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REACTIONS OF SODIUM HYDROGEN SELENIDE WITH α , β -UNSATURATED COMPOUNDS.

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Abstract: Sodium hydrogen selenide (NaHSe) reacts with α , β unsaturated compounds, under mild conditions, *via* a Michael type of addition to yield the corresponding monoselenides.

Much attention has recently been given to the role of organoselenium reagents in organic synthesis. Sodium hydrogen selenide, prepared *in situ* from the reaction of selenium powder and sodium borohydride in ethanol¹, has been used to prepare a variety of monoselenides and diselenides by its reaction with alkyl and aromatic halides^{1,2}.

In this paper we report that activated α , β -unsaturated compounds (1, X = CN,CHO, COOH, COOEt) react under mild conditions with sodium hydrogen selenide in a Michael type of addition to afford the corresponding selenides (2) in good yields. Sodium

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hydrogen selenide adds to the double bond to afford the corresponding selenol which subsequently reacts with another molecule of the α , β unsaturated compound to afford, after workup, the selenide (2). Table 1 shows the results obtained in these experiments. Aromatic α , β -unsaturated compounds, when reacted with the selenium reagent at room temperature, afforded the selenides in good yield (based on recovered starting material). In attempts to drive reactions



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to completion, higher temperatures provided only decomposition products. Cinnamyl alcohol and methyl 1- cyclohexenecarboxylate did not react with sodium hydrogen selenide indicating that an extended conjugated system may be necessary for the reaction. Products from the reduction of the double bond and/or the carbonyl group were not obtained in any case. Selenides are versatile synthetic intermediates^{3,4,5}. They can be converted into selenonium ylides *via* the selenonium salts. They can also be converted into selenoxides, selenones and selenide dihalides, each of which may be used for other synthetic transformations.

Unsaturated compound.	% Yield Selenide	% Recovered Starting Material
Ph-CH=CH-CN	66	21
Ph-CH=CH-CHO	74	0
Ph-CH=CH-COOCH ₂ CH ₃	70	10
Ph-CH=CH-COOH	73	11
Methyl 1-cyclohexenecarboxylate	0	100
Ph-CH=CH-CH ₂ OH	0	100

Table 1. Reactions of conjugated compounds with NaHSe.

Experimental

Melting points were taken on a Fisher-Johns melting point apparatus or on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Proton nuclear magnetic resonance (¹H NMR) spectra were obtained using a Varian EM 360A NMR spectrometer or a Varian 200 MHz spectrometer. Chemical shifts, δ , are expressed in parts per million (ppm) downfield from the tetramethylsilane (TMS) internal standard. Infrared spectra were taken on a Perkin-Elmer 1330 infrared spectrophotometer. Gas Chromatography/Mass Spectrometry (GC/MS) data were obtained using a Hewlett-Packard 5995A with Direct Injection Port (DIP) or a Chemical Ionization Finnigan model 4500.

General procedure for the preparation of Selenides (2).

Sodium borohydride (1.05 mmol) was added under nitrogen to a suspension of selenium powder (99%, 1.00 mmol) in ethanol. An exothermic reaction occurred and it was controlled by the use of an ice bath. After stirring for 1 h at room temperature the α , β -unsaturated compound (1.00 mmol) was added and the reaction mixture was stirred at room temperature for 24 h under nitrogen. After that time water (20.0 mL) was added and the mixture was extracted with diethyl ether (4 x 20.0 mL). The combined organic extracts were dried over anhydrous MgSO₄, filtered, and evaporated *in vacuo* to afford the crude product. The product was purified by silica gel chromatography (flash column) using mixtures of hexane:ethyl acetate as eluent. The selenides were characterized by ¹H NMR, IR and MS.

Reaction with trans-Cinnamonitrile.

The general procedure was followed and after workup and purification of the product by flash chromatography using hexane:ethyl acetate (4:1) as eluent afforded, 0.134 g, (21.0 %) recovery of starting material and 0.534 g (66.0 % yield) of the corresponding selenide: mp 36° C; IR (neat) 3059, 3028, 2927, 2246, 1491, 1452, 1415, 1075, 910, 762, 733 and 697 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.3 (m, 5H), 4.05 (m, 1H), 2.95 (m, 2H); MS (chemical ionization) m/z: 341 (M+1), 340 (M), 339 (M-1), 338 (M-2), 337 (M-3), 130 (M-210).

Reaction with trans-Cinnamaldehyde.

The general procedure was followed and after 75 min TLC analysis indicated no starting material was present. Workup and purification of the product by flash chromatography using hexane:ethyl acetate (4:1) afforded 0.483 g (74.0 % yield) of the corresponding selenide: mp 71-73°C; IR (KBr pellet) 3052, 3021, 2890, 1710, 1632, 1515, 1191, 1149, 1027, 976, 756 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 9.6 (s, 1H), 7.15 (m, 5H), 4.8 (m, 1H), 2.45 (m, 2H); MS (DIP) m/z: 346 (M+1), 345 (M), 344 (M-1), 343 (M-2), 131 (M-214).

Reaction with Ethyl trans-Cinnamate.

The general procedure was followed and after workup and purification of the product by flash chromatography using hexane:ethyl acetate (6:1) afforded 0.043 g (10.0 %) recovery of starting material and 0.337 g (70.0 % yield) of the corresponding selenide. IR (neat) 3083, 3060, 3028, 2980, 2868, 1731, 1635, 1600, 1539, 1475, 1390, 1320, 1077, 954, 765 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.25 (m, 5H), 4.2 (m, 1H), 3.95 (q, 2H, J=7Hz), 2.95 (m, 2H), 1.1 (t, 3H, J=7Hz); MS (DIP) m/z: 434 (M+1), 433 (M), 432 (M-1), 431 (M-2), 131 (M-302).

Reaction with trans-Cinnamic acid.

The general procedure was followed and after 36 h at room temperature, acidic workup and purification by flash chromatography using hexane:ethyl acetate 1:1 and then ethyl acetate as eluents afforded 0.104 g (11.0%) recovery of the starting material and 0.732 g (73.0% yield) of the desired selenide: mp 92°C; IR (KBr pellet) 3410,
3022, 2968, 1699, 1560 cm⁻¹; ¹H NMR (60 MHz, CDCl₃) δ 9.8 (br s, 2H),
7.35 (s, 10 H), 4.7 (m, 2H) and 3.0 (m, 4H). MS (DIP) m/z: 378 (M+1),
377 (M), 376 (M-1), 375 (M-2).

Reaction with Methyl 1-Cyclohexenecarboxylate.

The general procedure was followed and after 72 h at room temperature workup afforded 100% of the starting material.

Reaction with Cinnamyl alcohol.

The general procedure was followed and after 72 h at room temperature workup afforded 100% recovery of starting material.

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