leaving a yellow band behind and the solution obtained was evaporated to dryness under reduced pressure. The solid was twice recrystallized from methanol–water, using charcoal to remove tarry material. The product showed m.p. 175.5-177°, which was depressed to m.p. 155-170° by admixture with D-glucose phenylosazone, and $[\alpha]^{25}\text{D}$ $-21.8°$ (0.25 hr.) and $-19.8°$ (21 hr.) (*c* 0.253, pyridine). Melting points reported for D-psicose phenylosazone are 162-163°,[14] 165°,[15] 173-174°,[16] 178°,[17] and 183-185°.[18]

The material resembled D-psicose phenylosazone and differed from D-glucose phenylosazone in that it was readily soluble in hot water and acetone. In addition, its infrared absorption spectrum (Nujol mull) differed markedly from that of D-glucose phenylosazone. The following X-ray powder diffraction data[19] were obtained for the osazone: 3.21[20] (m),[21] 3.51 (vw), 3.74 (m), 4.34 (s), 4.72 (m), 5.56 (m), 6.82 (vw), 8.72 (m) and 10.27 (m). These values are in good agreement with those recorded by Clark, Gardner, Sattler and Zerban[22] for D-psicose phenylosazone but differ from the following values obtained[19] for D-glucose phenylosazone: 2.59 (vw), 3.14 (w), 3.40 (m), 4.14 (vw), 4.55 (m), 5.02 (s), 6.93 (vw) and 9.28 (m).

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[14] M. L. Wolfrom, A. Thompson and E. F. Evans, THIS JOURNAL, **67**, 1793 (1945).

[15] W. C. Austin and F. L. Humoller, *ibid.*, **56**, 1153 (1934).

[16] M. Steiger and T. Reichstein, *Helv. Chim. Acta*, **19**, 184 (1936).

[17] F. W. Zerban and L. Sattler, *Ind. Eng. Chem.*, **34**, 1180 (1942).

[18] P. A. Levene and W. A. Jacobs, *Ber.*, **43**, 3141 (1910).

[19] We are indebted to Dr. J. H. Dusenbury, Textile Research Institute, Princeton, N. J., for these measurements.

[20] Interplanar spacing, Å., CuK$\alpha$ radiation.

[21] Relative intensity: s strong, m medium, w weak and vw very weak.

[22] G. L. Clark, J. O. Gardner, L. Sattler and F. W. Zerban, *Sugar*, **47**, 40 (1952).

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## Substitution Positions in the Nitration of Dibenzoselenophene

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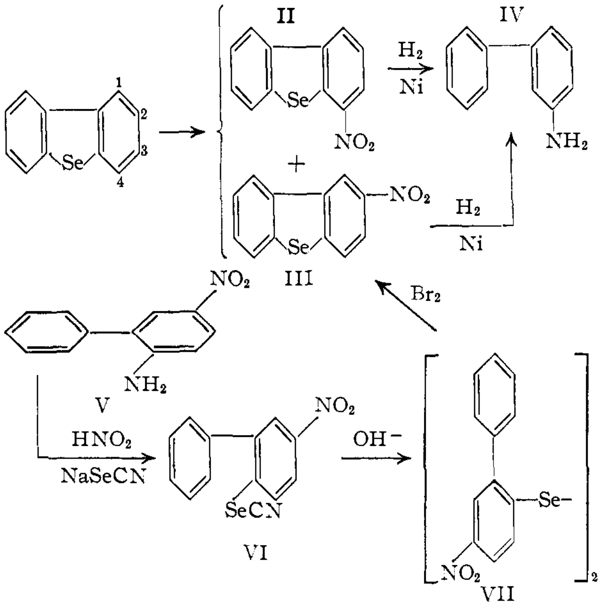
The nitration of dibenzoselenophene (I) in glacial acetic acid gives as the major product a mononitro derivative. Sawicki and Ray[1] compared the ultraviolet absorption spectrum of this compound with the spectra of known mononitrodibenzothiophenes, and on this basis assigned the nitro group to the 2-position (*i.e.*, *para* to the selenium atom). Subsequently, more detailed examination of the nitration products by Sawicki[2] indicated the presence of at least one additional mononitro derivative and at least one dinitro derivative.

Starting with 2-amino-5-nitrobiphenyl (V), and using a modification of a method for preparation of dibenzoselenophene,[3] we have synthesized 2-nitrodibenzoselenophene (III). This compound has been found to be identical to the major product formed from nitration of dibenzoselenophene, thus confirming the position assignment by Sawicki and Ray. It appears that our 2-nitro compound is the first dibenzoselenophene derivative made by methods other than substitution reactions on the parent heterocycle, and that this is the first chemical proof of the position of substitution on dibenzoselenophene.

Both the 2-nitro compound and a second mononitro compound (isolated in fair yield from the nitration mixture) yield 3-aminobiphenyl (IV) when subjected to simultaneous reduction and deselenization[4] with hydrogen and Raney nickel. The second mononitro derivative is thus 4-nitrodibenzoselenophene (II), for the 1-nitro compound would yield 2-aminobiphenyl and the 3-nitro compound would yield 4-aminobiphenyl.

We have found also that the deselenization procedure previously described[4] may be improved simply by carrying out the reaction in a Parr low-pressure hydrogenator. This modification permits the use of less active Raney nickel in a somewhat smaller quantity and lowers the necessary reaction time considerably. By careful control of conditions, the nitrodibenzoselenophenes may be reduced to the corresponding amines without removal of selenium from the molecules. The reactions reported here are summarized



### Experimental[5]

**2-Selenocyano-5-nitrobiphenyl (VI).**—To 28 ml. of concentrated sulfuric acid in a 3-liter beaker cooled in an ice-bath, there was slowly added 4 g. of powdered sodium nitrite. The mixture was very carefully heated and agitated until all solid dissolved, then cooled to 0°. Nine grams of 2-amino-5-nitrobiphenyl[6] was dissolved in 90 ml. of glacial acetic acid. This solution was slowly added to the cold solution of sodium nitrite in sulfuric acid. The reaction was allowed to proceed for 20 minutes, after which was added 1 g. of urea (to destroy excess nitrous acid) and 800 ml. of ice-water. The mixture was made basic to congo red paper with sodium acetate, then 16 ml. of 3 *M* sodium selenocyanate added. The brown precipitate formed was allowed to stand overnight, then filtered off and recrystallized from carbon tetrachloride. By cooling the crystallizing solution to 0°, there was obtained 5.4 g. (43%) of pale brown crystals (m.p. 159-161°). Recrystallization from acetone-alcohol raised the melting point to 162-163°.

*Anal.* Calcd. for $C_{13}H_8N_2O_2Se$: Se, 26.0. Found: Se, 25.5.

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[1] E. Sawicki and F. E. Ray, THIS JOURNAL, **74**, 4120 (1952).

[2] E. Sawicki, *ibid.*, **77**, 957 (1955).

[3] J. D. McCullough, T. W. Campbell and E. S. Gould, *ibid.*, **72**, 5753 (1950).

[4] G. E. Wiseman and E. S. Gould, *ibid.*, **76**, 1706 (1954).

[5] All melting points are corrected.

[6] (a) F. Bell, *J. Chem. Soc.*, 2770 (1928); (b) F. H. Case, THIS JOURNAL, **65**, 2137 (1943).

**Bis-(5-nitro-2)-biphenylyl Diselenide (VII).**—To a solution of 6 g. of potassium hydroxide in 30 ml. of methanol was added 2.8 g. of 2-selenocyano-5-nitrobiphenyl. The mixture was agitated and allowed to stand for one hour, then poured into a mixture of 200 ml. of benzene and 200 ml. of a saturated solution of aqueous boric acid. The yellow benzene layer was separated and the benzene evaporated. The product was recrystallized from acetone. There was obtained 1.9 g. (74%) of yellow crystals, m.p. 192–193°.

*Anal.* Calcd. for $C_{24}H_{16}N_2O_4Se$: Se, 28.4. Found: Se, 28.2

**2-Nitrodibenzoselenophene (III).**—To a solution of 1.5 ml. of bromine in 60 ml. of carbon tetrachloride was added 1.9 g. of the diselenide VII prepared above. The solution was warmed and then allowed to cool. Thirty ml. of acetone was added *cautiously* to remove excess bromine. The solution was refluxed for two hours. Then the solvents were evaporated, during which time hydrogen bromide was evolved. Thirty ml. of carbon tetrachloride was added to the residue and refluxing resumed for an additional two hours. The solvent was removed, during which time no hydrogen bromide fumes were evolved. The residue was extracted with two 200-ml. portions of hot methanol. The extractions were decolorized with Norit, and the volume reduced to about 100 ml. The cooled solution yielded 0.91 g. (49%) of yellow needles, m.p. 184–185°.

*Anal.* Calcd. for $C_{12}H_7NO_2Se$: Se, 28.5. Found: Se, 28.3.

**Nitration of Dibenzoselenophene.**—To a solution of 20 g. of dibenzoselenophene in 130 ml. of glacial acetic acid was added 8 ml. of fuming nitric acid. The solution was maintained at 65° until precipitation occurred. The mixture was cooled and filtered. The precipitate so obtained was recrystallized twice from benzene, yielding 11.5 g. (44%) of yellow needles, m.p. 184–185° (reported[1] 180°). This compound gave no depression in melting point when mixed with 2-nitrodibenzoselenophene prepared above.

The benzene filtrate was evaporated and the residue recrystallized three times from alcohol. Six grams (25%) of yellow solid, 4-nitrodibenzoselenophene, m.p. 133–134°, was obtained.

*Anal.* Calcd. for $C_{12}H_7NO_2Se$: Se, 28.5. Found: Se, 28.3.

**2-Aminodibenzoselenophene.**—Ten grams of Raney nickel in 150 ml. of benzene was placed in a Parr low-pressure hydrogenator for 15 minutes to reactivate the catalyst. To the container was added 6 g. of 2-nitrodibenzoselenophene, and the container was then reconnected to the hydrogenator. When the hydrogen pressure drop remained constant for 15 minutes, the charge was removed and filtered. Hydrogen chloride gas was passed through the colorless filtrate. The white precipitate formed was filtered and suspended in water, then an excess of ammonium hydroxide added. The precipitate was filtered and recrystallized from hexane, yielding 4.7 g. (86%) of colorless crystals, m.p. 92° (reported[2] 99°).

**Deselenization.**—To a hot solution of 1 g. of 2-nitrobenzoselenophene in 120 ml. of benzene was added 10 g. of Raney nickel. The mixture was heated on the Parr apparatus for 2 hours under 50 lb. pressure of hydrogen. The solution was then cooled and filtered. Hydrogen chloride gas was passed through the colorless filtrate, yielding 0.35 g. of a white precipitate (3-aminobiphenyl hydrochloride). Recrystallization of a portion of the hydrochloride from alcohol–ether brought the m.p. to 199–200°.

*Anal.* Calcd. for $C_{12}H_{12}NCl$: neut. equiv., 206. Found: neut. equiv., 212.

This amine was acetylated with acetic anhydride yielding 3-acetamidobiphenyl, m.p. 147° (reported[7] 148°). From the similar deselenization of 4-nitrodibenzoselenophene (II), was obtained a 63% yield of 3-aminobiphenyl hydrochloride. Mixtures of the hydrochlorides from deselenizations of the two nitro compounds showed no melting point depression. Mixtures of the two acetamidobiphenyls showed no melting point depression.

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(7) F. Fichter and A. Sulzberger, *Ber.*, **37**, 882 (1904).

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# COMMUNICATIONS TO THE EDITOR

## IDENTIFICATION OF 3-KETOPENTOSE ARISING FROM RIBOSE PHOSPHATE

*Sirs:*

The formation of xylulose phosphate from ribose phosphate has been recently demonstrated in spleen extracts.[1] The present report is concerned with the isolation and tentative identification of *erythro*-3-ketopentose (*erythro*-3-pentulose) in the same system. Definitive identification must await synthesis of this compound.

Ribose 5-phosphate was incubated with a mouse spleen extract and the reaction product dephosphorylated and de-ionized as described previously.[1] The resulting free sugars were chromatographed on a Dowex-1–borate column. Xylulose and unreacted ribose were separated by elution with 0.02 *M* borate and ribulose by 0.04 *M* borate. The column was then eluted with 0.1 *M* borate and finally with 0.1 borate plus 0.25 *M* NaCl. Two small symmetrical peaks were located by means of reducing sugar assay.[2] These peaks were not observed when pure ribulose and xylulose were chromatographed under identical conditions.

The first of these peaks was lyophilized, freed from borate[3] and taken up in a small amount of water. The clear, slightly yellow solution contained approximately 17 μmoles determined as reducing sugar with either ribulose or arabinose as standard. Colorimetric analysis indicated that it was not glycolaldehyde, nor was it any recognizable triose, tetrose or hexose. The compound did give an orcinol and cysteine–carbazole reaction. In the latter case, a blue color was formed with a maximum at 600 mμ.[4] Paper electrophoresis in borate buffer yielded a single negatively charged spot.

The compound was subjected to periodic acid oxidation[5] as follows: 0.10 μ mole was incubated

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(1) G. Ashwell and J. Hickman, THIS JOURNAL, **76**, 5889 (1954).

(2) J. T. Park and M. J. Johnson, *J. Biol. Chem.*, **181**, 149 (1949).

(3) L. P. Zill, J. X. Khym and G. M. Cheniae, THIS JOURNAL, **75**, 1339 (1953).

(4) A new and apparently specific colorimetric procedure has been devised whereby it is now possible to detect the compound in the original incubation mixture and to follow it throughout the isolation procedure.

(5) J. MacGee and M. Doudoroff, *J. Biol. Chem.*, **210**, 617 (1954).