saturated nitriles) even without optimization of reaction conditions. The gentleness of the method is illustrated both by the sensitive nature of the systems that can be formed, as well as its compatibility with various functionality. Several of the compounds formed using geranyl bromide and citronellyl iodide have interest as juvenile hormone mimics.[13]

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Department of Chemistry
University of Wisconsin
Madison, Wisconsin 53706

Barry M. Trost*[14]
Alex J. Bridges

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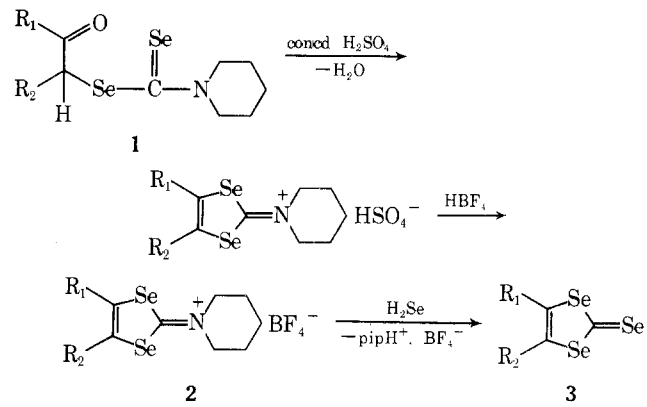
A Safe Preparation of Mono- and Disubstituted 1,3-Diselenole-2-selones

Summary: The preparation of 2-(*N,N*-pentamethylenimino)-1,3-diselenolium fluoroborate as nonhazardous intermediates in the synthesis of 1,3-diselenole-2-selones and tetraselenafulvalenes is described.

Sir: 1,3-Diselenole-2-selones[1-4] have recently gained interest as intermediates in the synthesis of certain tetraselenafulvalenes, which form highly conducting organic solids with 7,7′,8,8′-tetracyanoquinodimethane.[2,3,5,6] Two different synthetic routes to 1,3-diselenole-2-selones have been reported. The first[2,4] involves the reaction of selenium and carbon diselenide with sodium acetylides leading to unsubstituted or monosubstituted selones. In the second[1,3] mono- and disubstituted 1,3-diselenole-2-selones are obtained by passing hydrogen selenide through a methanolic solution of 2-(*N,N*-pentamethylenimino)-1,3-diselenolium perchlorates. These salts do, however, detonate upon ignition, heating, and shock and, although we have not so far observed any spontaneous detonations as reported for related systems,[7] their handling in larger quantities constitutes a potential hazard. In spite of this, the use of perchlorates as intermediates was justified by their ready isolation in high yield and purity.

Scheme I

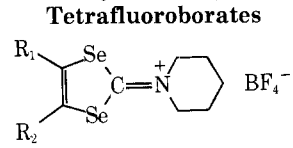


1 2 3

Previous attempts to prepare the fluoroborates (**2**) by treating the hydrosulfates, obtained by ring closure of 2-oxoalkyl piperidinodiselenocarbamates (**1**),[1,3] in concentrated H_2SO_4 with an excess of an ethanolic solution of 48% aqueous HBF_4 resulted in a rather poor yield of a deliquescent product.[8]

We have now found that addition of the reaction mixture containing the hydrosulfate to a stirred ethanolic solution containing a 2–3-fold molar excess of HBF_4, prepared from an etheral solution of HBF_4 (54%, Merck-Schuchardt, Munich), gives well-defined, nonhygroscopic fluoroborates in excellent yields (Table I). This procedure makes the corresponding selones available in large quantities without the safety hazards of the earlier procedure.

Table I
2-(*N,N*-Pentamethylenimino)-1,3-diselenolium Tetrafluoroborates



2

R_1	R_2	Yield, %[a]	Mp, °C
CH_3	H	90[b]	111–112
CH_3	CH_3	91	178–179
Ph	H	93	176–177
$-CH_2CH_2CH_2-$		89	210–212 dec

[a] Satisfactory analytical data (±0.3% for C, H, N) were obtained for all compounds listed in the table. [b] A crystalline product was obtained by addition of ether until turbidity, followed by storage overnight at −30°.

In the general procedure, 0.05 mol of the 2-oxoalkyl piperidinodiselenocarbamate (**1**)[1,3] (Scheme I) was dissolved slowly in 50 g of concentrated H_2SO_4 over 1 hr. Enough ethyl acetate to cause starting precipitation of the hydrosulfate was added cautiously to the now cooled reaction mixture, which was then filtered through a

coarse glass filter funnel into a vigorously stirred, cooled solution of 0.15 mol of HBF_4 (54% in ether) in 500 ml of absolute ethanol. The fluoroborate **2** was precipitated by addition of dry ether, filtered off, washed with dry ether, and dried in vacuo. If necessary the product may be purified by dissolving it in a minimum amount of methanol, filtering, and reprecipitating with dry ether.

The fluoroborates were converted to the corresponding selones **3** by a procedure identical with that earlier reported for the perchlorates.[1,3] This step is facilitated by the fact that the fluoroborates are more readily soluble in methanol than are the perchlorates.

Melting points are uncorrected. Elemental analyses were performed by Mr. Preben Hansen, Department of General and Organic Chemistry.

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Department of Chemistry **Jan R. Andersen**
Danish Atomic Energy Commission
Research Establishment Risø
DK-4000 Roskilde, Denmark

Department of General and Organic Chemistry **Klaus Bechgaard***
H. C. Ørsted Institute
DK-2100 Copenhagen, Denmark

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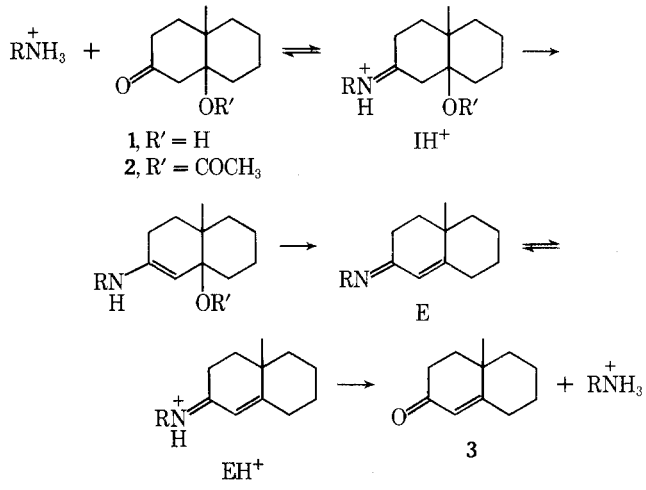
Detection and Characterization of Eniminium Ion Intermediates in Nucleophilic Amine Catalyzed β-Ketol Dehydration

Summary: Previously undetected chromophoric ($\lambda_{max}^{H_2O}$ ~270 nm, ϵ ~16,000) intermediates in nucleophilic amine catalyzed dehydration of β-ketol **1** have been detected (when a large concentration of catalyst is used), isolated, and characterized as eniminium ions (e.g., **4**).

Sir: Nucleophilic amine catalysis of the conversions of β-ketol **1** and β-acetoxy ketone **2** to enone **3** in aqueous solution has been reported by us[1] to proceed without appreciable accumulation of intermediate species according to the mechanism shown in Scheme I, with α-deprotonation of iminium ion IH^+ as the rate-limiting step. We have now found that under appropriate conditions eniminium ion EH^+ is formed in significant concentrations. Since, as discussed below, this species is an intermediate in the sequence **1** → EH^+ → **3**, its detection constitutes important corroboration that catalysis is occurring via amine-carbonyl condensation.[2]

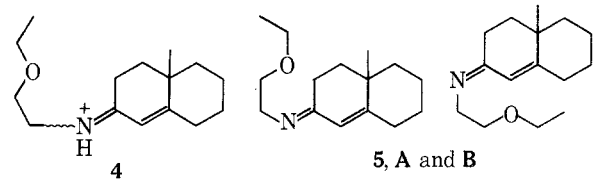
Intermediate EH^+ is characterized by an ultraviolet absorption maximum at ~270 nm. Our failure to detect this species earlier resulted from the use of conditions (low substrate and catalyst concentrations) which tend not to lead to appreciable accumulation of EH^+.[3] Absorption at ~270 nm is readily detectable, however, when relatively high concentrations of reactant and catalyst (pseudo-zero-order conditions) are used at pH ≤ catalyst pK_a. For example, an

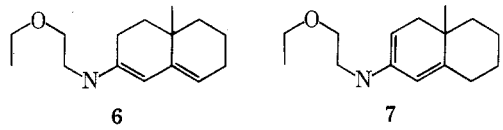
Scheme I



aqueous solution of **1** (5.85×10^{-3} *M*) and ethoxyethylamine (pK_a = 9.44; 0.52 *M*) at pH 8.65 develops absorption predominantly at 270 nm through approximately the first 10% of consumption of **1**.

Identification of this chromophoric species as **4** was accomplished by extraction of the reaction mixture with deuteriochloroform and determination of the mass spectrum [*m/e* 235.1938 (calcd for $C_{15}H_{15}NO$ 235.1936)] and the NMR spectrum of the extract. In addition to a peak at δ 5.70 in the latter due to the vinyl proton peak of **3**, two peaks appeared at δ 5.92 and 6.09 (area ratio of ~2:1) which can only reasonably be assigned to the vinyl protons of the geometrical isomers **5A** and **5B** of the neutral enimine derived from **4**.[4,5]





If the extracted species were dienamine **6**,[6] the olefinic protons should appear at ~5 ppm,[7,8] and a mixture of **5** and **6** prepared by the method of Malhotra[9] did indeed show the expected additional resonances of equal intensity at δ 4.89 and 5.06.[10] If the species were dienamine **7**, it should have an NMR peak at about δ 4.25.[7] The vinyl proton of **4** itself would be expected to appear well below 6 ppm,[8,11] and, when DCl was added to a CD_3OD solution of the synthesized mixture of **5** and **6**, peaks at δ 5.85 and 6.18 were replaced by ones at δ 6.30 and 6.55. The ir spectrum of the extract showed ν 1630 and 1615 cm^{-1}, consistent with the postulated imine structure.[12]

The fact that **4** is observed in reactions run at a pH near the pK_a of the catalyst means that this species must be at least comparable in basicity to ethoxyethylamine. This is not unreasonable. Although imines are generally believed to be ~10^3 less basic than the corresponding amines,[13-16] the additional double bond in the enimine should help to stabilize its protonated form.[17] Unsaturated ketones are ~10^3 more basic than saturated ketones.[18]

The pH-dependent equilibrium between **4** and neutral enimine can be easily demonstrated. A chloroform solution of **5**, prepared in the manner described above, was extract-