addition was immediate. After the reflux period, equal volumes of water and ether were added to either the entire reaction mixture or a half-aliquot (as indicated in Table II), and the organic layer was washed three times each with water, with 10% sodium hydroxide, and again with water. It was then dried and distilled.

When applied to **5** (0.33 mole) this procedure gave a mixture of products shown in Table I. Application of **9–12** involved either this procedure or the initial use of wet phosphorus pentoxide as indicated in Table II and gave no rearrangement.

Method B.—This procedure is the original one of Rindfusz.[3] The conditions and molar quantities were initially those of method A, followed by direct distillation of the reaction mixture from the phosphorus pentoxide residue. When applied to **2** (64.3 g., 0.33 mole) this procedure gave 6-*t*-butylchroman, 47.3 g., 0.25 mole, 75%, b.p. 115–116° (1.0 mm.). *Anal.* Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 82.26; H, 9.78.

The procedure applied to **5** gave fraction 1, 12 g., b.p. 45–116° (15 mm.), 9% *t*-butylbenzene and 91% chroman by v.p.c. Redistillation gave chroman, b.p. 89–90° (9 mm.), which was identified by comparing n.m.r. and infrared spectra and v.p.c. retention time with those of a genuine sample of chroman[3] as well as by correct elemental analysis.

Fraction 2, 42 g., b.p. 116–117° (1.5 mm.), was shown by v.p.c. to contain 5% of a component which was most likely 8-*t*-butylchroman and 95% 6-*t*-butylchroman **3** (Table I). The infrared and n.m.r. spectra of this mixture were identical with those of genuine **3**. *Anal.* Found: C, 82.06; H, 9.40.

Application of this method to compounds **9–12** gave mixtures as described in Table II.

Method C.—The reaction of **5** (69.3 g., 0.33 mole) with phosphorus pentoxide (22 g., 0.15 mole) was carried out in carbon disulfide (100 ml.) in a manner similar to the method B procedure. After a 2-hr. reflux period the method B work-up was used. Distillation of the dried organic solution gave a mixture, 41.8 g., b.p. 35–111° (1.0 mm.), whose composition was established by v.p.c. (Table I).

Method D.—This procedure involved heating a mixture of either **11** (10.4 g., 0.063 mole) or **12** (10.4 g., 0.05 mole) with phosphorus pentoxide (3.44 g., 0.025 mole) and water (0.9 g., 0.05 mole) at a bath temperature of 150° for 0.5 hr. The resulting mixtures were distilled directly to give 4.9 g. (b.p. 55–99° at 12 mm.) or 5.8 g. (b.p. 82–119° at 9 mm.), respectively. The v.p.c. analyses of these mixtures are given in Table II.

Chemistry of Carbon Diselenide. II. Alkylation of Substituted Selenoureas[1]

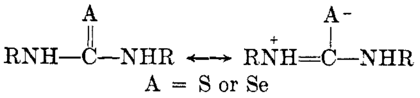
J. S. Warner and T. F. Page, Jr.

Organic Chemistry Division, Battelle Memorial Institute,
Columbus Laboratories, Columbus, Ohio 43201

Received July 30, 1965

It was previously reported[2] that carbon diselenide reacts readily with primary amines to give substituted selenoureas or analogous cyclic products with diselenocarbamate salts and isoselenocyanates serving as intermediates in the reaction. We have since studied the alkylation of those products.

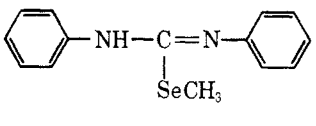
Although infrared studies[3–5] of analogous thioureas have provided no evidence for the existence of the thiol form in solution or in the solid state, alkylation yields only S-substituted products as though the thiol form were indeed present. This course of reaction can be readily explained, however, by assuming a partial polarization[6] of the molecule to such an extent that the sulfur atom rather than the nitrogen atom is the more nucleophilic center.



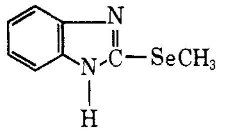
$$\mathrm{RNH{-}\overset{\overset{\displaystyle A}{\|}}{C}{-}NHR \longleftrightarrow R\overset{+}{N}H{=}\overset{\overset{\displaystyle A^-}{|}}{C}{-}NHR}$$

$$A = S \text{ or } Se$$

Since selenium is more polarizable than sulfur, Se-alkylation of selenoureas should be even more likely than S-alkylation of thioureas. It was found, as thus expected, that 1,3-diphenylselenourea, and seleno-2-benzimidazolinone gave only the corresponding Se-methyl derivatives, I and II, respectively, upon alkylation with methyl iodide.



I



II

The methylated products were shown to be Se-methyl rather than N-methyl derivatives by n.m.r. analysis and by synthesis of N-methyl derivatives by a different route. In the n.m.r. spectra of both products, satellite peaks arising from the spin–spin interaction of the methyl protons with the naturally occurring Se^{77} nuclei (7.50% abundant), were observed as expected for Se-methyl products. The Se^{77}–H couplings for I and II were 11.2 and 11.5 c.p.s., respectively.

The N-methyl derivative of 1,3-diphenylselenourea was prepared by reacting carbon diselenide with aniline in the presence of a large excess of N-methylaniline. The intermediate phenyl isoselenocyanate would thus be much more likely to react with N-methylaniline than with aniline to give the desired N-methyl product instead of 1,3-diphenylselenourea. The N-methyl derivative of seleno-2-benzimidazolinone was prepared by reaction of carbon diselenide with N-methyl-*o*-phenylenediamine. Infrared spectra and mixture melting point determinations indicated that these N-methyl derivatives were not the same as the methyl iodide alkylation products.

Although a detailed analysis of the infrared spectra was not made, it is of interest to note that strong absorption bands in the region of 3300–3100 cm.$^{-1}$, attributed to the N–H stretching vibrations, were found for both N-methyl derivatives. This evidence suggests that selenoureas of this type, like thioureas, exist primarily, if not totally, in the keto form in the solid state.

Experimental Section[7]

2-(Methylseleno)benzimidazole.—A solution of 0.59 g. (0.003 mole) of seleno-2-benzimidazolinone in 25 ml. of ethanol was mixed with a solution of 0.43 g. (0.003 mole) of methyl iodide in 10 ml. of ethanol and left overnight at room temperature. The mixture was filtered to remove a small amount of insoluble material, concentrated to 10 ml., and treated with 100 ml. of 1% aqueous sodium bicarbonate. The crystalline precipitate, after being washed with water and dried, weighed 0.52 g. (82%)

---

(1) This work was supported by a research contract with the Selenium-Tellurium Development Association, Inc., New York, N. Y. 10004.

(2) J. S. Warner, *J. Org. Chem.*, **28**, 1642 (1963).

(3) C. N. R. Rao, *Can. J. Chem.*, **42**, 36 (1964).

(4) A. K. Chibisov and Y. A. Pentin, *J. Gen. Chem. USSR*, **31**, 16 (1961).

(5) A. K. Chibisov and Y. A. Pentin, *ibid.*, **31**, 323 (1961).

(6) H. G. Mautner and W. D. Kumber, *J. Am. Chem. Soc.*, **78**, 97 (1956).

(7) N.m.r. spectra were obtained with a Varian Associates Model HR-60 n.m.r. spectrometer, and infrared spectra were run on a Perkin-Elmer Model 137 infrared spectrometer. N.m.r. spectra were calibrated by the well-known side-band technique using internal $Si(CH_3)_4$ as a reference and chemical shifts are reported in parts per million downfield from the $Si(CH_3)_4$ signal.

and melted at 196–197°. Recrystallization from ethanol did not change its melting point. The n.m.r. spectrum in methanol-d_4 consisted of a symmetrical, complex multiplet between 7.75 and 7.00 p.p.m. due to the aromatic protons, a broad concentration-dependent resonance at 3.90 p.p.m. due to the NH proton; and a sharp singlet at 2.58 p.p.m., with Se^{77}–H satellites, due to the methyl protons.

Anal. Calcd. for $C_8H_8N_2Se$: C, 45.5; H, 3.8; N, 13.3; Se, 37.4. Found: C, 45.7; H 3.8; H, 13.2; Se, 37.3.

Se-Methyl-1,3-diphenylpseudoselenourea.—The similar treatment of 0.83 g. (0.003 mole) of 1,3-diphenylselenourea with methyl iodide yielded 0.66 g. (73%) which melted at 92–93°. Recrystallization from ethanol raised the melting point to 94–95°.

Anal. Calcd. for $C_{14}H_{14}N_2Se$: C, 58.1; H, 4.8; N, 9.7; Se, 27.4. Found: C, 58.7; H, 4.8; N, 9.6; Se, 26.9.

The n.m.r. spectrum in $CDCl_3$ consisted of a complex multiplet centered near 7.25 p.p.m. due to the aromatic protons, a very broad, concentration-dependent resonance near 5.6 p.p.m. due to the NH proton, and a sharp singlet at 2.12 p.p.m., with Se^{77}–H satellites, due to the methyl protons.

N-Methylseleno-2-benzimidazolinone.—A solution of 3.4 g. (1.28 ml., 0.02 mole) of carbon diselenide in 150 ml. of carbon tetrachloride was added dropwise over a 2-hr. period with stirring to a refluxing solution of 3.0 g. (0.025 mole) of N-methyl-*o*-phenylenediamine[8] in 150 ml. of carbon tetrachloride. Refluxing was continued for 16 hr. A slow stream of nitrogen was passed through the reaction mixture during the entire period. The mixture was then cooled and filtered to yield 2.1 g. (50%) of product, m.p. 173–174° dec. Recrystallization from ethanol under nitrogen gave fine colorless needles, m.p. 184–185° dec. When mixed with the product from the direct methylation of seleno-2-benzimidazolinone, the melting point was depressed to 166–177° dec.

Anal. Calcd. for $C_8H_8N_2Se$: C, 45.5; H, 3.8; N, 13.3; Se, 37.4. Found: C, 45.6; H, 4.2; N, 13.4; Se, 37.3.

1-Methyl-1,3-diphenylselenourea.—A solution of 1.7 g. (0.64 ml., 0.01 mole) of carbon diselenide in 100 ml. of carbon tetrachloride was added dropwise over a 2-hr. period with stirring to a refluxing solution of 1.1 g. (0.012 mole) of aniline and 44 ml. (0.40 mole) of N-methylaniline in 200 ml. of carbon tetrachloride. Refluxing was continued for an additional 3 hr. A slow stream of nitrogen was passed through the mixture during the entire period. The resulting solution was concentrated at reduced pressure at 50°, treated with 250 ml. of ice-cold 2 *N* hydrochloric acid, and extracted with ether. The ether extract was washed with water, dried over anhydrous magnesium sulfate, and concentrated to a syrup. The syrup was dissolved in 25 ml. of hot carbon tetrachloride and treated with hexane until a slight cloudiness appeared. Cooling to 0° overnight yielded 1.7 g. (59%) of dense pale yellow crystals, m.p. 98–99°. When mixed with the product from the direct methylation of 1,3-diphenylselenourea, the melting point was depressed to 68–78°.

Anal. Calcd. for $C_{14}H_{14}N_2Se$: C, 58.1, H, 4.8; N, 9.7; Se, 27.4. Found: C, 58.1; H, 4.9; N, 9.7; Se, 27.9.

---

[8] N-Methyl-*o*-phenylenediamine, b.p. 87–87.5° (0.3 mm.), $n^{27}\text{D}$ 1.6111, was prepared by the method of H. Irving and O. Weber [*J. Chem. Soc.*, 2296 (1959)]. Its identity was confirmed by n.m.r. analysis.

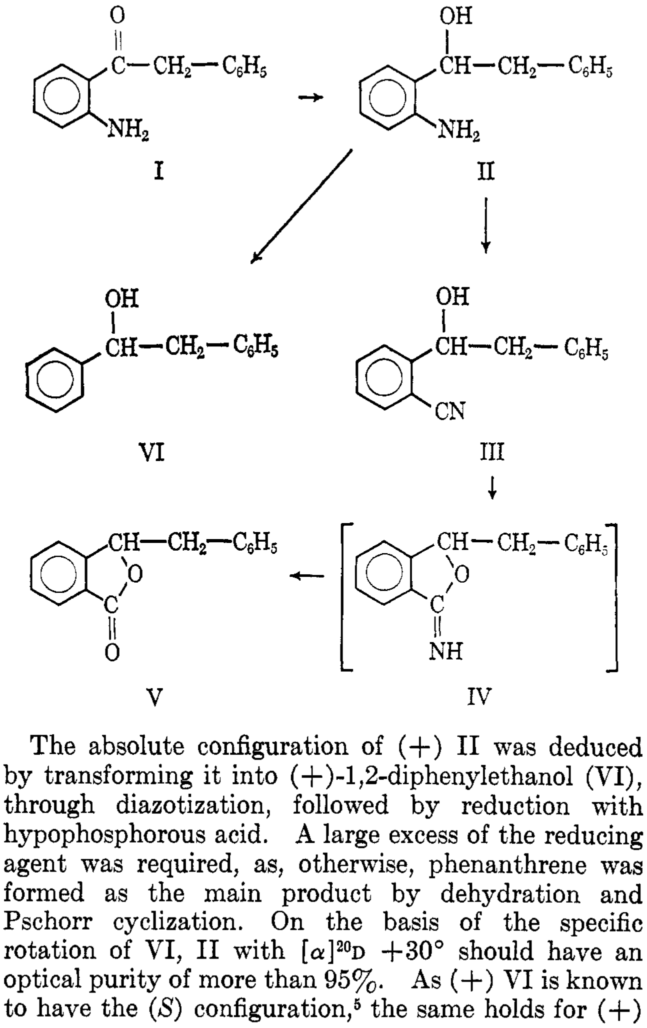
Synthesis and Absolute Configuration of the Enantiomeric 3-Benzylphthalides

G. BERTI, N. MACCHIONI,[1] AND A. MARSILI

Institutes of Organic and Pharmaceutical Chemistry, University of Pisa, Pisa, Italy

Received August 9, 1965

In connection with an investigation of the preparation of optically active bromo lactones by asymmetric bromination of unsaturated acids in the presence of Cinchona alkaloids,[2] we were interested in determining the absolute configuration of 3-benzylphthalide (V). Usual methods of resolution could not be used on V, which lacks basic or acidic groups, nor on the corresponding hydroxy acid, which is stable only as a salt in strongly basic solutions. Optically active V was therefore prepared by the following route. The known ketone I[3] was reduced to the amino alcohol II, which was easily resolved through its salts with (−)-dibenzoyltartaric acid. Diazotization of (−) II, followed by reaction with cyanocuprate (I), gave a crude product with strong —OH and C≡N bands in the infrared, evidently III. Chromatography of crude III over alumina yielded (+)-3-benzylphthalide (V). The ease of cyclization of III to V is not exceptional, as several γ- or δ-hydroxynitriles are known to be transformed into lactones under very mild conditions: thus, for instance, *o*-hydroxy-α-phenylcinnamonitrile gives 3-phenylcoumarin simply on refluxing with water.[4] Such an easy transformation of the nitrile group in III can only be explained with an intramolecular attack by the hydroxyl on the nitrile group to give V, through the imine IV. It is almost certain that the optically active lactone is formed with retention of configuration, as no logical mechanism involving inversion can be hypothesized for such a reaction.



The absolute configuration of (+) II was deduced by transforming it into (+)-1,2-diphenylethanol (VI), through diazotization, followed by reduction with hypophosphorous acid. A large excess of the reducing agent was required, as, otherwise, phenanthrene was formed as the main product by dehydration and Pschorr cyclization. On the basis of the specific rotation of VI, II with $[\alpha]^{20}\text{D}$ +30° should have an optical purity of more than 95%. As (+) VI is known to have the (*S*) configuration,[5] the same holds for (+)

---

[1] Taken in part from the Ph.D. Thesis of N. Macchioni.

[2] G. Berti and A. Marsili, *Angew. Chem.*, **75**, 1026 (1963); *Chim. Ind.* (Milan), **46**, 312 (1964).

[3] D. W. Ockenden and K. Schofield, *J. Chem. Soc.*, 3440 (1953).

[4] W. Borsche and F. Streitberger, *Ber.*, **37**, 3163 (1904).

[5] G. Berti, F. Bottari, and B. Macchia, *Chim. Ind.* (Milan), **45**, 1527 (1963).