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GENERATION OF α-OXO SELENOALDEHYDES BY TREATMENT OF α,α'-DIKETO SELENIDES WITH BASE

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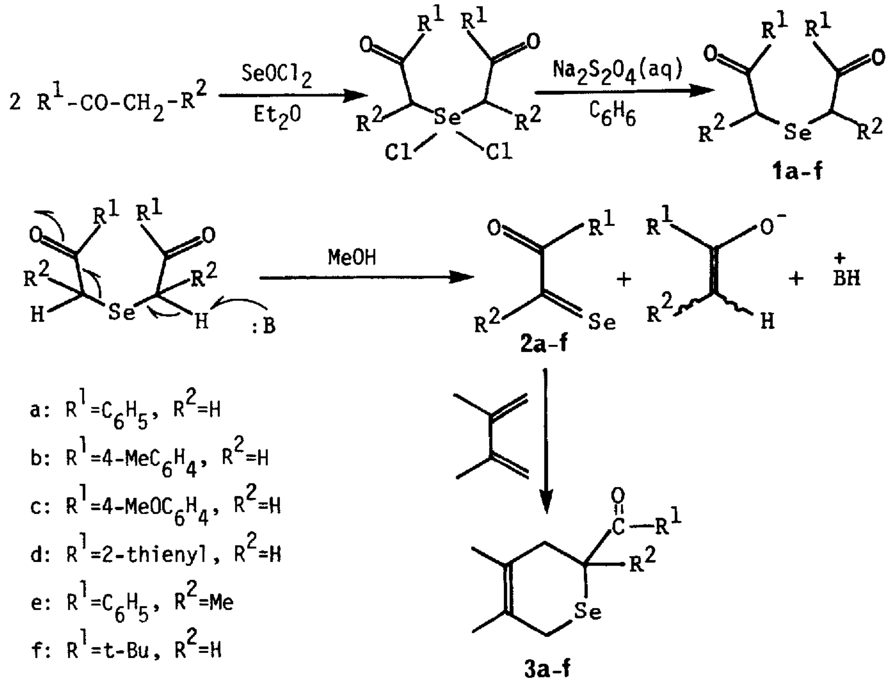
ABSTRACT

Treatment of α,α'-diketo selenides, which recently became readily obtainable, with base affords α-oxo selenoaldehydes and ketones. The seleno-carbonyl compounds thus formed are reactive transient species, but can be trapped by Diels–Alder reaction to give 3,6-dihydro-2*H*-selenapyran derivatives in moderate to good yields.

Chemistry of selenoaldehydes is of current interest.[1–5] We have recently reported a convenient modified synthesis of α,α'-diketo selenides (**1**).[6] Herein we report that treatment of **1** with base generates α-oxo selenoaldehydes and selenoketones (**2**), which can be trapped by Diels–Alder reaction to give 3,6-dihydro-2*H*-selenapyran derivatives (**3**) in moderate to good yields.



a: $R^1=C_6H_5$, $R^2=H$
b: $R^1=4\text{-}MeC_6H_4$, $R^2=H$
c: $R^1=4\text{-}MeOC_6H_4$, $R^2=H$
d: R^1=2-thienyl, $R^2=H$
e: $R^1=C_6H_5$, $R^2=Me$
f: R^1=t-Bu, $R^2=H$

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Table 1. Generation of seleno-carbonyl compounds **2** from diketo selenides **1** and their trapping by Diels–Alder reaction[a]

run	diketo selenide	base (equiv.)	time (h)	adduct[b] (yield, %)
1	**1a**	Et_3N (1·1)	6	**3a** (70)
2	**1b**	Et_3N (1·1)	10	**3b** (62)
3	**1c**	Et_3N (1·1)	11	**3c** (65)
4	**1d**	Et_3N (1·1)	5	**3d** (72·5)
5	**1e**	KOH (0·1)	1	**3e** (33)
6	**1f**	KOH (0·1)	2	**3f** (58)

[a] The reaction was carried out in the presence of 5 equiv. of 2,3-dimethyl-1,3-butadiene in refluxing methanol.
[b] In every case the ketones ($R^1COCH_2R^2$) were isolated in 62–107% yields except run 6.

Treatment of diphenacyl selenide (**1a**, 2 mmol) with triethylamine (2·2 mmol) in boiling methanol (30 ml) for 6 h affords an intractable mixture containing acetophenone as the only identifiable product. However, the reaction carried out under the same conditions in the presence of 2,3-dimethyl-1,3-butadiene (10 mmol) affords the selenapyran derivative (**3a**) in 70% yield.* Compound **3a** corresponds to the Diels–Alder adduct of the selenoaldehyde (**2a**) with the diene. Acetophenone (104%) is another product.† The reaction seems to occur in an E2 mechanism as depicted in the scheme since the reaction rate depends on the amount of triethylamine used. Diphenacyl sulfide does not undergo the corresponding thioaldehyde-forming reaction. Therefore, the driving force of the present reaction stems from the weaker bond strength of the C—Se bond compared with the C—S bond. Although the reaction was examined by using a variety of bases and solvents, the yield of **3a** was the best when **1a** was simply heated with triethylamine in refluxing methanol.‡

In a similar way, several diketo selenides (**1**) were treated with bases in refluxing methanol and the resulting seleno-carbonyl compounds were trapped by 2,3-dimethyl-1,3-butadiene. Results are summarized in Table 1. Run 5 shows that the present method is also applicable to the generation of selenoketones. But in this case and in run 6, better yields of adducts were obtained by use of 0·1 equiv. of potassium hydroxide as the base instead of 1·1 equiv. of triethylamine.§

In summary readily accessible diketo selenides serve as convenient precursors for generation of reactive dienophilic α-oxo selenoaldehydes and ketones.

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***3a**: ^{1}H-NMR (90 MHz, $CDCl_3$) δ 1·84 (6H, broad s, Me), 2·3–2·9 (2H, m, CH_2), 3·06 (1H, d, J = 14 Hz, CH_2Se), 3·18 (1H, d, J = 14 Hz, CH_2Se), 4·68 (1H, dd, J = 7 and 5 Hz, methine), 7·2–8·0 (5H, m, Ph). Compounds **3b–d** and **3f** also showed similar absorption patterns in their ^{1}H-NMR spectra.

†Since the yields of ketones often exceed 100% (see note b in Table 1) and the precipitation of elemental selenium is observed during the reaction, the reductive cleavage of the C—Se bonds which affords two molecules of ketones and selenium seems to occur as the side reaction.

‡The following bases were examined in varying amounts: triethylamine in methanol and benzene, 1,4-diazabicyclo-[2.2.2]octane in methanol, 1,8-diazabicyclo[5.4.0]undec-7-ene in benzene, and potassium hydroxide in methanol.

§The reaction with triethylamine is too sluggish in these cases.

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