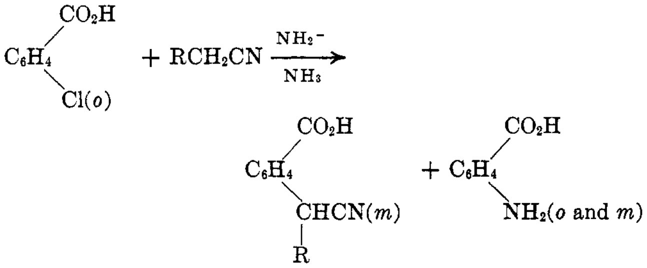
TABLE I

REACTION OF *o*-CHLOROBENZOIC ACID AND ACTIVE HYDROGEN COMPOUNDS

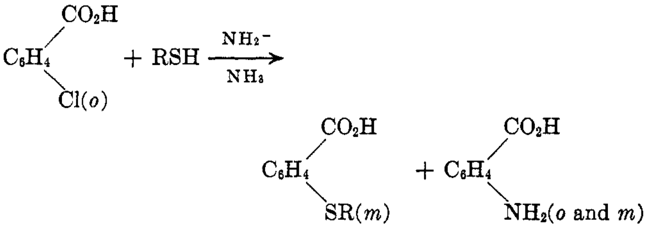
| Active hydrogen compd. | M.p., °C.[a] | I or II, % yield | C, % |  | H, % |  | N, % |  |
|---|---|---|---|---|---|---|---|---|
|  |  |  | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| $CH_3CN$ | 176–177 | 70 | 67.07 | 66.70 | 4.38 | 4.34 | 8.69 | 8.47 |
| $CH_3CH_2CN$ | 134–135 | 49 | 68.55 | 68.61 | 5.17 | 5.27 | 7.99 | 7.80 |
| $CH_3(CH_2)_3CN$ | 130–131 | 71 | 70.91 | 70.77 | 6.44 | 6.42 | 6.89 | 6.87 |
| $C_6H_5SH$ | 107–108[b] | 56 |  |  |  |  |  |  |
| $CH_3SH$ | 126–127[c] | 62 |  |  |  |  |  |  |
| $C_2H_5SH$ | 98[d] | 61 |  |  |  |  |  |  |

[a] Melting points are uncorrected. [b] Lit.[6] m.p. 107–109°. [c] C. C. Price and J. J. Hydock [*J. Am. Chem. Soc.*, **74**, 1943 (1952)] reported m.p. 126–127°. [d] J. J. Donleavy and J. English, Jr. [*ibid.*, **62**, 221 (1940)] reported m.p. 98–99°.



I

no case has any *o*-carboxyphenylated active hydrogen compound been isolated. The isomeric aminobenzoic acids were separated, identified, and quantitatively analyzed. The isomeric aminobenzoic acid distribution in all reactions was approximately 1:2 *ortho*:*meta*. Table I shows the yields of the compounds I and II that have been prepared using a reaction time of 1 hr. and a molar ratio of 0.6 mole of sodamide to 0.3 mole of active hydrogen compound to 0.1 mole of *o*-chlorobenzoic acid.



II

To show that no *ortho* isomer was present, authentic samples of both the *ortho* and *meta* isomer were prepared and a comparison was made of the respective infrared spectra. In all cases, the infrared spectra of the products were identical in all respects with the spectra of the corresponding known *meta* isomer.

From these results it appears that this reaction is an excellent method for substituting the active hydrogen atom by a *m*-carboxyphenyl group.[5] Thus, in the single previously reported synthesis of *m*-carboxydiphenyl sulfide,[6] the von Richter reaction provided a yield of only 5%. We are currently trying to extend this reaction to other active hydrogen compounds.

## Experimental Section

**General Procedure for the Reaction of *o*-Chlorobenzoic Acid with Active Hydrogen Compounds and Sodamide in Liquid Ammonia.**—Sodamide (0.6 mole) was prepared by adding 0.6 g.-atom (18.2 g.) of cleanly cut sodium to a 1-l. flask equipped with a stirrer and Dry Ice condenser and containing about 600 ml. of liquid ammonia and 0.1 g. of ferric nitrate. The active hydrogen compound (0.3 mole) was added over a period of 5 min. and allowed to react for 30 min. to ensure anion formation. Then 0.1 mole (15.6 g.) of *o*-chlorobenzoic acid was added portionwise over a period of 5–7 min., and the solution was stirred for 1 hr. At this time, 0.65 mole of ammonium chloride was added and the ammonia was removed by heating with a steam bath. The residue was slurried with a little ether and poured into about 150 ml. of ice–water slurry. The basic mixture was treated with charcoal, filtered, and added to 50 ml. of concentrated hydrochloric acid. The solid material was recovered by filtration and purified by recrystallization from a water-methanol mixture. Table I summarizes pertinent physical data for the compounds.

The isomeric aminobenzoic acids were separated and the ratio of the isomers was estimated by paper chromatography.

---

[5] The reactions of *m*- or *p*-chlorobenzoic acid with active hydrogen compounds yield a mixture of *m*- and *p*-carboxyphenylated active hydrogen compounds in a ratio of approximately 1:1 *meta*:*para*, as determined by infrared analysis.

[6] J. F. Bunnett and M. M. Rauhut, *J. Org. Chem.*, **21**, 934 (1956).

---

# The Isomerization and Disproportionation of 8-*t*-Butylchroman and Related *t*-Butyl phenyl Ethers[1]

IRVING J. BOROWITZ AND GREGORY J. WILLIAMS

*Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania*

*Received August 17, 1965*

In relation to our recent syntheses of 6-ketononanolides from tetrahydrochromans,[2] it was desired to prepare the 6- and 8-*t*-butyl derivatives of chroman. A standard synthesis of chromans substituted in the aromatic ring involves the alkylation of the appropriate sodium phenoxide with 3-chloro-1-propanol to give the corresponding 3-phenoxy-1-propanol which is then cyclized by dehydration in boiling benzene with phosphorus pentoxide followed by direct distillation.[3] We have utilized this method previously to synthesize several monomethylchromans and 5,8-dimethylchroman.[2b] Application of this method to 4-*t*-butylphenol (**1**) gave 3′-hydroxypropyl 4-*t*-butylphenyl ether (**2**) which was cyclized to 6-*t*-butylchroman (**3**).

Similar reaction of 2-*t*-butylphenol (**4**) gave 3′-hydroxypropyl 2-*t*-butylphenyl ether (**5**). Cyclization of **5** with phosphorus pentoxide by the previously utilized procedure (method B) gave a mixture which

---

[1] This investigation was supported in whole by Public Health Service Research Grant AI 06303-01 to I. J. B. from the National Institute of Allergy and Infectious Diseases.

[2] (a) I. J. Borowitz and G. Gonis, *Tetrahedron Letters*, **No. 19**, 1151 (1964); (b) R. Kelsey, Lehigh University, unpublished results.

[3] R. E. Rindfusz, *J. Am. Chem. Soc.*, **41**, 667 (1919); (b) R. E. Rindfusz, P. M. Gennings, and V. L. Harnack, *ibid.*, **42**, 157 (1920).

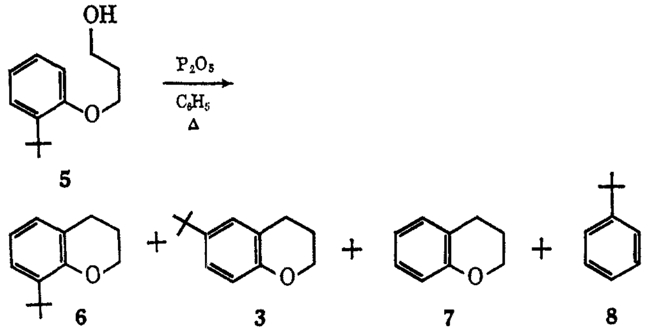
TABLE I

THE REACTIONS OF 3′-HYDROXYPROPYL 2-*t*-BUTYLPHENYL ETHER (5) WITH PHOSPHORUS PENTOXIDE

| Method[a] | Total wt. of product,[b] g. | Products | V.p.c. ratio[c] | Ret. time,[d] min. | Wt.,[e] g. | Mole[e] | Yield,[e] % |
|---|---|---|---|---|---|---|---|
| A | 49.5 | **8** | 15 | 0.5 | 7.4 | 0.055 | 16 |
| | | **7** | 11 | 1.05 | 5.5 | 0.041 | 12 |
| | | Unident. | 6 | 1.8 | | | |
| | | **6** | 18 | 2.6 | 8.9 | 0.047 | 14 |
| | | **3** | 39 | 3.0 | 19.3 | 0.101 | 30 |
| | | Unident. | 11 | 5.05 | | | |
| B | 54 | | | | | | |
| | 12 (fraction 1) | **8** | 9 | 0.5 | 1.1 | 0.008 | 2 |
| | | **7** | 91 | 1.05 | 10.9 | 0.081 | 24 |
| | 42 (fraction 2) | **6** | 5 | 2.6 | 2.0 | 0.011 | 3 |
| | | **3** | 95 | 3.0 | 39.9 | 0.210 | 62 |
| C | 41.8 | **7** | 9 | 1.05 | 3.8 | 0.028 | 9 |
| | | Unident.[f] | 9 | | | | |
| | | **6** | 19 | 2.6 | 8.0 | 0.042 | 13 |
| | | **3** | 48 | 3.0 | 20 | 0.105 | 32 |
| | | Unident. | 15 | 5.05 | | | |

[a] Methods A–C are described in the Experimental Section. [b] Since the total product obtained may vary with the distillation procedure, it is felt that the v.p.c. ratios within a particular run are a more reliable index of the distribution of products than the actual yields. [c] Ratios are based on a total area summation method. [d] Retention times (v.p.c.) are measured from a diethyl ether peak and were determined on a 20% SE-30 HMDS on Chromosorb W stainless steel column at an oven temperature of 225°. [e] The weight, moles, and yields of products are based on the v.p.c. ratio and the total weight of products obtained. [f] Two close peaks are observed.

contained 8-*t*-butylchroman (**6**) only as a minor component, 6-*t*-butylchroman (**3**) as the major component, chroman (**7**), and *t*-butylbenzene (**8**) (Table I).



It was found that a related mixture arose if the work-up of the cyclization reaction was changed to avoid direct distillation from the phosphoric acids formed (method A). Significantly, however, the ratio of the rearranged **3** to **6** was now only 2.2 rather than 11.5 as resulted from the direct distillation without removal of acidic species. Thus, the various products already had formed in part during the reflux period. Cyclization of **5** in carbon disulfide (method C) still gave a mixture of **7**, **6**, and **3**. Thus the presence of benzene as a *t*-butyl acceptor was not necessary.

That part of the *t*-butyl isomerization from the 8 position (corresponding to an *ortho* position) to the 6 position (corresponding to *para*) of the chroman occurs during the initial reflux period is in contrast to the results obtained for *o*-*t*-butylanisole (**9**) and *o*-*t*-butylphenyl *n*-butyl ether (**10**). In the latter cases *ortho*–*para* isomerization and loss of the *t*-butyl group occurred only during distillation of the *o*-*t*-butyl ether from the phosphorus pentoxide residues and not during the initial reflux period in benzene (Table II). The corresponding *p*-*t*-butyl ethers, **11** and **12**, exhibited loss of the *t*-butyl group to only a small extent and gave no rearrangement to the corresponding *ortho* isomer.

The formation of chroman, rearranged 6-*t*-butylchroman, and *t*-butylbenzene at the expense of the presumably initially formed 8-*t*-butylchroman is thus related to other acid-catalyzed *ortho–para* *t*-butyl isomerizations and disproportionation reactions.[4–9] The observation that the *ortho–para* *t*-butyl rearrangement occurs more readily in the *t*-butylchroman case than with **9** or **10** may reflect the fact that the chroman cyclization involves more carbonium ion character than do the rearrangements of **9** or **10**. It may also indicate a different extent of interaction of the chroman with acidic species and/or a different extent of rearrangement of such species compared with the anisole or phenyl *n*-butyl ether cases.

In summary this work reaffirms the acid-catalyzed mobility of a *t*-butyl group on an aromatic ring. It cites a limitation on the chroman synthesis of Rindfusz[3] and it represents the first demonstration, to our knowledge, of such reactions on a chroman nucleus.

### Experimental Section

Microanalyses were performed by Professor V. B. Fish of the Department of Chemistry, Lehigh University. Infrared spectra were recorded on a Beckman IR-8 infrared spectrophotometer. Vapor phase chromatograms were recorded on a Wilkens A-700 chromatograph with column conditions as noted in the tables. N.m.r. spectra were recorded on a Varian A-60 spectrometer with tetramethylsilane ($\tau$ 10) as an internal standard. The identification of *t*-butylbenzene, anisole, *n*-butyl phenyl ether, and compounds **9–12** in the various mixtures encountered was based on v.p.c. retention times compared with those of genuine samples.

**Alkylations of *o*- and *p*-*t*-Butylphenol. A. Reactions with 3-Chloro-1-propanol.**—*o*-*t*-Butylphenol (75 g., 0.50 mole) was added to a solution of sodium (11.5 g., 0.50 g.-atom) in absolute

---

[4] One unidentified product, formed in both the reactions of **11** and **12**, may be a corresponding di-*t*-butyl ether but was not further studied.

[5] H. Hart and E. A. Haglund, *J. Org. Chem.*, **15**, 396 (1950).

[6] For a discussion of the mechanisms of disproportionation and isomerization, see D. A. McCaulay, "Friedel-Crafts and Related Reactions," Vol. II, Part 2, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, Chapter 24.

[7] M. J. Schlatter and R. D. Clark, *J. Am. Chem. Soc.*, **75**, 361 (1953).

[8] P. H. Gore in "Friedel-Crafts and Related Reactions," Vol. III, Part 1, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p. 140.

[9] A. W. Burgstahler, P.-L. Chien, and M. O. Abdel-Rahman, *J. Am. Chem. Soc.*, **86**, 5281 (1964).

TABLE II

THE REACTIONS OF *t*-BUTYLAROMATIC ETHERS WITH PHOSPHORUS PENTOXIDE

| Compound | Moles[a] | Method[b] | Products | | V.p.c. ratio | Ret. time,[c] min. | Wt. g. | Mole | Yield, % |
|---|---|---|---|---|---|---|---|---|---|
| *o*-*t*-Butylanisole (**9**) | 0.050 | A[d] | **9** | | 100 | 1.65 | 8.0 | 0.0486 | 97.5 |
| **9** | 0.050 | B[d] | Anisole | 6.4 g. | 14 | 0.6 | 0.9 | 0.0083 | 17 |
| | | | **9** | | 50 | 1.65 | 3.2 | 0.0195 | 39 |
| | | | **11** | | 22 | 2.00 | 1.4 | 0.0086 | 17 |
| | | | Unident. | | 14 | 3.10 | | | |
| **9** | 0.050 | A[e] | **9** | | 100 | 1.65 | 6.0 | 0.0366 | 73 |
| **9** | 0.050 | B[e] | Anisole | 4.9 g. | 16 | 0.6 | 0.78 | 0.0073 | 14.5 |
| | | | **9** | | 50 | 1.65 | 2.45 | 0.0149 | 30 |
| | | | **11** | | 21 | 2.00 | 1.03 | 0.0063 | 12.5 |
| | | | Unident. | | 13 | 3.10 | | | |
| *o*-*t*-Butylphenyl *n*-butyl ether (**10**) | 0.050 | A[d] | **10** | | 100 | 2.5 | 9.5 | 0.0460 | 92 |
| **10** | 0.050 | B[d] | *n*-Bu phenyl ether | 7.7 g. | 15 | 1.0 | 1.15 | 0.0077 | 15 |
| | | | **10** | | 60 | 2.5 | 4.60 | 0.0220 | 44 |
| | | | **12** | | 15 | 3.0 | 1.15 | 0.0056 | 11 |
| | | | Unident. | | 10 | 5.1 | | | |
| **10** | 0.050 | B[e] | *n*-Bu phenyl ether | 7 g. | 17 | 1.0 | 1.19 | 0.0079 | 16 |
| | | | 10 | | 56 | 2.5 | 3.92 | 0.0190 | 38 |
| | | | 12 | | 16 | 3.0 | 1.12 | 0.0054 | 11 |
| | | | Unident. | | 11 | 5.1 | | | |
| *p*-*t*-Butylanisole (**11**) | 0.050 | A[d] | **11** | | 100 | 2.0 | 7.9 | 0.048 | 96 |
| **11** | 0.050 | B[d] | Anisole | | 7 | 0.6 | | | |
| | | | **11** | | 87 | 2.0 | | | |
| | | | Unident. | | 6 | 3.1 | | | |
| **11** | 0.063 | D | Anisole | 4.9 g. | 72 | 0.6 | 3.53 | 0.033 | 52 |
| | | | **11** | | 16 | 2.0 | 0.78 | 0.005 | 8 |
| | | | Unident. | | 12 | 3.1 | | | |
| *p*-*t*-Butylphenyl *n*-butyl ether (**12**) | 0.050 | A[d] | **12** | | 100 | 3.0 | 9.5 | 0.046 | 92 |
| **12** | 0.050 | B[d] | *n*-Bu phenyl ether | 8.6 g. | 9 | 1.0 | 0.78 | 0.005 | 10 |
| | | | **12** | | 85 | 3.0 | 7.3 | 0.035 | 71 |
| | | | Unident. | | 6 | 5.1 | | | |
| **12** | 0.050 | D | *n*-Bu phenyl ether | 5.8 g. | 75 | 1.0 | 4.35 | 0.029 | 58 |
| | | | Unident. | | 8 | 1.75 | | | |
| | | | **12** | | 10 | 3.0 | 0.58 | 0.003 | 6 |
| | | | Unident. | | 7 | 5.1 | | | |

[a] All 0.050-mole runs were actually performed as follows. A 0.100-mole run was performed; the reaction mixture was divided into two halves; the half-aliquots were worked up *via* method A or B as indicated. [b] Methods A, B, and D are described in text and Experimental Section. The methods used and the column captions have the same meaning as in Table I. [c] Retention times for **9** and **11** are based on v.p.c. work with the 20% SE-30 column (225°) (footnote *c*, Table I) while values for **10** and **12** were obtained on an Apiezon L column (250°). [d] Reaction was performed with 0.05 mole of phosphorus pentoxide/0.10 mole of water. [e] Reaction was performed with 0.05 mole of dry phosphorus pentoxide.

ethanol (300 ml.). 3-Chloro-1-propanol (47 g., 0.50 mole) then was added with vigorous stirring over 0.5 hr. The mixture then was heated at reflux for 12 hr., most of the ethanol was removed, water (100 ml.) was added, and the residue was extracted with ether (150 ml., three 75-ml. portions). The combined ether extracts were washed with 10% sodium hydroxide (two 75-ml. portions), then with water, and finally distilled to give 3′-hydroxypropyl 2-*t*-butylphenyl ether **5**, 78 g., 0.38 mole, 75%, b.p. 128° (0.25 mm.) as a pure compound (v.p.c.). The n.m.r. spectrum (neat) of **5** exhibited a complex multiplet at $\tau$ 2.68–3.33 for an *ortho*-disubstituted benzene (4 H), a singlet at 5.60 (OH proton), a multiplet centered at 6.16 (4H of C-1′ and C-3′), a multiplet centered at 6.34 (2 H of C-2′), and a singlet at 8.63 (9 H of *t*-butyl). *Anal.* Calcd. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.97; H, 9.69.

Similar reaction of *p*-*t*-butylphenol (75 g., 0.50 mole) gave 3′-hydroxypropyl 4-*t*-butylphenyl ether **2**, 94 g., 0.45 mole, 90%, b.p. 163° (3 mm.) as a pure compound (v.p.c.). The n.m.r. spectrum (neat) of **2** exhibits an AB quartet (4 H) centered at $\tau$ 3.02 typical of two dissimilar groups *para* substituted on a benzene ring, a singlet at 5.57 (OH proton), a multiplet of two overlapping triplets centered at 6.16 (4 H on C-1′ and C-3′), a multiplet centered at 6.44 (2 H of C-2′), and a singlet at 8.77 (9 H of *t*-butyl). *Anal.* Found: C, 75.11; H, 9.63.

**B. *o*- and *p*-*t*-Butylanisoles.**—The *ortho* isomer was prepared from sodium *o*-*t*-butylphenolate and methyl iodide in 85% yield, b.p. 85.5° (9 mm.). *Anal.* Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.37; H, 9.64.

The *para* isomer was similarly prepared for *p*-*t*-butylphenol in 93% yield, b.p. 97° (9 mm.). *Anal.* Found: C, 80.38; H, 9.60.

**C. *o*- and *p*-*t*-Butylphenyl *n*-Butylphenyl *n*-Butyl Ethers.**—The *ortho* isomer was prepared from sodium *o*-*t*-butylphenolate and *n*-butyl iodide in 74% yield, b.p. 117° (10 mm.). *Anal.* Calcd. for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.66; H, 10.91. The *para* isomer was similarly prepared in 95% yield, b.p. 133–134° (9 mm.). *Anal.* Found: C, 81.47; H, 10.70.

**D. *n*-Butyl Phenyl Ether.**—This was prepared in a similar alkylation reaction in 93% yield, b.p. 89–90° (9 mm.). *Anal.* Calcd. for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.60; H, 7.65.

**Reactions of Alkyl Phenyl Ethers with Phosphorus Pentoxide. Method A.**—In a typical reaction a solution of 3′-hydroxypropyl 2-*t*-butylphenyl ether (69.3 g., 0.33 mole) in benzene (50 ml.) was added dropwise with stirring to a suspension of phosphorus pentoxide (22 g., 0.15 mole) in benzene (100 ml.). In the case of the hydroxypropyl ethers the addition was moderated at such a rate as to maintain reflux. This was followed by a 3-hr. reflux period. In the isomerization reactions with **9**–**12** initial 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]

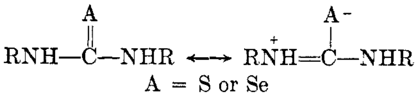
J. S. WARNER AND T. F. PAGE, JR.

*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.

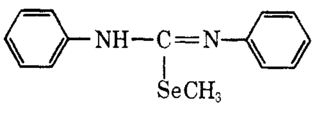
Although infrared studies[3-5] of analogous thioureas have provided no evidence for the existence of the thiol form in solution or in the solid state, alkylation yields only S-substituted products as though the thiol form were indeed present. This course of reaction can be readily explained, however, 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.



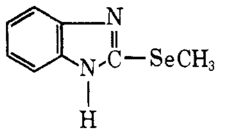
$$\mathrm{RNH{-}\overset{\overset{A}{\|}}{C}{-}NHR \longleftrightarrow R\overset{+}{N}H{=}\overset{\overset{A^-}{|}}{C}{-}NHR}$$

A = S 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.