

A Photochemical Route to Some Substituted Benzyl Isoselenocyanates¹

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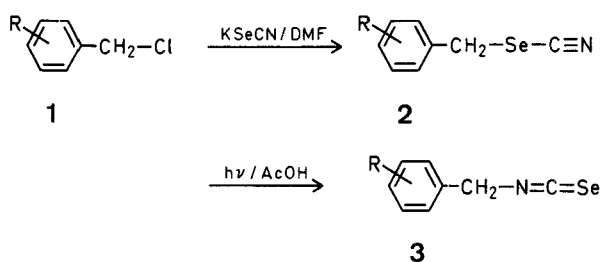
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In connection with our continued studies on the side-chain substitution of arenes, it became necessary to prepare some substituted benzyl isoselenocyanates as reference compounds. However, the literature to date contains few descriptions of the preparation of these compounds. The classical method of synthesis of organic isoselenocyanates involves the addition of elementary selenium to isonitriles². A recent, and seemingly more convenient, procedure consists of the formation and subsequent cleavage of *N*-alkyl-diselenocarbamates^{3,4}. Other methods of only limited applicability include the reaction of *N*-substituted imidoyl dichlorides with sodium selenide^{5,6}, alkylation of the selenocyanate ion^{7,8}, and the treatment of isocyanates with phosphorus pentaselenide⁶. However, none of these methods is attractive for our purpose, since they require compounds which are not readily available as starting materials.

We now wish to report on the photochemical transformation of the benzyl selenocyanates to isoselenocyanates, by which variously substituted benzyl isoselenocyanates can be easily obtained via three stages from the parent arenes. The overall process consists in the reaction of benzyl chlorides with potassium selenocyanate, followed by a short irradiation of the resulting benzyl selenocyanates in acetic acid.

When 0.1–1.0 mmolar solutions of benzyl selenocyanates **2a–f** and 1-naphthylmethyl selenocyanate (**2g**) were irradiated in dry acetic acid with a high-pressure mercury lamp, photo-equilibria which were composed mostly of the corresponding isoselenocyanates **3a–g** were obtained. Photo-equilibrium was reached within 10–20 min, when these



dilute solutions were used⁹. Longer irradiations were not advantageous, since the liberation of free selenium became significant. The separation of the isoselenocyanate from the accompanying starting material was easily achieved by preparative T.L.C. on silica gel; yields ranged from 26 to 40%. Disappointingly, this method was not applicable to aliphatic selenocyanates nor to aryl selenocyanates¹⁰.

The benzyl and 1-naphthylmethyl isoselenocyanates obtained are pale yellow oils or colorless crystalline solids, which can be stored for months without appreciable deterioration when kept in the dark. They can be easily distinguished from the parent selenocyanates by a strong, wide I.R. band appearing at around 2100–2160 cm⁻¹.

The ease of performance, mild reaction conditions, and acceptable yield suggest this procedure may become a method of choice for a simple laboratory synthesis of various benzyl isoselenocyanates.

Melting points were taken on a hot stage apparatus and are uncorrected. The I.R. spectra were recorded in Nujol mulls on a Hitachi 215 spectrophotometer. The ¹H-N.M.R. spectra were obtained on a Varian T-60 spectrometer, using deuteriochloroform as solvent and TMS as internal standard, unless otherwise stated. Preparative T.L.C. separations were carried out with silica gel GF-254 coated glass plates (20 × 20 cm), which were prepared by using a MRK spreader with a thickness of 0.25 mm and activated at 120° for 3 h. The solvent system was hexane containing 4–5% ether unless otherwise stated, and ultraviolet light was used for detection.

All photochemical reactions were conducted using a Halos P1H 100 high-pressure mercury lamp in a water-cooled quartz immersion well. The solution was flushed with dry nitrogen prior to irradiation and was stirred during the reaction by a magnetic stirring bar. The progress of the reaction was monitored by T.L.C. and ¹H-N.M.R. until the photo-equilibrium was reached.

Benzyl selenocyanates were prepared by the reaction of the corresponding chlorides with potassium selenocyanate and recrystallized from hexane or ethanol prior to use. All the new benzyl selenocyanates and isoselenocyanates were characterized by microanalyses as well as by the spectral data summarized in the Tables. The following examples illustrate typical preparations.

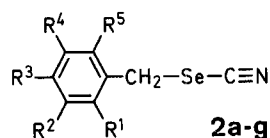
Pentamethylbenzyl Selenocyanate (2f):

To a well-stirred solution of pentamethylbenzyl chloride (1.00 g, 5.1 mmol) in dimethylformamide (20 ml), potassium selenocyanate (1.00 g, 6.9 mmol) is added in one portion, and the resultant mixture is stirred at room temperature overnight in the dark. The mixture is then poured into water (200 ml) to afford a white precipitate, which is collected by filtration and recrystallized from hexane, giving 2f as white fine needles; yield: 0.89 g (66%); m.p. 149–151° (see Table 1).

p-Chlorobenzyl Isoselenocyanate (3b):

A solution of *p*-chlorobenzyl selenocyanate (2b; 0.100 g, 0.43 mmol) in acetic acid (90 ml) is irradiated under nitrogen with a

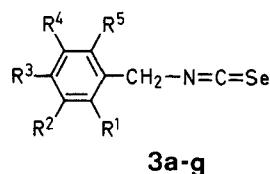
Table 1. Benzyl and 1-Naphthylmethyl Selenocyanates 2



Product No.	R ¹	R ²	R ³	R ⁴	R ⁵	Yield [%]	m.p. (solvent)	Molecular formula ^a or Lit. m.p.	I.R. (Nujol) ν [cm ⁻¹]	¹ H-N.M.R. (CDCl ₃ /TMS) δ [ppm]
2a	H	H	H	H	H	84	71–72° (hexane)	C ₇ H ₇ SeN	2145; 1490; 1215; 1190; 1065; 755; 685	4.27 (s, 2H, CH ₂); 7.33 (m, 5H _{arom})
2b	H	H	Cl	H	H	84	55–56° (hexane)	C ₇ H ₆ ClSeN	2140; 1485; 1185; 1085; 1005; 820; 795	4.25 (s, 2H, CH ₂); 7.32 (m, 4H _{arom})
2c	CH ₃	CH ₃	Br	CH ₃	CH ₃	67	179–180° (ethanol)	C ₁₂ H ₁₄ BrNSe (331.1)	2140; 1180; 995; 920; 785	2.37 (s, 6H, 2CH ₃); 2.48 (s, 6H, 2CH ₃); 4.55 (s, 2H, CH ₂)
2d	CH ₃	CH ₃	CH ₃	Cl	CH ₃	83	169–170° (hexane/CHCl ₃ , 9:1)	C ₁₃ H ₁₄ ClNSe (286.7)	2140; 1220; 1185; 1005; 950; 860	2.22 (s, 3H, CH ₃); 2.33 (s, 3H, CH ₃); 2.37 (s, 3H, CH ₃); 2.48 (s, 3H, CH ₃); 4.53 (s, 2H, CH ₂)
2e	CH ₃	H	CH ₃	H	CH ₃	78	81–82° (ethanol)	C ₁₁ H ₁₃ NSe (238.2)	2140; 1185; 840; 775	2.23 (s, 3H, CH ₃); 2.37 (s, 6H, 2CH ₃); 4.45 (s, 2H, CH ₂); 6.80 (m, 2H _{arom})
2f	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	66	149–151° (hexane)	C ₁₃ H ₁₇ NSe (266.3)	2150; 1195; 1060; 1005; 795; 770	2.20 (s, 9H, 3CH ₃); 2.32 (s, 6H, 2CH ₃); 4.53 (s, 4H, CH ₂)
2g	(CH ₃) ₂	(CH ₃) ₂	CH ₃	CH ₃	CH ₃	72	134–135° (hexane/CHCl ₃ , 9:1)	C ₁₅ H ₁₅ NSe (288.3)	2140; 1200; 1180; 1020; 790; 770; 745	2.42 (s, 3H, CH ₃); 2.52 (s, 3H, CH ₃); 2.62 (s, 3H, CH ₃); 4.97 (s, 2H, CH ₂); 7.37–8.13 (m, 4H _{arom})

^a The microanalyses were in satisfactory agreement with the calculated values (C ± 0.29, H ± 0.09, N ± 0.14).

Table 2. Benzyl and 1-Naphthylmethyl Isoselenocyanates 3



Product No.	R ¹	R ²	R ³	R ⁴	R ⁵	Yield [%]	m.p. (solvent)	Molecular formula ^a or Lit. m.p.	I.R. (nujol) ν [cm ⁻¹]	¹ H-N.M.R. (CDCl ₃ /TMS) δ [ppm]
3a	H	H	H	H	H	39	-8°	~ -8° ^d	2140; 1450; 1345; 725; 685 ^b	4.73 (s, 2H, CH ₂); 7.27 (m, 5H _{arom}) ^c
3b	H	H	Cl	H	H	40	oil ^d	C ₈ H ₆ ClNSe (230.6)	2130; 1330; 1085; 1010; 790 ^b	4.77 (s, 2H, CH ₂); 7.28 (m, 4H _{arom}) ^c
3c	CH ₃	CH ₃	Br	CH ₃	CH ₃	27	143-145° (hexane)	C ₁₂ H ₁₄ BrNSe (331.1)	2150; 1330; 1205; 1005; 915	2.37 (s, 6H, 2CH ₃); 2.48 (s, 6H, 2CH ₃); 4.75 (s, 2H, CH ₂)
3d	CH ₃	CH ₃	CH ₃	Cl	CH ₃	36	118-119° (hexane)	C ₁₂ H ₁₄ ClNSe (286.7)	2160; 1335; 1215; 1005; 920; 820	2.27 (s, 3H, CH ₃); 2.33 (s, 3H, CH ₃); 2.38 (s, 3H, CH ₃); 2.48 (s, 3H, CH ₃); 4.75 (s, 2H, CH ₂)
3e	CH ₃	H	CH ₃	H	CH ₃	35	66-68° (hexane)	C ₁₁ H ₁₃ NSe (238.2)	2150; 1615; 1330; 850; 775; 710	2.23 (s, 3H, CH ₃); 2.37 (s, 6H, 2CH ₃); 4.63 (s, 2H, CH ₂); 6.77 (m, 2H _{arom}) ^c
3f	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	26	123-125° (hexane)	C ₁₃ H ₁₇ NSe (266.3)	2160; 1325	2.23 (s, 9H, 3CH ₃); 2.32 (s, 6H, 2CH ₃); 4.77 (m, 2H, CH ₂)
3g	(CH ₃ -CH) ₂		CH ₃	CH ₃	CH ₃	30	125-128° (hexane)	C ₁₅ H ₁₅ NSe (288.3)	2140; 1325; 1245; 1195; 1060; 785; 750	2.37 (s, 3H, CH ₃); 2.47 (s, 3H, CH ₃); 2.57 (s, 3H, CH ₃); 5.23 (s, 2H, CH ₂); 7.27-8.03 (m, 4H _{arom}) ^c

^a The microanalyses were in satisfactory agreement with the calculated values (C \pm 0.44, H \pm 0.27, N \pm 0.44).

^b Liquid film.

^c CCl₄ solution.

^d Pale yellow oil which solidifies to a white mass at -78°.

high-pressure mercury lamp for about 20 min. The solution turned to a pale yellow with some deposition of elemental selenium on the wall of reaction vessel. The mixture is diluted with water (200 ml) and the product is extracted with ether (3 \times 60 ml). The combined extracts are washed thoroughly with water and saturated aqueous sodium hydrogen carbonate, dried with anhydrous magnesium sulfate, and the solvent removed in vacuo at less than 40° to give a yellow liquid residue which, according to ¹H-N.M.R. analysis, consists of **3b**, **2b**, and *p*-chlorobenzyl acetate in an approximate ratio of 90:10:1. The mixture is then chromatographed on silica gel column with 4% ether in hexane as eluent, giving **3b** as early eluate; yield: 40 mg (40%) (see Table 2). With this solvent system, the unchanged selenocyanate and acetate are retained on the column.

Pentamethylbenzyl Isoselenocyanate (3f):

A solution of pentamethylbenzyl selenocyanate (**2f**; 0.160 g, 0.60 mmol) in acetic acid (120 ml) is irradiated under nitrogen for ~10 min. When a deposit of free selenium begins to appear, the irradiation is interrupted and a pale yellow solution is diluted with water. The product is extracted with ether and the extract is washed successively with water, aqueous sodium hydrogen carbonate and water, and dried with magnesium sulfate. The solvent is removed under reduced pressure, and the yellow solid residue is chromatographed on a thick-layer silica gel plate using 5% ether in hexane as eluent. The fast moving yellow band is scraped off from the glass plate and extracted with ether to give **3f**; yield: 41 mg (26%). From the slower moving band, the unchanged **2f** could be recovered.

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- ¹⁰ The use of more concentrated solutions was not advantageous, since it often necessitated frequent cleaning of the mercury lamp from deposited selenium.
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