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A series of 1-(2-arylethynylselenomercapto)-2,3-epoxypropane and 1,3-di(2-arylethynylselenomercapto)-2-propanol were synthesized starting from 1,2,3-selenadiazoles and epichlorohydrin.

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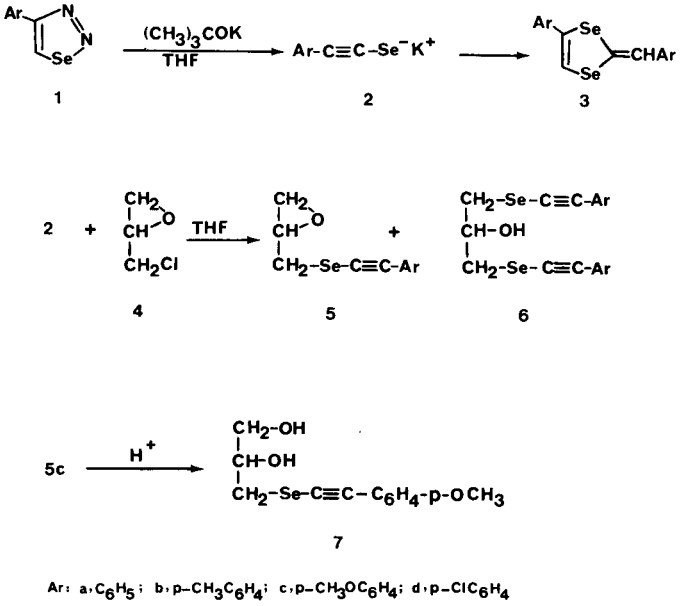
In a previous communication we reported that the reaction of potassium 2-arylethynylselenolate (**2**) with α-bromoesters would result in the nucleophilic displacement of the halogen and after hydrolysis the corresponding carboxylic acids could be generated [1]. We now describe the reaction of the selenolate anion **2** with epichlorohydrin (**4**) (Scheme 1).

Selenium dioxide oxidation of arylketone semicarbazones in acetic acid affords 1,2,3-selenadiazoles [2]. When potassium *t*-butoxide was added to a tetrahydrofuran solution of 4-aryl-1,2,3-selenadiazoles (**1**) a gas was liberated and subsquent addition of epichlorohydrin (**4**) to the reaction mixture afforded 1-(2-arylethynylselenomercapto)-2,3-epoxypropane (**5**) and 1,3-di(2-arylethynylselenomercapto)-2-propanol (**6**) in 69-94% total yield. Generation of selenolate anion **2** and addition of epichlorohydrin (**4**) could result in two competing reactions: dimerization [3] (**3**) or nucleophilic attack on epichlorohydrin [4] (**5** and **6**). The anion **2** is a powerful nucleophile and the reactions with epichlorohydrin were carried out at room temperature and were completed in less than 2 minutes, as evidenced by tlc, and without the formation of any dimerization products. It appeared that the rate of dimerization of potassium 2-arylethynylselenolates **2** leading to the formation of 1,4-diselenafulvenes **3** was suppressed in favor of the reaction with epichlorohydrin.

We have examined the reaction of equivalent amounts of selenolate anion **2** with epichlorohydrin (**4**) and found that the crude mixture consisted of two products: compound **5** which was the result of direct displacement and compound **6** which was due to the "normal opening" [5] of the epoxide in compound **5**, by the selenolate anion **2** as a nulceophile. On using epibromohydrin instead of epichlorohydrin an increase in the ratio of displacement to epoxide attack was observed. Hydrolysis of compound **5** in acidic solution gave a selenium analog of glycerol ether, 3-(2-*p*-methoxyphenylethynylselenomercapto)-1,2-propanediol (**7**).

The structures of all compounds were confirmed by analytical and spectroscopic methods. The results are tabulated in Table I.

Scheme 1



Ar: a, C_6H_5; b, p-$CH_3C_6H_4$; c, p-$CH_3OC_6H_4$; d, p-ClC_6H_4

EXPERIMENTAL

Melting points were taken on Fisher-Johns hot stage apparatus. Infrared spectra were obtained on a Perkin Elmer Infracord spectrophotometer using mineral oil mulls or as a thin film. The ^1H nmr spectra were recorded on a Varian M-360 instrument. Chemical shifts are reported on δ scale relative to TMS in deuteriochloroform. The 4-aryl-1,2,3-selenadiazoles used as starting material were otained by previously described methods [2].

Reaction of Potassium 2-Arylethynylselenolate **2** with Epichlorohydrin (**4**). General Procedure.

To a stirred solution of 4-aryl-1,2,3-selenadiazole (**1**, 0.01 mole) in dry tetrahydrofuran (30-50 ml), potassium *t*-butoxide (0.01 mole) was added. Immediately after the evolution of nitrogen ceased (20-30 seconds) epi-

Table I

No.	Ar	Mp °C or Bp °C/mm Hg	Yield % [c]	Formula	C% Calcd.	C% Found	H% Calcd.	H% Found	IR, cm^{-1} C≡C	IR, cm^{-1} OH	^{1}H-NMR, ppm
5a	C_6H_5	88/0.1	46	$C_{11}H_{10}OSe$	55.71	55.45	4.25	4.23	2175		2.8 (m, 4H), 3.6 (m, 1H), 7.5 (br s, 5H)
5b	*p*-$CH_3C_6H_4$	98/0.2	61	$C_{12}H_{12}OSe$	57.38	57.41	4.82	4.83	2160		2.4 (s, 3H), 2.8 (m, 4H), 3.5 (m, 1H), 7.4 (m, 4H)
5c	*p*-$CH_3OC_6H_4$	103/0.1	49	$C_{12}H_{12}O_2Se$	53.94	53.73	4.53	4.51	2170		3.0 (m, 4H), 3.5 (m, 1H), 3.9 (s, 3H), 7.0 (d, 2H)
5d	*p*-ClC_6H_4	104/0.2	44	$C_{11}H_9ClOSe$	48.64	48.55	3.34	3.33	2175		2.9 (m, 4H), 3.4 (m, 1H), 7.4 (s, 4H)
6a	C_6H_5	oil [a]	31	$C_{19}H_{16}OSe_2$	54.56	54.35	3.86	3.85	2170	3500	3.1 (m, 5H), 4.5 (m, 1H), 7.5 (s, 10H)
6b	*p*-$CH_3C_6H_4$	oil [a]	31	$C_{21}H_{20}OSe_2$	56.51	56.62	4.52	4.50	2160	3500	2.4 (s, 6H), 3.2 (m, 5H), 4.5 (m, 1H), 7.4 (m, 8H)
6c	*p*-$CH_3OC_6H_4$	oil [a]	45	$C_{21}H_{20}O_3Se_2$	52.73	52.50	4.21	4.19	2170	3600	3.2 (m, 5H), 3.9 (s, 6H), 4.5 (m, 1H), 7.0 (d, 4H), 7.6 (d, 4H)
6d	*p*-ClC_6H_4	115 [b]	25	$C_{19}H_{14}Cl_2OSe_2$	46.84	46.93	2.90	2.89		3600	3.1 (m, 5H), 4.5 (m, 1H), 7.4 (s, 8H)

[a] Although stable at room temperature extensive decomposition was evidenced when distillation in 0.1-0.2 torr was tried. [b] Recrystallized from hexane-ethyl acetate. [c] The values are based on the recovery of pure compounds from flash chromatography.

chlorohydrin (**4**, 0.01 mole) was added in one portion and stirring was continued for one hour at room temperature. The solvent was evaporated under reduced pressure, water (50 ml) was added to the residue and the mixture was extracted with ether (3 × 50 ml). The solution was dried on magnesium sulfate. The solvent was removed and the dark oily residue was purified by flash chromatography [6] using hexane-ethyl acetate (3:1) as eluent. For physical and spectroscopic data see Table I.

The above reaction was performed with epibromohydrin instead of **4** and when potassium 2-(*p*-methoxyphenyl)ethynylselenolate was used as a nucleophile compounds **5c** and **6c** were obtained in 92% total yield and with a ratio of **5c/6c** = 6.8.

Acid Catalyzed Hydrolysis of 1-(2-[*p*-Methoxyphenyl]ethynylselenomercapto)-2,3-epoxypropane (**5c**) to Compound (**7**).

A sample of 0.140 g of 1-(2-[*p*-methoxyphenyl]ethynylselenomercapto]-2,3-epoxypropane (**5c**) was treated with 5 ml of 1% sulfuric acid in 8 ml of acetone. The clear solution was left at room temperature for 24 hours. The product was taken up in ether (30 ml), washed with saturated bicarbonate (10 ml), dried on anhydrous magnesium sulfate and evaporated to give 0.140 g of 3-(2-[*p*-methoxyphenyl]ethynylselenomercapto)-1,2-propanediol (**7**) as an oil which was further purified by flash chromatography (ethyl acetate:hexane 7:3); ir (film): ν max = 3500 (OH); 2170 cm^{-1} (C≡C); nmr (deuteriochloroform): δ = 3.4 (br s, 2H), 3.9 (s, 3H), 3.5-4.3 (m, 5H), 7.0 (d, 2H), 7.6 ppm (d, 2H).

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