SYNTHESIS AND PROPERTIES OF SOME SIX-MEMBERED HETEROAROMATIC BETAINES

Yasumitsu Tamura, Masafumi Yamagishi, and Masazumi Ikeda
Faculty of Pharmaceutical Sciences, Osaka University
1-6 Yamada-oka, Suita, Osaka, Japan
Yasuyoshi Miki
Faculty of Pharmaceutical Sciences, Kinki University
3-4-1 Kawakoe, Higashi-Osaka, Japan

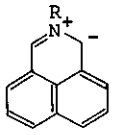
Synthesis and some properties of two types of six-membered heteroaromatic betaines are described.

(I) Benz[de]isoquinolinium-1-ides (1a,b)

Compounds (1) were prepared in situ by treatment of 2-substituted 2,3-dihydro-1H-benzisoquinoline N-oxides with acetic anhydride. They reacted with dimethyl acetylenedicarboxylate and with maleimides to give 1:1 cycloadducts. The stereochemistry of the maleimide cycloadducts was determined by nmr spectroscopy. Exclusive or predominant formation of the endo-adducts is in sharp contrast with the case of naphtho[1,8-cd]thiopyran, which reacts with maleimides to give exclusively or predominantly exo-adducts. The adducts were converted into cyclohepta[de]naphthalene derivatives.

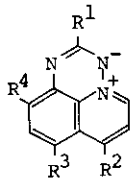
(II) 3H-Pyrido[3,2,1-ij][1,2,4]benzotriazin-4-ium-3-ides (2a-g)

A series of compounds (2) was synthesized by reaction of 8-acylaminoquinolines with O-mesitylenesulfonylhydroxylamine followed by treatment with aqueous alkali. The spectral (uv, ^{1}H-nmr, and ^{13}C-nmr spectra) and chemical properties (bromination and 1,3-dipolar cycloaddition) of the new mesomeric betaines were investigated.



(1)

a, R=Me; b, R=Ph



(2)

a, $R^1=R^2=R^3=R^4=H$; b, $R^1=Me$, $R^2=R^3=R^4=H$;
c, $R^2=Me$, $R^1=R^3=R^4=H$; d, $R^3=Me$, $R^1=R^2=R^4=H$;
e, $R^4=Me$, $R^1=R^2=R^3=H$; f, $R^4=Br$, $R^1=R^2=R^3=H$;
g, $R^1=Ph$, $R^2=R^3=R^4=H$