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

Tetsuji Kametani,* Kimio Takahashi, Masataka Ihara,
and Keiichiro Fukumoto
Pharmaceutical Institute, Tohoku University, Aobayama,
Sendai 980, Japan

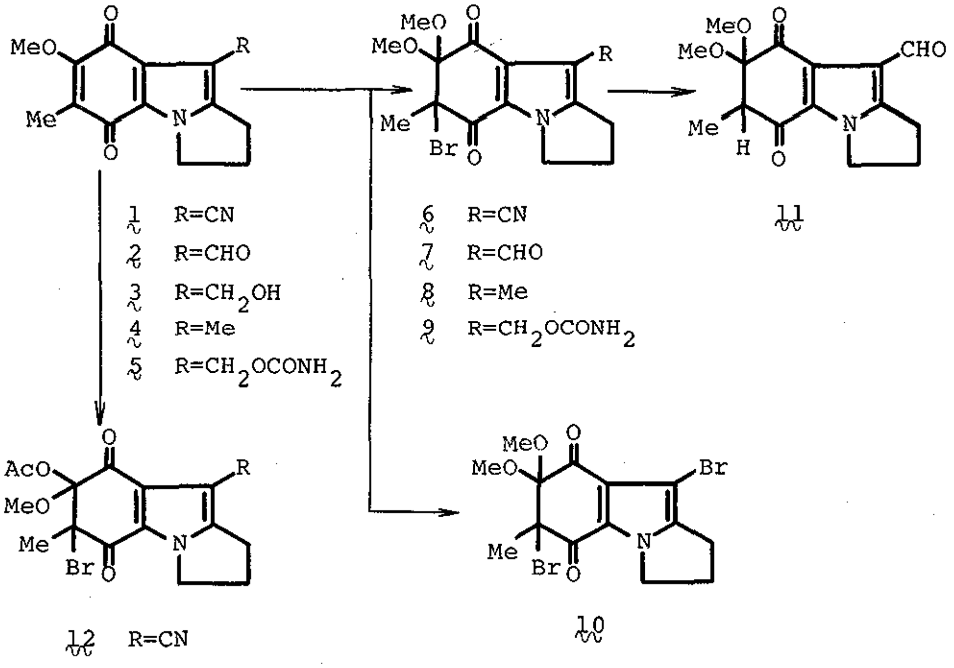
Treatment of the pyrrolo[1,2-*a*]indole-5,8-diones (**1** ∿ **5**) with N-bromosuccinimide in protic solvents such as methanol and acetic acid yielded the adducts (**6** ∿ **10** and **12** ∿ **13**) in good yield. Debromination of the adduct **7** with tri-*n*-butyltin hydride to give **11** was also 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$_2$CH$_2$-), 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-CH$_3$), 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, $\gtrdot$C-CH$_3$), 2.30 - 3.50 (4H, m, -CH$_2$CH$_2$-), 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°; nmr δ (CDCl$_3$) 2.02 and 2.08 (each 3H, each s, COCH$_3$ and $\geqq$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°, in the similar conditions.



1 R=CN
2 R=CHO
3 R=CH$_2$OH
4 R=Me
5 R=CH$_2$OCONH$_2$

6 R=CN
7 R=CHO
8 R=Me
9 R=CH$_2$OCONH$_2$

11

12 R=CN
13 R=CHO

10

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