Acylations of 1*H*-1,2-Thieno- and 1*H*-1,2-Benzo-diazepines: Ring-conversion into 1,3-Diazepines

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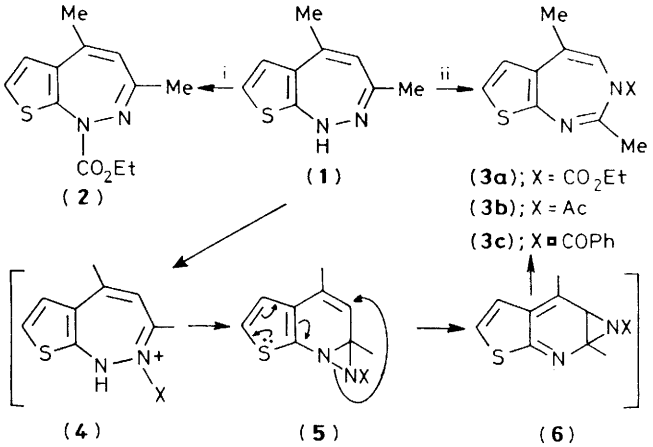
Treatment of the 1*H*-1,2-thienodiazepine (**1**) and the 1*H*-1,2-benzodiazepines (**7**) having an electron-donating substituent in the 7-position with ethyl chloroformate, acetyl chloride, or benzoyl chloride in benzene results in ring-conversion to give the corresponding 1,3-diazepines (**3**) and (**12**).

The acylations of 5*H*-2,3-benzodiazepines[1] and 4*H*-1,2-diazepines[2] prompted us to examine such reactions of 1*H*-1,2-benzodiazepines and related fused 1*H*-1,2-diazepines, and we now report the first examples of the ring-conversion of 1,2-diazepines into 1,3-diazepines by acylating reagents.

Treating the thienodiazepine (**1**)[3] with ethyl chloroformate in pyridine gave only the 1-ethoxycarbonyl-1*H*-1,2-diazepine (**2**), whereas treatment of (**1**) with the same reagent in benzene at room temperature resulted in rearrangement with ring-conversion to give the 3*H*-1,3-diazepine (**3a**) in *ca.* 40% yield.† Similar results were obtained with acetyl chloride or benzoyl chloride in benzene but no reaction was obtained with acetic anhydride, tosyl chloride, or methyl iodide even on heating at 60—70 °C.

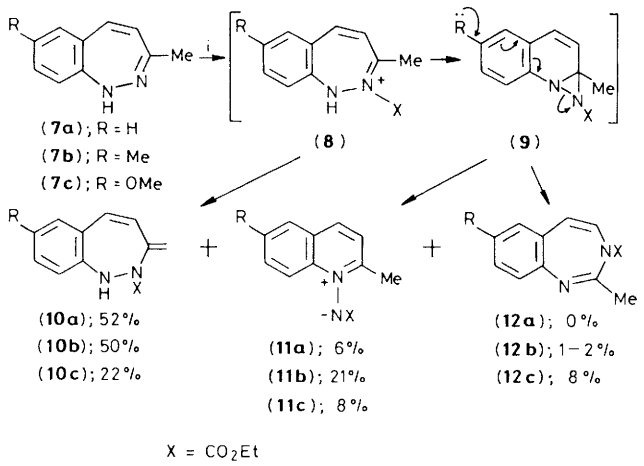
The ring-conversion of (**1**) into (**3**) may involve the diaziridine intermediates (**5**) formed *via* the 2-acyl salts (**4**). The intermediates (**5**) may then rearrange to the aziridines (**6**) followed by ring-expansion to the products (**3**) (Scheme 1),



Scheme 1. *Reagents:* i, $ClCO_2Et$–pyridine, ii, $ClCO_2Et$, AcCl, or PhCOCl–benzene.

which is analogous to that observed for the direct formation of 3*H*-1,3-thienodiazepines from thieno[*b*]pyridine *N*-imides by irradiation.[3]

† The diazepine (**2**) was also prepared from (**1**) by treatment with $ClCO_2Et$ in the presence of n-butyl-lithium at −60 °C and the 1,3-diazepines (**3**) have been prepared by irradiation of the corresponding thienopyridine *N*-acylimides.[3]



Scheme 2. *Reagents:* i, $ClCO_2Et$, AcCl, or PhCOCl–benzene.

In contrast, 3-methyl-1*H*-1,2-benzodiazepine (**7a**),[4] upon treatment with ethyl chloroformate in benzene gave the *exo*-methylene compound (**10a**)‡ and the quinoline *N*-imide (**11a**), but no 1,3-diazepine derivative. However, the benzodiazepines (**7b**) and (**7c**) having an electron-donating group in the 7-position gave the 1,3-diazepines (**12**), in addition to (**10**) and (**11**), in the yields shown in Scheme 2.

‡ Satisfactory elemental analyses and spectral data were obtained for the new compounds (**10**), *e.g.*, (**10a**): yellow oil; λ_{max} (ϵ) (EtOH) 224 (11700), 241 (12200), 289 (10400), and 299 nm (9600); ν_{max} ($CHCl_3$) 1700 (C=O) and 3350 (NH) cm^{-1}; δ ($CDCl_3$) 5.09 and 5.17 (each 1H, s, $C=CH_2$), 6.34 (2H, s, 4- and 5-H), 6.4 (1H, br., NH), 6.9—7.3 (4H, m, Ph–H), 1.19 and 4.09 (3H, t, and 2H, q, CO_2Et); (**10b**): yellow oil; (**10c**): yellow prisms, m.p. 85—86 °C.

In this benzo-series, the reaction could proceed by two competing pathways from the initially formed 2-acyl salts (**8**): (i) deprotonation of the methyl group to give (**10**), and (ii) elimination of the NH proton to give the diaziridines (**9**) followed by either C–N bond fission to give (**11**) or N–N bond fission to give (**12**). The substituent effect on the ring-conversion is illustrated by structures (**5**) and (**9**). The electron-donating group may provide assistance for breaking the N–N bond in the diaziridines and for cyclisation of the resulting dipolar intermediates into aziridines. This effect is analogous to those observed for the thermal ring-conversion of monocyclic 1,2-diazepines into 1,3-diazepines[5] and the photochemical formation of 1,3-benzodiazepines from quinoline *N*-acylimides.[6]

In addition, similar reactions of 3-unsubstituted 1,2-thieno- and 1,2-benzo-diazepines gave the corresponding fused 2-acylaminopyridines and pyridine *N*-imides, but no diazepines.

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