REACTION OF PYRROLO[1,2-a]INDOLE-5,8-DIONE DERIVATIVES WITH N-BROMOSUCCINIMIDE IN PROTIC SOLVENTS

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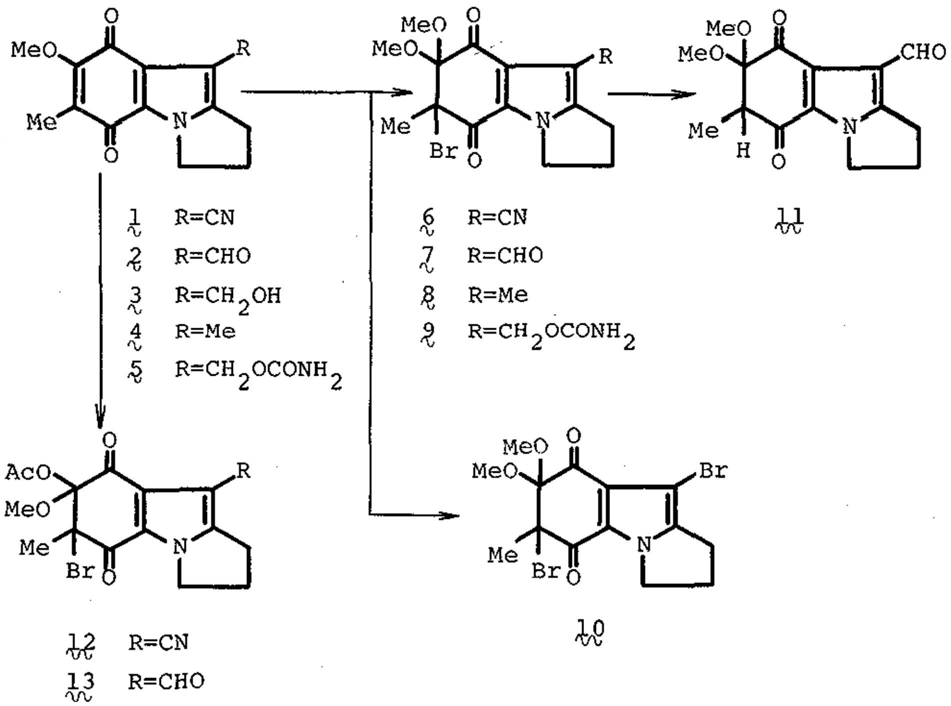
Treatment of the pyrrolo[1,2-a]indole-5,8-diones (1 ∿ 5) with N-bromosuccinimide in protic solvents such as methanol and acetic acid yielded the adducts (6 ∿ 10 and 12 ∿ 13) in good yield. Debromination of the adduct 7 with tri-n-butyltin hydride to give 11 was also described.

In the previous paper[1], we have mentioned the reaction of 9-cyano-2,3-dihydro-7-methoxy-6-methylpyrrolo[1,2-a]indole with N-bromosuccinimide (NBS) in methanol to give 8-bromo-9-cyano-2,3-dihydro-5,7-dimethoxy-6-methylpyrrolo[1,2-a]indole. Although the reactions of simply substituted indoles[2] and 1,4-benzoquinone derivatives[3] with NBS in protic solvents had been reported, the reaction of pyrrolo[1,2-a]indole-5,8-diones with NBS has not yet been reported. In this paper, we wish to describe the reactions of some pyrrolo[1,2-a]indole-5,8-diones with NBS in protic solvents.

The aldehyde 2 was treated with two equivalents of NBS in methanol-dichloromethane (1 : 1 v/v) at room temperature for 20 min to give the adduct **7**[4] in a good yield, mp 188 - 189°; nmr δ ($CDCl_3$) 2.04 (3H, s, C-CH_3), 2.50 - 3.50 (4H, m, -CH_2CH_2-), 3.34 and 3.80 (each 3H, each s, OCH_3 x 2), 4.36 (2H, t, *J* = 7 Hz, >NCH_2), 10.34 (1H, s, CHO); ir $\nu_{max}^{CHCl_3}$ 1710, 1670 cm^{-1} (C=O); m/e 371, 369 (M^+), 290 (M^+-Br). Introduction of bromine and methoxy groups to C-6 and 7 positions was suggested by the uv spectrum [λ_{max}^{EtOH} nm (log ε) 254 (4.23), 290 (3.76), 336 (4.02)] which is similar to that of the 6,7-dihydropyrrolo[1,2-*a*]indole-5,8-dione.[5] The structure of **7** was further supported by the debromination of **7**. Namely, treatment of the adduct **7** with tri-*n*-butyltin hydride in the presence of catalytic amount of azobisisobutyronitrile[6] afforded the debrominated compound **11**, mp 185 - 186°; nmr δ ($CDCl_3$) 1.20 (3H, d, *J* = 7 Hz, >CH-C*H*$_3$), 3.18 and 3.34 (each 3H, each s, each OCH_3 x 2), 4.30 (2H, t, *J* = 7 Hz, >NCH_2-); ir $\nu_{max}^{CHCl_3}$ 1700, 1660 cm^{-1} (C=O); m/e 291 (M^+); uv λ_{max}^{EtOH} nm (log ε) 230 (4.31), 285 (3.83), 325 (4.09).

The similar reactions of **1**,**4** and **5** with NBS furnished the corresponding adducts **6**,**8** and **9**, respectively, in excellent yields. Interestingly, in the case of the alcohol **3**, the desired adduct could not be obtained but the dibromide **10** was formed in a good yield, mp 197 - 199°; nmr δ ($CDCl_3$) 2.00 (3H, s, $\geq$C-CH_3), 2.30 - 3.50 (4H, m, -CH_2CH_2-), 3.30 and 3.74 (each 3H, each s, OCH_3 x 2), 4.34 (2H, t, *J* = 7 Hz, >NCH_2-); ir $\nu_{max}^{CHCl_3}$ 1700, 1675 cm^{-1} (C=O); uv λ_{max}^{EtOH} nm (log ε) 254 (3.82), 294 (3.60), 346 (3.84). The dibromide **10** was also obtained by treatment of the aldehyde **2** with a large excess of NBS for a longer reaction time (15 hr).

When the reaction was carried out in acetic acid, 1 and 2 yielded the 7-acetoxylated bromides (12 and 13). Thus, treatment of the aldehyde 2 with an excess of NBS in acetic acid-dichloromethane (1 : 1 v/v) at room temperature for 6 hr gave the acetate 13 in high yield, mp 183 - 184^{o}; nmr δ ($CDCl_3$) 2.02 and 2.08 (each 3H, each s, $COCH_3$ and $\geq CCH_3$), 2.50 - 3.50 (4H, m, $-CH_2-CH_2-$), 3.84 (3H, s, OCH_3), 4.34 (2H, t, $\underline{J}$ = 7 Hz, $>N-CH_2-$), 10.24 (1H, s, CHO); ir $\nu_{max}^{CHCl_3}$ 1775, 1720, 1665 cm^{-1} (C=O); uv λ_{max}^{EtOH} nm (log ε) 254 (4.60), 328 (4.36). The nitrile 1 gave the acetate 12, mp 178 - 179^{o}, in the similar conditions.



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