SIX-MEMBERED ZWITTERIONIC MALONYLHETEROCYCLES

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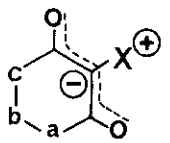
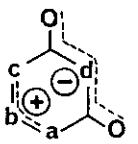
Malonylheterocycles, such as 4-hydroxy-2-pyrones and -2-pyridones, 6-hydroxy-pyrimidin-4-ones, 4-hydroxy-coumarins and -2-quinolones, or barbituric acids are acidic compounds with pK_a values ranging usually between 4,0 and 6,0. The negative charge localized in the malonate anion moiety of a heterocyclic system can be compensated in two different ways yielding zwitterionic compounds:

A 

B 

a=O, b-c = C=C	Pyrones	a=c=N, b=d=C	Pyrimidines	(2)
a=NR, b-c = C=C	Pyridones	a=N, c=S, b=d=C	1,3-Thiazines	(3)
a=c=N, b = C	Pyrimidones	a=N, c=O, b=d=C	1,3-Oxazines	(4)
a=O, b-c = benzo	Coumarins	a=c=d=N, b=C	1,3,5-Triazines	(5)
a=NR, b-c = benzo	Quinolones (1)	a=b=c=N, d=C	1,2,3-Triazines	(6)

X = N<, SR_2, PR_3, I-Aryl

Both types of compounds have been studied by us in recent years. Synthetic routes to pyridinium-, sulfonium, phosphonium- and iodonium-ylides have been developed. Especially the reactive iodonium-ylides were found to be versatile synthons in the chemistry of malonylheterocycles (and generally in the field of 1,3-dicarbonyl systems); the 2-quinolone system (1) beeing most thoroughly studied.

Since about 1971 a number of six-membered mesoionic compounds of the general formula B have been prepared by us and others and their chemistry studied[1]. The synthesis of these compounds requires appropriate substituted amidines or α-amino-N-heterocycles (for 2 and 5), thioamides (for 3), amides (for 4) and triazenes (for 6) as substrates, and reactive malonic acid derivatives (such as carbon suboxide, chlorocarbonyl ketenes or trichlorophenyl malonates) or "azamalonyl" derivatives (for 5), respectively, as reagents. Some of the mesomeric betaines undergo 1,4-dipolar cycloadditions with acetylenic or ethylenic dipolarophiles. A number of type B compounds are rearranged at higher temperatures via ketene intermediates to other heterocyclic ring systems.

[1] *W. Friedrichsen, Th. Kappe and A. Böttcher, HETEROCYCLES 19, 1083-1148 (1982).*