Pergamon

Tetrahedron Letters 43 (2002) 5285–5286

TETRAHEDRON LETTERS

Synthesis of pyridothietone by flash vacuum pyrolysis of 2-mercaptonicotinic acid

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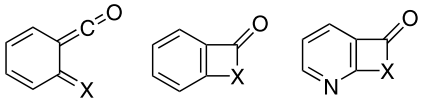
Received 25 March 2002; revised 25 May 2002; accepted 31 May 2002

Abstract—The temperature dependence of products formed from flash vacuum pyrolysis (FVP) of 2-mercaptonicotinic acid **4** has been studied. FVP of **4** at 550°C and ca. 1×10^{-2} torr gave pyridothietone **3b** and a trimer **5** as the major products. At higher temperature (800°C), FVP of **4** gave 2-mercaptopyridine **6** as the major product and 2,2′-dipyridyl disulphide **7** as the minor one.

The short-lived α-oxo-*o*-quinodimethane **1a** and its heteroanalogues **1b–d** have been shown to be transient intermediates in many reactions and have attracted much attention as a result of their non-aromatic structural features.[1] Although **1a–d** have never been isolated successfully due to their high reactivities, the closed forms of **1a–d**, benzocyclobutenone **2a**,[1c] benzopropiolactone **2b**,[1d] benzothietone **2c**,[1g,1h] and benzoazetinone **2d**,[1i] have been shown to be somewhat more stable and can be isolated at low temperature. To extend the chemistry of **2** to their pyridine analogues, we have previously synthesized pyridocyclobutenone **3a** by the flash vacuum pyrolysis (FVP) of 3-chloroformyl-2-methylpyridine.[2] We now wish to report the synthesis of the previously unknown pyridothietone **3b** by FVP of 2-mercaptonicotinic acid **4**.



1a, X = CH_2 **2a**, X = CH_2 **3a**, X = CH_2
1b, X = O **2b**, X = O **3b**, X = S
1c, X = S **2c**, X = S
1d, X = NH **2d**, X = NH

FVP of **4** at 550°C and ca. 1×10^{-2} torr produced a pale-yellow band in the cold trap at 77 K. After warming to room temperature, the ^{1}H and ^{13}C NMR spectra revealed that pyridothietone **3b** was present as the major product (41%),[3] along with a trimer **5** (30%)[4] and recovered **4** (19%). Unlike **2d** and **3a**, which can only be isolated at low temperature, **3b** is stable at room temperature and can be separated from **4** and **5** by fractional distillation under vacuum. When the pyrolysis temperature was raised to 800°C, FVP of **4** gave 2-mercaptopyridine **6** and 2,2′-dipyridyl disulphide **7**[5] in 58% and 11% yields, respectively, along with a small amount of **3b** (4%) and some polymers. The formation of these products via FVP of **4** is summarized in Scheme 1.

It is noteworthy that although FVP of **4** at high temperatures (>800°C) does not give 2-thiocarbonyl-2*H*-pyrrole **10**, such a ring-contraction reaction is not uncommon in related systems.[2,6] Our recent study on the chemistry of 3-hydroxypyridine-2-carboxylic acid **11** indicates that FVP of **11** at 550°C and 1×10^{-2} torr gives a dimer of 2-carbonyl-2*H*-pyrrole **12**, dipyrrolo[1,2-*a*;1′,2′-*a*]pyrazine-5,10-dione **13**,[7] as the major product (38%) (Scheme 2). This result demonstrates another example of a ring contraction reaction.

We are currently applying this approach to the preparation of other heterocyclic analogues of benzocylobutenone.

Acknowledgements

We thank the National Science Council of the Republic of China for financial support.

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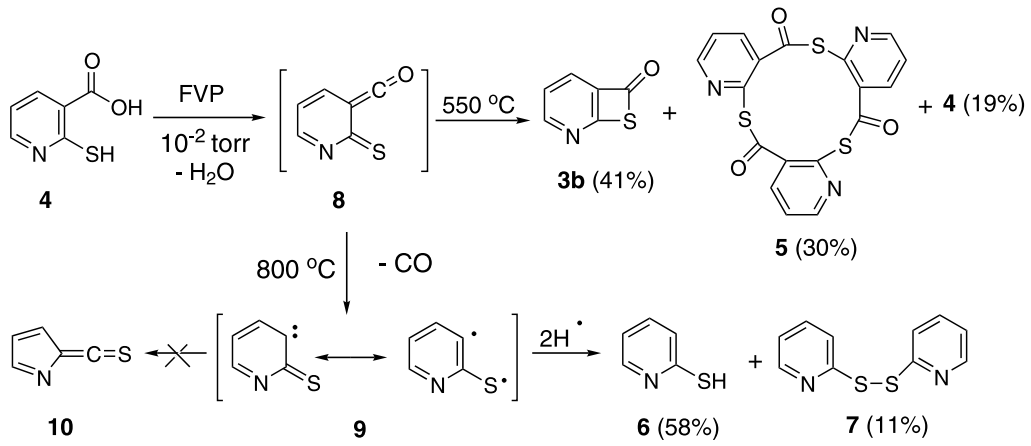
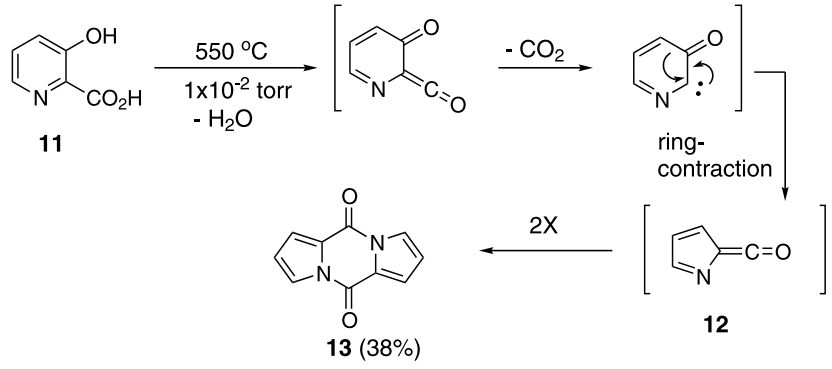
PII: S0040-4039(02)01044-4



Scheme 1.



Scheme 2.

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2. Chou, C. H.; Wu, C. C.; Chen, W. K. *Tetrahedron Lett.* **1995**, *36*, 5065.
3. **3b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.82 (dd, $J=4.5$ and 1.8 Hz, 1H), 8.23 (dd, $J=8.1$ and 1.8 Hz, 1H), 7.39 (dd, $J=8.1$ and 4.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 190.62, 168.56, 154.77, 135.47, 122.82, 120.07; MS(FAB) m/z (%) 138 ($M+1^+$, 13); IR ($CDCl_3$, cm^{-1}) 1686.
4. **5**: ^{1}H NMR (acetone-d_6) δ 8.73 (dd, $J=7.8$ and 1.8 Hz, 1H), 8.26 (dd, $J=6.0$ and 1.8 Hz, 1H), 7.23 (dd, $J=7.8$ and 6.0 Hz, 1H); ^{13}C NMR (acetone-d_6) δ 205.42, 165.45, 145.91, 143.68, 130.68, 115.64; MS(FAB) m/z (%) 412 ($M+1^+$, 1.0); IR ($CDCl_3$, cm^{-1}) 1744, 1709.
5. **7**:^{1}H NMR ($CDCl_3$) δ 8.47 (d, $J=4.8$ Hz, 2H), 7.62 (dd, $J=4.8$, 1.2 Hz, 4H), 7.12 (m, 2H); ^{13}C NMR ($CDCl_3$) 170.69, 149.22, 137.17, 120.87, 119.43; MS (LR, 70 eV) m/z (%) 220 (M^+, 79).
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