons at 73.0 (s) and 48.3 (s). In wet acetic acid, (4a) is the major product (80% yield). These reactions appear to be general for 3*H*-indoles having methyl or methylene substituents at C-2, as (1b) gives rise to the analogous compounds (2b), (3b) and (4b), under the appropriate reaction conditions. The isolation of the carbinolamines (3a) and (3b), further confirms such compounds as reaction intermediates in indole-acetylenic ester reactions[2], and also suggests that the formation of (2) is via N-substitution followed by enamine reaction with DMAD at the carbon attached to C-2 of the indole, and not vice-versa. The pyrido-indoles (4a) and (4b) appear to be the first reported compounds in which MP has provided four of the carbon atoms in a pyridine ring formed by cyclo-addition.

In acetonitrile, (3a) reacts with DMAD to give a yellow (1IND + 1MP + 1DMAD) adduct (5) [35%; m.p. 192-193°C; $\lambda_{max.}$ 340nm (ϵ 17500); δ_H(90 MHz, $CDCl_3$) 7.72 (1H, s, olefinic H), 7.1-6.8 (4H, m, aryl H), 3.65 (9H, s, OMe), 3.90 (1H, d, *J* 9.6 Hz, H-9), 3.5-3.2 (1H, m, H-10), 1.8-1.2 (6H, m, 3 x CH_2), 1.22 (3H, s, CMe); δ_C (22.5 MHz, $CDCl_3$) 171.7 (s), 170.9 (s), 164.7 (s), 145.5 (d), 141.4 (s), 140.0 (s), 128.1 (d), 123.0 (d), 122.7 (d), 112.0 (s), 110.6 (d), 85.1 (s), 61.3 (s), 52.4 (q), 51.7 (q), 50.9 (q), 49.2 (d), 45.5 (s), 41.4 (d), 37.1 (t), 28.0 (t), 24.8 (q), and 18.7 (t); *m/z* 411 (55%), 380 (100), and 352 (35)] with the three sp^3 quaternary carbon resonances, and two sp^3 CH resonances being particularly diagnostic. Structure (5) is further confirmed by spin decoupling: irradiation at δ_H 3.30 causes the doublet at δ_H 3.90 to collapse to a singlet. (5) may arise either via cycloaddition of a 1,5-dipole[2], formed in much the same way as the intermediate leading to (2) is formed, or via enaminic addition of the N-vinyl ester to the cyclobutene formed by DMAD addition to the cyclohexene obtained from (3a) by the loss of water. (Analogous cyclobutenes formed from 1*H*-indoles and DMAD have actually been isolated in the ring opened form[3], but in the present case, ring opening is precluded due to ring strain.) The generality of this reaction is being studied.

References

1. R.M. Acheson, and G. Procter, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1924.
2. R.M. Letcher, M.C.K. Choi, T.C.W. Mak, and R.M. Acheson, *J. Chem. Soc., Perkin Trans. 1*, 1983, 505.
3. R.M. Letcher, M.C.K. Choi, and J.S.M. Wai, *J. Chem. Research*, 1985, (S) 280; (M) 3138.

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