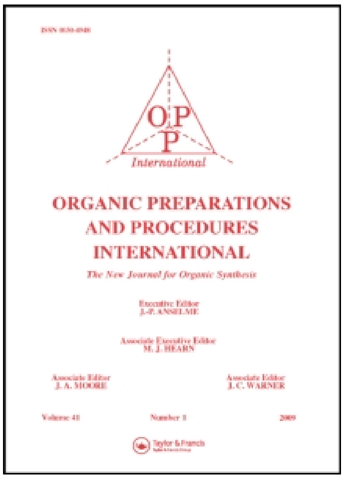

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A MODIFIED PROCEDURE FOR THE PREPARATION OF 5H, 7H-DIBENZO[c,e]SELENEPIN

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A MODIFIED PROCEDURE FOR THE PREPARATION OF 5H, 7H-DIBENZO[c,e]SELENEPIN

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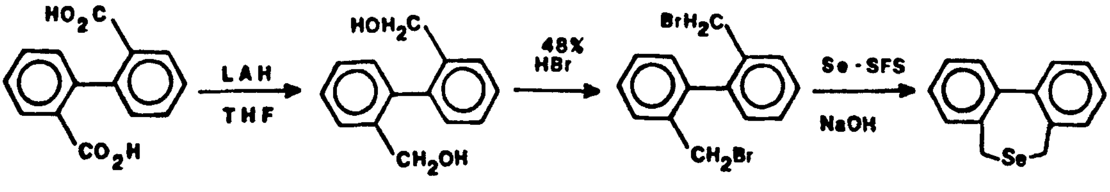
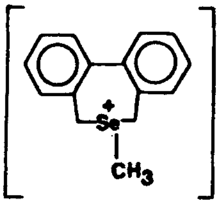
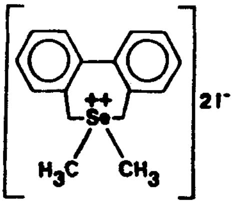
The original procedure of Truce and Emrick[1] describes the preparation of the title compound (IV) by the reaction of H_2Se with 2,2'-bis-(bromomethyl)-biphenyl (III). An alternative route to III was also reported by Hall et al. and incorporated a lithium tetrahydroaluminate (LAH) reduction of either the dimethyl or diethyl ester diphenate to give the diol (II) which in turn was brominated in hot concentrated hydrogen bromide.[2]



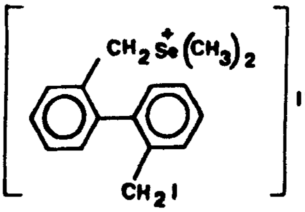
I II III IV



V



VI



VII

Several difficulties were encountered in attempting to repeat the above procedures due primarily to the lack of appropriate detail in the literature. For example, several different attempts at the Ullman coupling of 2-iodotoluene led to failure since detail was lacking on the correct type of "copper-bronze" to use. The alternate route employing the diphenates appeared reasonable, but again detailed information concerning the preparation of these substances was lacking in the literature. We therefore devised a modified scheme starting with relatively inexpensive diphenic acid (I) which is directly reduced using LAH to yield II followed by bromination.[2] The selenepin (IV) was obtained by an adaptation of the method of Bird and Challenger[3] to generate sodium selenide <u>in situ</u> with sodium formaldehyde sulfoxylate (SFS, "Rongalite") and elemental selenium.

The main advantages to this route is that it bypasses the esterification step thereby saving time and eliminates the need to generate hydrogen selenide whose odor is revolting and which is a hazardous compound.[4] The only disadvantage is the lower yield of III from the direct reduction of the acid (50%) versus the much higher yields realized when the esters are reduced (100%); however, since the acid is commercially available (or easily prepared), this generally is not a major problem. The best method to prepare the diphenates was to bubble anhydrous hydrogen chloride through the appropriate alcoholic solution of I followed by one hour reflux and evaporation of half the solvent. Refrigeration to 5° yielded almost quantitative amounts of the esters whose melting points matched perfectly those reported in the literature (dimethyl ester, 73°; diethyl ester, 42°).[2] The detailed conversions of I to II and of III to IV which were worked out in our laboratory are described below. Hitherto unpublished spectral data are also included for the title compound.

Several attempts to reproduce the synthesis of the methyl selenonium iodide derivative (6-methyl-5H,7H-dibenzo[c,e]selenepinium iodide, V) and the unusual quaternary dication dimethyl derivative (6,6-dimethyl-5H,7H-dibenzo[c,e]selenepinium diiodide, VI),[1] led only to V and elemental analyses matched with that expected for $C_{15}H_{15}ISe$.[5] Our melting point, however, for V was 95-96° which differs greatly from the reported melting point of 123-125°.[1] No explanation is offered at this time for the discrepancy, but our findings are suspiciously close to the reported melting point of VI (97-98°).[6]

EXPERIMENTAL SECTION

Melting points (uncorrected) were taken on a Fisher-Johns Melting Point Apparatus (stage type). Infrared spectra were recorded as Nujol mulls between NaCl plates on a Perkin-Elmer Model 237 Infrared Spectrophotometer. Proton NMR data were obtained on a 60 MHz Varian Model EM360A Spectrometer. The sample was run in CCl_4, and shifts in ppm (δ) are reported relative to TMS standard.

2,2'-bis(Hydroxymethyl)biphenyl (III).- A 7.5 g (0.20 mol) suspension of $LiAlH_4$ in 100 ml of tetrahydrofuran was prepared in a three-necked 500 ml flask fitted with reflux condenser and a 250 ml dropping funnel. To the funnel was added a suspension of 40 g (170 mmoles) of I in 100 ml THF. The diphenic acid was normally powdery enough that the dropping funnel orifice did not clog, but a small wire was used occasionally to insure constant flow. Small portions of THF were used to rinse the remaining diphenic acid from the funnel into the flask. The mixture was refluxed for 1 hr. After cooling, excess $LiAlH_4$ was destroyed with 50 ml of 95% EtOH and worked up by first adding 8 ml H_2O, then 8 ml of 15% NaOH, then finally 24 ml of H_2O again. The solid was filtered, washed with a few small portions of THF, and discarded. All but ca. 10 ml of the filtrate was boiled off, and the residue was allowed to air dry completely. The product was recrystallized from hot benzene (hood!) to yield 11 g (50%) of colorless product, mp. 109-111°, lit.[2] 112-113°.

5H,7H-dibenzo[c,e]selenepin (V).- This procedure was also carried out in a fume hood. In a 125 ml round-bottomed flask fitted with reflux condenser and heating mantle was placed a mixture of 15 g (0.10 mol) sodium formaldehyde sulfoxylate ("Rongalite"),[3] 12 g (0.30 mol) NaOH pellets, and 5 g of selenium (0.06 mol, red or grey) in 50 ml H_2O. The mixture was brought to 50° and 16 g (0.047 mol) of III was added and the mixture was refluxed for 3 hrs. Upon cooling, the grey congealed plastic-like lump of crude product was manually removed from the reaction mixture, agitated in cold wate,r placed over $CaCl_2$ in a vacuum dessicator, and then was continuously extracted (Soxhlet extractor) with 200 ml CCl_4 for ca. 1 hr. The CCl_4 was evaporated and a small portion of the product was recrystallized from hot hexanes for melting point and spectral characterization. The product tended to oil out on cooling, but scratching the side of the recrystallization flask induced solid formation immediately. The yield was 7.0 g (60%) of yellow solid, mp. 65-67°, lit.[1] 65-66°. ^{1}H-NMR (CCl_4): δ 7.20 (s, 4, H-phenyl) 3.32 (dd, 1, J_{gem} = 12Hz, H-benzyl). IR(Mull): 3080m, 1210w, 1180w, 1130w, 1000w, 940w, 880m, 740s, 610m.

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5. Calcd for $C_{15}H_{15}ISe$: C, 44.91; H, 3.77; I, 31.64. Found: C, 44.67; H, 3.70; I, 30.33.

6. W. E. Truce (personal communication) suggests the more reasonable conceptual structure VII for a product that might arise from incorporation of two equivalents of methyl iodide into the selenepin V; he also presumes the mp of 95-96° recorded here to be correct.