(dried over concentrated sulfuric acid for 24 hr.) added. At reflux temperature, the reaction was complete after 20 min.—as indicated by the discharge of the color—and a grayish precipitate had formed. The heating was continued for another 15 min. and the product decomposed with ice and 25% sulfuric acid. The aqueous layer was extracted with ether and chloroform, and the combined organic solutions were washed with sodium bicarbonate solution, dried and concentrated to a volume of 30 ml. Then 100 ml. of cyclohexane was added and the mixture heated to the boiling point and filtered. From the solution crystallized 30 g. of the product (75%); by concentration of the mother liquor a little more product could be obtained. Recrystallization from cyclohexane gave colorless needles, m.p. 110–111°.

*Anal.* Calcd. for $C_{14}H_{12}OS$: C, 73.7; H, 5.3. Found: C, 73.9; H, 5.6.

*p-Toluenesulfonate.* To a solution of 11 g. of the foregoing substance in 30 ml. of pyridine, 10 g. of *p*-toluenesulfochloride was added slowly at 0 to −5°. After 18 hr. at 0°, the product was poured into a mixture of ice and 30% hydrochloric acid. The oil which precipitated solidified upon standing or trituration with alcohol, and the product was recrystallized from methanol. It melted at 95°; yield, 15 g. (78%).

*Anal.* Calcd. for $C_{21}H_{18}O_3S_2$: C, 66.0; H, 4.7. Found: C, 65.8; H, 4.6.

*Dibenzo*[*bf*]*thiepin* (I). The following conditions have been found the most advantageous for the rearrangement: A solution of 9.5 g. of the *p*-toluenesulfonate in 75 ml. of 95% formic acid was refluxed for 30 min. and slowly poured into an excess of sodium carbonate solution, so that the reaction was alkaline all the time. The product was extracted three times with benzene and the benzene extract washed with dilute hydrochloric acid and 5% sodium bicarbonate solution, dried, and concentrated to a volume of 15 ml. After a first chromatography on alumina, 4 g. (77%) of a product was obtained which melted at 73–75° after recrystallization from cyclohexane. For the final purification, 2 g. of product in petroleum ether–benzene (5:1) was chromatographed on 35 g. of alumina. Of the 50-ml. fractions of eluate, the second fraction contained the pure compound, which was recrystallized from methanol and formed yellowish needles, m.p. 89–90°, yield, 1.2 g. (44%). The infrared spectrum showed the absence of a hydroxyl or ester group. The ultraviolet spectrum showed $\lambda_{max}^{ethanol}$ (log $\epsilon$): 227 m$\mu$ (4.36); 262 m$\mu$ (4.47); 295 m$\mu$ (3.70).

*Anal.* Calcd. for $C_{14}H_{10}S$: C, 80.0; H, 4.8. Found: C, 80.2; H, 4.9.

*Dibenzo*[*bf*]*thiepin-sulfone.* A mixture of 1 g. of the foregoing compound in 18 ml. of 95% formic acid and 2.1 g. of 30% hydrogen peroxide, was heated at 40° for 30 min. with magnetic stirring, whereupon a clear solution resulted, and at 98° for 4 hr., and poured into water. The product crystallized from ethanol and melted at 171–172°. It was not affected by alkali or periodic acid and showed no hydroxyl absorption in the infrared. The ultraviolet spectrum showed $\lambda_{max}^{ethanol}$ (log $\epsilon$): 229 m$\mu$ (4.54); 264 m$\mu$ (3.85); 300 m$\mu$ (4.08).

The infrared spectrum showed $\bar{\nu}_{max}^{KBr}$: 1600, 1562, 1481, 1440, 1307 (s), 1260, 1180 (s), 1126, 1087, 1064, 818, 813 (s), 784, 763 (s), 725, 700 cm.$^{-1}$

*Anal.* Calcd. for $C_{14}H_{10}SO_2$: C, 69.4; H, 4.1. Found: C, 69.2; H, 4.1.

*Diphenylsulfide-o,o′-dicarboxylic acid* (VI). To a solution of 1 g. of the dibenzothiepin in 25 ml. of acetone (and a few drops of water), powdered potassium permanganate was added in small portions; after each addition, we waited until the color disappeared. When the permanganate color did not change for 3 hr., the solution was filtered and the solid phase washed with 2 ml. of acetone. The residue was then extracted twice with 10 ml. of boiling water and the combined extracts were acidified with dilute hydrochloric acid. The product was reprecipitated from dilute potassium hydroxide solution and finally recrystallized from aqueous alcohol. It melted at 230° (lit.,[14] m.p. 229°) and was identified by mixed melting point with a sample prepared according to Rosenmund and Harms.[14] The ultraviolet spectrum showed $\lambda_{max}^{ethanol}$ (log $\epsilon$): 226 m$\mu$ (4.51); 255 m$\mu$ (3.98); 322 m$\mu$ (3.70).[15]

The infrared spectrum showed $\bar{\nu}_{max}^{KBr}$: 2940, 1700 (s), 1600 (*o*-disubstituted benzene), 1568, 1475, 1418 (carboxyl), 1307 (s), 1283 (s) (carboxyl), 1266 (s), 1136, 1064, 1047, 939, 810 (s), 755 (s) (superposition of C—S—C and *o*-disubstituted benzene), 724, 714 cm.$^{-1}$

*Anal.* Calcd. for $C_{14}H_{10}O_4S$: C, 61.3; H, 3.7. Found: C, 60.9; H, 4.1.

*Thioxanthone.* To a well stirred mixture of 1.4 g. of dibenzothiepin and 60 ml. of boiling water, a mixture of 5 g. of potassium permanganate and 3 g. of sodium carbonate was added slowly. When the color was no longer discharged, the product was acidified with 25% sulfuric acid and decolorized by addition of sodium sulfite. The yellow precipitate was dissolved in benzene and chromatographed on alumina. Thus, 0.6 g. (43%) of thioxanthone was obtained which melted alone and upon admixture of authentic material at 209°.

*Reaction of thioxanthone with methylmagnesium iodide.* A repetition of the experiment of Decker[7] led to somewhat different results. The whole sequence of operations was carried out in a nitrogen atmosphere.

A solution of methylmagnesium iodide prepared from 6 g. of magnesium and 33 g. of methyl iodide in anhydrous ether, was added to a suspension of 16 g. of thioxanthone in warm benzene. During 4 hr. the ether was distilled off and the resulting product refluxed. It was decomposed with ice and ammonium chloride.[16] From the benzene layer, some thioxanthone crystallized which was removed by filtration. The benzene solution was then washed with water, dried, and evaporated *in vacuo* at a temperature not exceeding 40°. The remaining reddish oil was chromatographed on alumina and eluted with a mixture of benzene and petroleum ether (1:1). Thus, a yellow oil was obtained which crystallized upon trituration with cyclohexane. 9-Methylthioxanthydrol melted at 82–83°.

*Anal.* Calcd. for $C_{14}H_{12}OS$: C, 73.7; H, 5.3. Found: C, 74.0; H, 5.8.

On standing in a vacuum desiccator (or on heating with a mixture of acetic acid and acetic anhydride) the crystals liquefied through dehydration. 9-Methylenethioxanthene is a liquid which could not be obtained in pure form, as it quickly began to autoxidize and deposit thioxanthone, m.p. 205° and mixed m.p. 207°. The product described by Decker[7] as a semisolid of undefined melting point was, therefore, undoubtedly not 9-methylenethioxanthene.

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[14] K. W. Rosenmund and H. Harms, *Ber.*, **53**, 2226 (1920).

[15] For diphenylsulfide, 2 maxima (at 252 and 278 m$\mu$) have been observed.

[16] Dehydration proceeds with great ease, if the decomposition is carried out with acid. Decker did not isolate the tertiary alcohol.

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## Dimer of 2-Pyridyl Isothiocyanate

JOHN C. HOWARD AND JULIAN G. MICHELS

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The synthesis of 2-pyridyl isothiocyanate, described as a brick-red solid, m.p. 110–111°, was

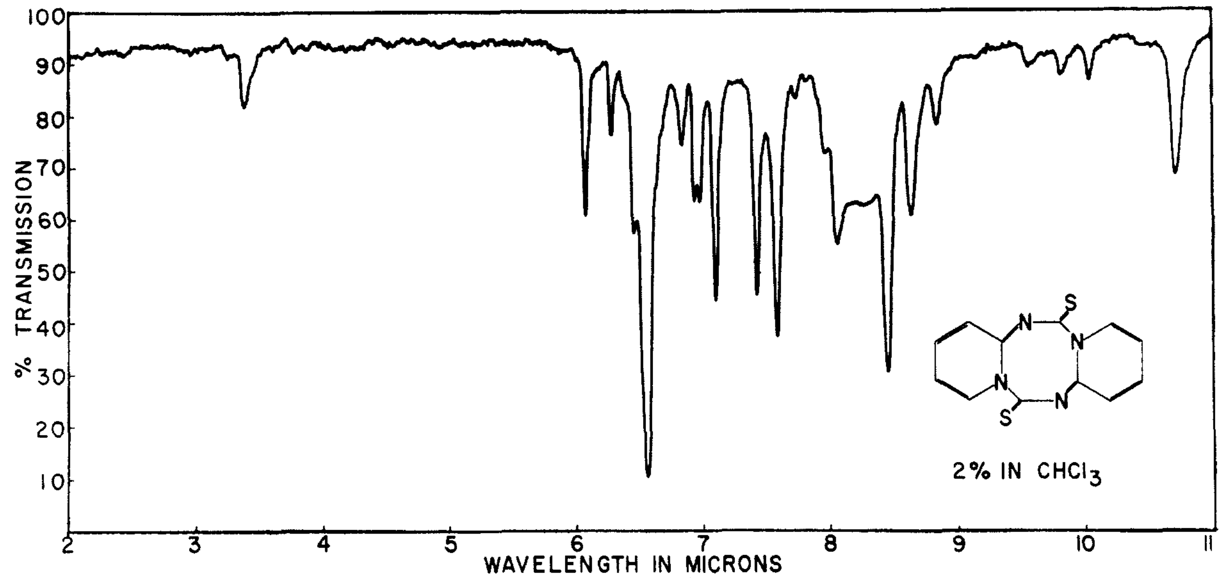


Fig. 1. Infrared spectrum of 2-pyridyl isothiocyanate dimer

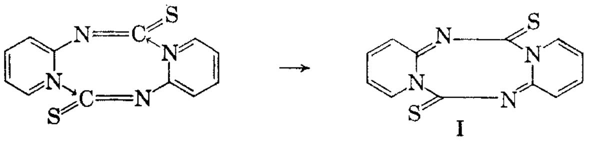
recently reported by Fairfull and Peak.[1] Structural assignment was made on the basis of a correct nitrogen analysis and conversion to the known *N*-phenyl-*N'*-2-pyridylthiourea by heating with aniline at 100°. It appeared to us that although the compound reacted at 100° as a typical isothiocyanate, its color and melting point were anomalous. Isothiocyanates are generally colorless liquids; in fact, 3-pyridyl isothiocyanate was so described by Fairfull and Peak.[1] We planned to use 2-pyridyl isothiocyanate as an intermediate and felt that the anomaly deserved closer examination. We have therefore repeated the synthesis following the published procedure and obtained a brick-red solid; our analytical sample melted at 119–120° after several reprecipitations from benzene-petroleum ether. A cyroscopic molecular weight determination corresponded to a *dimer* of 2-pyridyl isothiocyanate.

An infrared spectrum of a freshly prepared chloroform solution showed no characteristic isothiocyanate absorption at 5$\mu$ (Fig. 1). After thirty minutes refluxing, however, the solution became straw-colored and the infrared spectrum showed very intense absorption at 4.96$\mu$ (Figure 2). The ultraviolet spectrum also changed greatly after fifteen minutes heating; a fresh chloroform solution absorbed strongly at 295 m$\mu$, 335 m$\mu$, and 420 m$\mu$. After heating, only one major peak, at 287 m$\mu$, was observed.

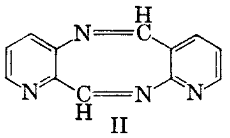
This physical evidence proves that the brick red solid is not 2-pyridyl isothiocyanate and indicates that the substance is a dimer which dissociates to the monomer in solution. Several attempts were made to isolate the monomer by distillation. A solution of the dimer was refluxed until the red color disappeared, concentrated and distilled at reduced pressure. Upon removal of the solvent, the red solid reappeared. The substance distilled as a pale yellow liquid, then solidified to the red solid in the receiver. The boiling point was similar to that of 3-pyridyl isothiocyanate and the pale yellow liquid was doubtless 2-pyridyl isothiocyanate.

Having established that the red solid was a dimer, we turned our attention to the question of its structure. It occurred to us that an eight-membered ring, I, could be formed from two isothiocyanate molecules by the "head to tail" attack of one pyridyl-nitrogen on the thiocarbonyl of the other.

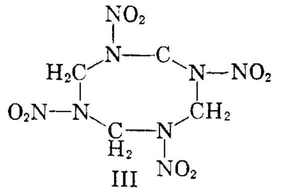
This tricyclic ring system[2] has not been described, although a similar type, II, was reported by Sucharda and Klisiecki.[3] The tetrazocine nucleus is



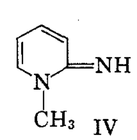
I



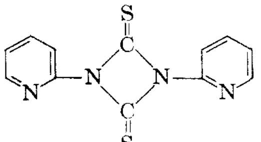
II



III



IV



V

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[1] A. E. S. Fairfull and D. A. Peak, *J. Chem. Soc.*, 796 (1955).

[2] We have named I "Dipyrido-[1,2-a,1',2'-e][1,3,5,7]-tetrazocine-6,13-dithione" in conformity with *Chemical Abstracts* usage.

[3] E. Sucharda and L. Klisiecki, *Roczniki Chem.*, 3, 251 (1923). *Chem. Abstr.*, 19, 72 (1925).

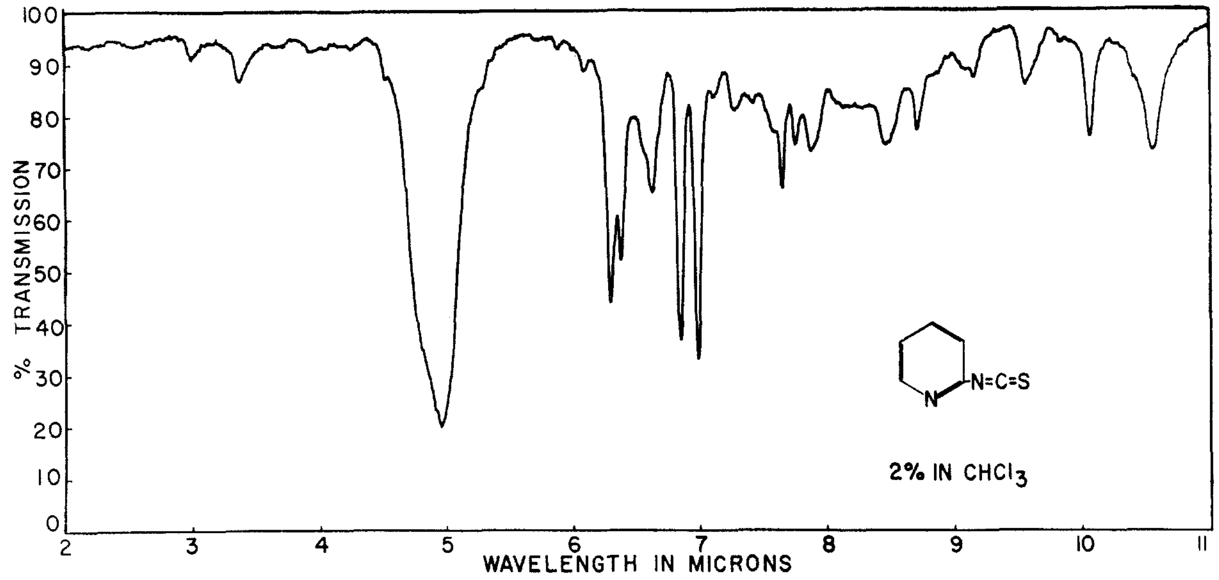

Fig. 2. Infrared spectrum of 2-pyridyl isothiocyanate

present in III, a derivative of hexamethylenetetramine.[4]

The infrared spectrum of the red solid is consistent with structure I. There is no absorption at 4.96μ (isothiocyanate); there is no typical pyridine ring absorption at 6.30 and 6.37μ (present in the monomer); and there is absorption at 6.07μ, a property shared with 1-methyl-2-pyridoneimine, IV.[5]

Because of the absence of model compounds containing the same chromophores, the ultraviolet spectrum of the dimer cannot be used with any confidence in the assignment of structure. However, IV absorbs at 350 mμ;[6] and extension of the chromophore by conjugation with a thiocarbonyl would be expected to have a bathochromic effect. This may account for the absorption above 400 mμ which gives the dimer its red color.

An alternative structure, V, analogous to the well-known aromatic isocyanate dimers,[7] was considered unlikely because it involved only the isothiocyanato group in its formation. Other isothiocyanate dimers have not been reported. The absence of pyridine ring absorption in the infrared spectrum of the dimer may also be evidence against V.

Dimers similar to I should be formed only by heterocyclic nitrogen compounds containing a 2-isothiocyanato group. A search for appropriate structures in the literature revealed mention of several polymeric 6-pyrimidinyl isothiocyanates which were not transformed to the monomer by distillation.[8] The synthesis and properties of similar compounds would be of interest.

## EXPERIMENTAL[9]

*2-Pyridyl isothiocyanate dimer* (I). The preparation was carried out according to Fairfull and Peak[1] except that the product was purified by dissolving it in a minimum amount of benzene at room temperature and precipitating with twice its volume of ligroin, m.p. 119–120°.

*Anal.* Calcd. for $(C_6H_4N_2S)_2$: C, 52.92; H, 2.96; N, 20.57; m.w. 272.36. Found: C, 53.1; H, 3.09; N, 20.41; m.w. 284 ± 15.

*Attempted isolation of 2-pyridyl isothiocyanate.* A chloroform solution containing 9.5 g. of the dimer was refluxed for 1 hr. and the solvent was then distilled. The residual red oil was distilled at reduced pressure. At the beginning of the distillation the red oil solidified, then melted when the temperature reached 110°, and distilled as a pale yellow liquid which turned red on cooling. Six grams of red oil was collected; b.p. 110–120° (10 mm.). After several minutes it began to crystallize and after standing overnight melted at 112–114°. The infrared spectrum was identical with the dimer.

*Effect of heat on the ultraviolet spectrum of* I. The spectrum of a freshly prepared solution of the dimer in chloroform was determined. The $\epsilon_{max}$ at 420 mμ, 335 mμ, and 290 mμ was 4350, 25,600, and 25,600 respectively. After the solution was refluxed for 15 min. the $\epsilon_{max}$ at 287 mμ was 30,000 and the two longer wave length maxima disappeared.

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(4) G. F. Wright, A. F. McKay, W. J. Chute, D. C. Downing, and G. S. Meyers, *Can. J. Res.*, **27**, 218 (1949).

(5) D. N. Shigarin, Ya. L. Danyushevskii, and Ya. L. Gol'dfarb, *Izvest. Akad. Nauk. S.S.S.R.*, *Otdel. Khim. Nauk.*, 120 (1956). *Chem. Abstr.*, **50**, 8329 (1956).

(6) L. C. Anderson and N. V. Seeger, *J. Am. Chem. Soc.*, **71**, 343 (1949).

(7) R. G. Arnold, J. A. Nelson, and J. J. Verbanc, *Chem. Rev.*, **57**, 54 (1957).

(8) T. B. Johnson and W. F. Storey, *Am. Chem. J.*, **40**, 131 (1908); Yuoh-Fong Chi and Chi Ming Ma, *J. Am. Chem. Soc.*, **55**, 4655 (1933).

(9) The melting points were determined on a calibrated Fisher-Johns block and the infrared spectra were determined on a Perkin-Elmer Model 21 equipped with sodium chloride optics; matched 0.1 mm. sodium chloride cells were used. The ultraviolet spectra were obtained on a Beckman DU quartz spectrophotometer. The elemental analyses and molecular weight determinations were performed by Mr. Gordon Ginther, Dr. Victor Ells, and associates of these laboratories and Schwarzkopf Analytical Laboratory, Woodside, New York.

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## An $O^{18}$ Tracer Study of the Acid-Catalyzed Formation of Enol Ethers

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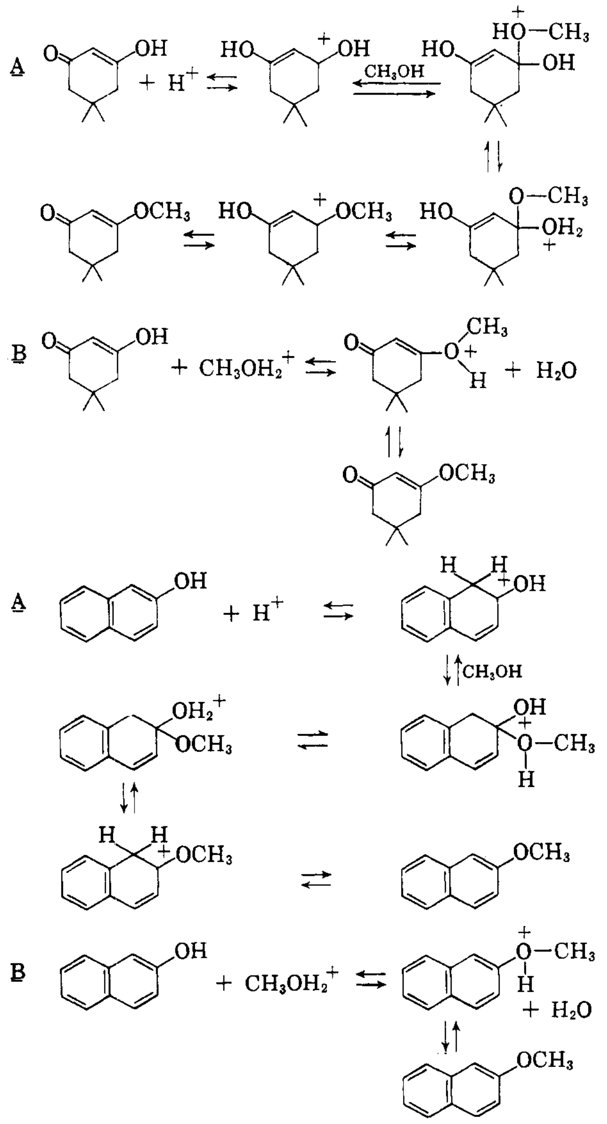
The conversion of enols, such as dimethyldihydroresorcinol,[1] and of some reactive phenols, such as β-naphthol[2] to the corresponding ethers may be effected by the acid-catalyzed reaction with the corresponding alcohol. In either case, there are two possible mechanisms:



The type A mechanism is, *a priori*, the more reasonable considering the facile formation of these ethers, and the small likelihood that the phenols are much more effective nucleophiles than is water. Further evidence for this mechanism may be found in the observation that resorcinol,[3] but not phenol, catechol, or hydroquinone, will form a monomethyl ether in this reaction, and that a dimethyl ether is not formed. Similarly, phloroglucinol reacts readily to form a dimethyl ether, but not a trimethyl ether.[4]

The two mechanisms are easily differentiated by using oxygen-18–labeled methanol, since mechanism A predicts incorporation of the label into the product ether, whereas mechanism B predicts that the ether will be devoid of isotope oxygen. The experiments were performed in the usual fashion and the results of the oxygen-18 analyses are given in Table I. It is readily apparent that nearly quantitative transfer of the label occurred, indicating the addition-elimination mechanism to be correct. The results also suggest that oxygen-18–labeling of these compounds should be easily effected by heating in acidified oxygen-18–enriched water, and that the ethers should be easily cleaved by acid-catalyzed hydrolysis.

TABLE I

Oxygen-18 Analytical Data

| Compound | % $O^{18}$ in $CO_2$ | % excess $O^{18}$ |
|---|---|---|
| Methanol | 0.742 | 1.08 |
| | 0.749 | 1.09 |
| 2-Methoxynaphthalene | 0.726 | 1.04 |
| | 0.726 | 1.04 |
| 5,5-Dimethyl-3-methoxy-cyclohexene-2-one | 0.448 | 0.972 |
| | 0.448 | 0.972 |

### EXPERIMENTAL

*Reaction of dimethyldihydrolrescrcinol.* To 5 g. (36 mmoles) of dimethyldihydroresorcinol was added 50 ml. of benzene, 3.0 ml. of methanol-$O^{18}$ (100% excess, containing 1.09 excess $O^{18}$), and 0.2 g. of *p*-toluenesulfonic acid. The solution was heated at reflux for 24 hr. in an apparatus in which the distilled solvent containing water was passed through potassium carbonate before being returned to the solution. Distillation gave 4.5 g. (81%) of the enol ether having b.p. 145–146° at 35 mm. Oxygen-18 analysis indicated the presence of 0.972 excess $O^{18}$.[5]

*Reaction of β-naphthol.* A solution of 1 g. of β-naphthol and 50 mg. of *p*-toluenesulfonic acid in 2.5 ml. of methanol was sealed in a tube and heated at 100° for 40 hr. The tube was opened and the contents were mixed with 10% potassium hydroxide solution and washed with same after filter-

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(1) D. Vorländer and M. Kohlmann, *Ann.*, **322**, 253 (1902).

(2) L. Gattermann, *Ann.*, **244**, 72 (1888)

(3) V. Merz, *J. prakt. Chem.*, **61**, 109 (1900).

(4) H. Weidel and J. Pollak, *Monatsh*, **21**, 22 (1900).

(5) Oxygen-18 analyses were performed by the method of W. E. Doering and E. Dorfman, *J. Am. Chem. Soc.*, **75**, 5595 (1953).