Spontaneous Deoxygenation of N-(3,4-Methylenedioxybenzyl)-Acetohydroxamic Acid: An Exceptionally Facile Process

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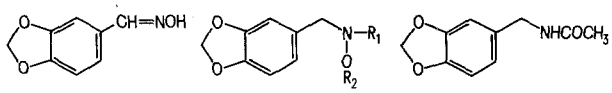
Summary. An exceptionally facile spontaneous deoxygenation of N-(3,4-methylenedioxybenzyl)-acetohydroxamic acid to its corresponding amide, without apparent literature precedent, is reported.

In the course of devising a new reductive rearrangement[2] for the synthesis of biologically important peptide derivatives, we had occasion to prepare N-(3,4-methylenedioxybenzyl)acetohydroxamic acid **4** and present here evidence for its unusually rapid thermal decomposition to the corresponding acetamide. In order to obtain an authentic sample of **4**, standard procedures were employed



1 **2** $R_1 = R_2 = H$; **3** $R_1 = R_2 = COCH_3$; **4** $R_1 = COCH_3$, $R_2 = H$; **5**

as outlined in Scheme I. Reduction of **1** (m.p. 110°) using diborane[3] afforded the hydroxylamine **2**, m.p. 43–45° [NMR ($CDCl_3$) δ 3.92 (s, 2H), 5.60 (broad s, 2H; NH, OH), 5.98 (s, 2H), 6.8 (narrow m, 3H); IR ($CHCl_3$) λ_{max} 2.9, 6.6, 6.9 μ; mass spectrum (C.I.) 167 (M^+), 135 (base, $C_8H_7O_2^+$)]. Exhaustive acetylation of **2** (Ac_2O) furnished the oily N,*O*-diacetyl derivative **3** [NMR ($CDCl_3$) 2.03 (s, 3H), 2.14 (s, 3H), 4.75 (s, 2H), 5.95 (s, 2H), 6.76 (narrow m, 3H); IR (film) 5.58, 6.0 μ]. This substance underwent rapid hydrolysis (0°, 30 min) in dilute aqueous NaOH to a monoacetyl derivative [NMR ($CDCl_3$) 1.98 (s, 3H), 4.2 (broad s, 2H), 5.92 (s, 2H), 6.76 (narrow m, 3H; underlying broad s, 1H); IR ($CHCl_3$) 3.0, 6.05 μ; mass spectrum 193 (M-16, base)] whose strongly positive reaction with $FeCl_3$ solution (deep burgundy in MeOH, EtOH) was characteristic of the hydroxamic acid **4**. Efforts to isolate **4** pure were unsuccessful. Whereas the substance appeared to be relatively stable at 0° in $CHCl_3$ solution (half-life ca. 2 days), efforts at chromatography (Florisil) or recrystallization yielded only the acetamide **5**, m.p. 104–105° (lit.[4] 103°) whose NMR-, IR-, and mass spectra matched perfectly those of an unambiguously prepared sample from piperonylamine and acetic anhydride.

Hydroxamic acids can be reduced to amides or lactams by a number of reagents[5]; however this remarkably facile deoxygenation of **4** is, to the best of our knowledge, unprecedented in the literature on hydroxamates.

[1] We acknowledge the Research Corporation for financial support.

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Species-Specific Protein Patterns in *Drosophila* Paragonial Glands[1]

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Summary. Electrophoretic analysis of the soluble proteins in the paragonial glands of 11 *Drosophila* species demonstrated that the patterns are highly species-specific. The possible functional significance of these proteins is discussed.

The paragonial glands (accessory glands) in the male flies of *Drosophila* have been studied by a number of investigators, mainly because of their specific roles in the reproductive process (see more recent reviews by CHEN[2] and FOWLER[3]). Extensive experiments carried out in our laboratory demonstrated that the secretory contents of these glands in *D. melanogaster*[4–6] and *D. funebris*[7–10] contain specific polypeptides and related amino acid derivatives which are responsible for the stimulation of oviposition and the reduction of receptivity in the mated females. We have also observed at least 12 electrophoretically separable proteins in the paragonial gland of *D. melanogaster*[11,12]. A polymorphism of one major protein band, which is autosomal in origin, could be detected. Recently, in a survey of the paragonial secretions in a total of 11 *Drosophila* species we found that the protein patterns are highly species-specific. This result will be dealt with in the present report.

Materials and methods. The flies of all *Drosophila* species were raised on a standard maize-agar-sugar-yeast diet at 25 °C. The males were separated from the females shortly after eclosion from the pupae and kept under the same condition with the diet renewed every 4 days. The classification of the 11 species included in this study is as follows: 1. subgenus *Sophophora* – *D. melanogaster*, *D.*

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