The free base was liberated from the dibenzoyl-*d*-tartrate salt in 100 ml. of 20% sodium hydroxide solution, which was repeatedly extracted with chloroform. After drying with sodium sulfate, the chloroform was evaporated and the residue (1 g.) was recrystallized, with charcoal treatment, from petroleum ether, b.p. 66–75°, to give 0.85 g. (20%) of white platelets of *trans*-*l*-decahydroquinoxaline, m.p. 175–175.5°; $[\alpha]^{26}_{D}$ −9.7° (*c*, 10.2, chloroform).

Anal. Calcd. for $C_8H_{16}N_2$: neut. equiv., 70.1. Found: neut. equiv., 70.1.

The residue of salt from the filtrates mentioned parenthetically above was quite soluble in water, and hence was not investigated further, but the base was liberated, recovered, and recrystallized from petroleum ether to give 2.0 g. partially resolved *trans*-*d*-decahydroquinoxaline, m.p. 160–171°, $[\alpha]^{26}_{D}$ +6.4° (*c*, 10.4, chloroform). This product was transformed into its dibenzoyl-*l*-tartrate salt, purified, and liberated exactly as described above for its enantiomer to give 0.5 g. (12%) of *trans*-*d*-decahydroquinoxaline, m.p. 175–175.5°; $[\alpha]^{26}_{D}$ +10.4° (*c*, 10, chloroform); same melting points, analyses of salt and base were observed.

The resolution was repeated exactly, except that the *trans*-*dl*-decahydroquinoxaline was *first* neutralized with dibenzoyl-*l*-tartaric acid, and the resolution of the more soluble salt eventually executed with dibenzoyl-*d*-tartaric acid. Again the same analyses, melting points, and approximate yields were observed. The observed values of the optical rotations of the resolved *trans*-decahydroquinoxalines were +10.3° and −10.1° at concentrations of 10 g./100 ml. of chloroform solutions; the infrared spectra were the same as for the racemic substance.

A Selenium Heterocyclic from the Reaction of Diphenylacetylene and Selenium Tetrachloride

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In the few cases studied, selenium tetrachloride has been shown to add to alkynes forming bis-2-chloroalkenylselenium dichlorides.[1,2] Our experiments show that diphenylacetylene reacts forming a substance of different selenium/alkyne ratio. The compound does not contain a Se–Cl linkage, as evidenced by the inactivity of the chlorine atom to water and even to Grignard reagents, and is very stable thermally and oxidatively, which suggests that it contains divalent selenium linked only to carbon. Several different methods (*vide infra*) have been used to characterize this material as 2-phenyl-3-chlorobenzoselenophene.

Several related substances containing the same heterocyclic ring system (*e.g.*, benzoselenophene,[3–7] 2-α(γ)-pyridylbenzoselenophene,[8] and 2-methylbenzoselenophene[9] have been reported previously but have been made in low yields, usually in a multistep syntheses. The one-step route to the 2-phenyl compound outlined represents a substantial improvement in both time and yield for the preparation of this ring system.

Experimental

2-Phenyl-3-chlorobenzoselenophene.—A 22.1-g. portion (0.1 mole) of selenium tetrachloride was treated with a Dry Ice-cooled solution containing 0.25 mole (36.0 g.) of diphenylacetylene dissolved in 100 ml. of ether. On warming to room temperature, a copious quantity of hydrogen chloride was evolved (in contrast to the other alkyne reactions). Partial evaporation and several days standing at −78° produced large yellow crystals which, on recrystallization from ether, yielded an 83% (based on $SeCl_4$) yield of off-white needles. Use of less than a 2:1 mole ratio led only to impure products from which only low yields of the desired compound were obtained.

Anal. Calcd. for $C_{14}H_9ClSe$ (291.1): C, 57.65; H, 3.11; Cl, 12.16; Se, 27.38. Found: C, 57.67; H, 3.26; Cl, 12.02; Se, 27.05; mol. wt. (Signer), 293.

Reduction with Raney Nickel.—A 2.9-g. portion (0.01 mole) of the compound was refluxed several hours with Raney Nickel under a hydrogen stream using the method of Gould and Wiseman.[10] Recovery and recrystallization of the product afforded a 61% yield of bibenzyl which was identified through its infrared spectrum and a mixture melting point determination with an authentic sample.

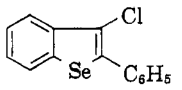
Spectral Work.—The ultraviolet spectrum (Cary Model 14) taken on 10^{-4} *M* solutions of the compound dissolved in spectral grade cyclohexane shows five peaks and shoulders: λ_{max} (log-ε); 212 (4.33), 244 (4.34); 253 (4.10 sh.), 283 (3.41 sh.), 298 (4.20).

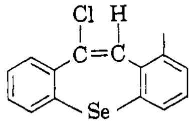
The infrared spectrum of a Nujol mull of the material, taken on a Perkin-Elmer, Model 21, spectrophotometer, showed the following peaks (all weak) between 1660 and 2000 cm.$^{-1}$: 1660, 1690, 1708, 1755, 1785, 1803, 1872, 1905, 1945, and 1965 cm.$^{-1}$.

The n.m.r. spectrum (taken at 60 Mc.) of the compound dissolved in carbon tetrachloride shows a complex array of overlapping peaks spread over 60 c.p.s. and centered at 0.9 p.p.m. downfield from the T_1 peak (aromatic protons) of toluene used as an internal standard.

Discussion

The analytical and molecular weight data suggest either I or II below as a possible structure for the compound. Formation of bibenzyl by the compound when reduced by Raney Nickel probably would not distinguish between the two structures, but Baufield, *et al.*,[11] have shown that 2-phenylbenzothiophene is similarly reduced.


I


II

Comparison of the ultraviolet spectrum of the compound with those of closely similar sulfur analogues of I and II, 2-phenylbenzothiophene[12] and dibenzo[*b*,*f*]thiepin[13] shows the closest similarity exists between the spectrum of the compound and that of 2-phenylbenzothiophene. However, the spectra of the two sulfur compounds are similar and the influence of the 3-chlorine is unknown, so conclusions from the ultraviolet spectra should be cautiously drawn.

The infrared absorptions in the 1600–2000-cm.$^{-1}$ region of phenyl compounds are reported to be characteristic of the type of ring substitution.[14] Nine of the ten low intensity infrared absorptions appearing between 1660 and 2000 cm.$^{-1}$ form a pattern which is characteristic of the combination expected for a monosubstituted and a disubstituted (*ortho*) ring. This indicates structure I rather than II.

Using concentrated solutions and carefully searching the spectral region in which olefinic hydrogen resonances

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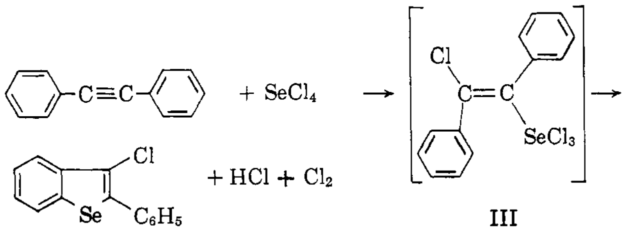
are known to occur[15] produced no other peaks than the ones reported above. Thus, the n.m.r. data also point to the exclusion of structure II.

Since evidence exists for addition of the selenium-trichloride group as a first step in addition reactions of selenium tetrachloride, reaction in this case probably proceeds by cyclization of the intermediate III.



Evidence that such an intermediate is involved is provided by the isolation of the tellurium analog of III from the reaction between tellurium tetrachloride and diphenylacetylene.[16] The authors do not report or consider the possibility of further conversion to 2-phenyl-3-chlorobenzotellurophene, so it can be assumed that the tellurium analog of III is more stable. However, it should be possible under appropriate conditions to produce the benzotellurophene analog of I.

Several experiments with sulfur tetrachloride substituting for selenium chloride have not led to an isolatable product, but further work will be carried out with this and other nonmetallic halides.

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Improved Synthesis of 3,3,3-Trifluoropropyne

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A novel synthesis of 3,3,3-trifluoropropyne, $CF_3C{\equiv}CH$, has been discovered which gives high product yields (75%) from a readily available starting material in conventional glass apparatus. 1,1,2-Trichloro-3,3,3-trifluoropropene, $CF_3CCl{=}CCl_2$,[1] reacts exothermically with zinc dust in solvents such as dimethylformamide, N,N-dimethylacetamide and N-methyl-2-pyrrolidone to give a zinc salt of 3,3,3-trifluoropropyne. (Anhydrous zinc chloride is normally added to reduce the induction period.) Addition of water liberates 3,3,3-trifluoropropyne in excellent yield and purity.

$$CF_3CCl{=}CCl_2 + 2Zn \xrightarrow[ZnCl_2]{\text{solvent}}$$

$$(CF_3C{\equiv}C)_2Zn \text{ or } CF_3C{\equiv}CZnCl + ZnCl_2 \xrightarrow{H_2O} CF_3C{\equiv}CH$$

Acetic acid and absolute ethanol were relatively ineffective as reaction solvents: yields of about 10% of 3,3,3-trifluoropropyne were obtained in forty-eight-hour reactions at steam bath temperatures and the balance of the starting material was recovered. With dry dioxane no reaction occurred at reflux temperature even after six hours. Solvents such as formamide and 95% ethanol alter the course of the reaction. Yields of 3,3,3-trifluoropropyne varied from 12% to 32% and a variety of partially reduced products were obtained, including the previously uncharacterized *cis*- and *trans*-1,2-dichloro-3,3,3-trifluoropropenes. Similar reductive eliminations of vinylic halogen from 1,1,1,-4,4,4-hexafluoro-2,3-dichlorobutene-2 in a zinc–absolute ethanol mixture[2] and in a zinc–formamide mixture[3] have been observed. The former reaction gave a 30% yield of 1,1,1,4,4,4-hexafluoro-2-chlorobutene-2. The latter yields an appreciable percentage (41.2%) of (*trans*) 1,1,1,4,4,4-hexafluorobutene-2. Dehalogenation to yield 1,1,1,4,4,4-hexafluorobutyne-2 also occurred in each case.

Procedures previously described for the preparation of 3,3,3-trifluoropropyne include the dehydrohalogenations of $CF_3CH{=}CHX$[4–7] and $CF_3CX{=}CH_2$,[6,7] dehalogenations of $CF_3{-}CX{=}CXH$[6,7] and the reaction of sulfur tetrafluoride with propiolic acid.[8] Although yields obtained in these reactions may be comparable with or even superior to those described herein, the usefulness of this new synthesis is readily apparent.

A logical mechanism for this reaction involves dehalogenation of 1,1,2-trichloro-3,3,3-trifluoropropene to yield 1-chloro-3,3,3-trifluoropropyne, which in turn immediately reacts with zinc to yield the zinc acetylide. The ready reaction of the trichlorotrifluoropropene with zinc may be contrasted to the sluggish reaction of 1,2-dichloro-3,3,3-trifluoropropene[6]; the electron withdrawing power of the additional 1-chloro atom apparently facilitates the initial reaction with the zinc.

Experimental

3,3,3-Trifluoropropyne.—Zinc dust (36.0 g., 0.5 mole 90% purity), 3.4 g. (0.025 mole) of fused zinc chloride, and 200 ml. of dry redistilled N,N-dimethylacetamide, were placed in a 500-ml. three-necked flask fitted with a thermometer, addition funnel, stirrer and water cooled condenser leading to a Dry Ice–acetone trap. The reaction mixture was heated to 100° and the slow addition of 50.0 g., (0.025 mole) of 1,1,2-trichloro-3,3,3-trifluoropropene was started. An exothermic reaction usually occurred within 10 min., raising the temperature above 100°. Heating was discontinued and the temperature was maintained at 95–105° by adjusting the olefin addition rate and by directing an air blast on the flask. Addition was complete in approximately 1 hr., and the solution was allowed to cool to 50–60°. An infrared spectrum of the reaction solution showed the presence of a strong C≡C absorption at 4.65 μ. No product was present in the Dry Ice trap at this time. The slow addition of 100 ml. of water with stirring was started and completed in 30 min.; the temperature was maintained at 50–60° by use of a heating mantle. An immediate vigorous gas evolution commenced and product collected in the Dry Ice trap. Heating was continued for an additional hour.

The product which collected in the Dry Ice trap was distilled directly into a steel sample cylinder and weighed; yield of $CF_3{-}C{\equiv}CH$, 17.7 g. (75.3%), b.p. −48° to −47°/705 mm. Identification was based on boiling point, infrared spectrum, and mass spectrographic analysis. The boiling point coincides with that reported in the literature.[5] The infrared spectrum shows a C—H band at 2.99 μ, a strong band at 4.62 μ (—C≡C—), and strong absorptions at 8.0 to 8.5 μ ($-CF_3$). The mass spectrum gave a parent peak at 94. Analysis by vapor phase chromatography (squalene–Pelletex) indicated a purity of at least 99%.

Reactions run using dimethylformamide and N-methyl-2-

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