duced a CO_2 containing only 0.01 atom per cent. excess O^{18}.

These results indicate that the oxygen atoms of carboxylic acids can exchange with those of acetic anhydride. This exchange is presumably due to reactions analogous to those involved in the formation of mixed anhydrides from acetic anhydride and other carboxylic acids at room temperature and their disproportionation on distillation.[5] It also resembles that observed[6,7] between acetic anhydride-1-C^{14} and acetyl chloride.

Experimental

Exchange Reactions of Phenylalanine.—Forty mg. of L-phenylalanine containing 1.28 atom per cent. excess O^{18} was added to 4 ml. of acetic anhydride and 2 ml. of pyridine and the mixture refluxed. After 2 to 4 minutes the phenylalanine went into solution. The system was flushed with oxygen-free nitrogen. When evolved CO_2 was being collected for O^{18} analysis the gases leaving the reaction vessel were passed through a trap cooled by CO_2–acetone and then into a trap cooled by liquid nitrogen. The CO_2 condensed in the latter trap was transferred to the gas manifold of a mass spectrometer by warming the trap to −80°. No contaminating gases were observed in the mass spectrometer.

In test experiments it was found that CO_2 began to be evolved about 7 minutes after the mixture was brought to reflux and the decarboxylation was completed in 15 minutes. These experiments show that the reaction is quantitative; from 98 to 101% of the theoretical was found for evolved CO_2.

When the phenylalanine was refluxed with acetic anhydride for 1 hour before addition of pyridine the amino acid went into solution but no CO_2 was formed until the pyridine was added.

Thirty mg. of the phenylalanine was added to 5 g. of benzoic anhydride and 2 ml. pyridine. The mixture was heated to reflux and the evolved CO_2 collected and analyzed as above. It contained 0.12 atom per cent. excess O^{18}.

Preparation of Benzoic Acid-O^{18}.—Ten cc. of benzotrichloride and 20 cc. of O^{18} labeled water were refluxed for 48 hours. The contents of the flask was chilled, normal water added, the benzoic acid filtered off and washed with cold water. The wet crystalline mass was dissolved with the aid of a minimum of 1 *N* NaOH and precipitated by acidification. The benzoic acid was promptly filtered off and washed with cold water. It was dried *in vacuo;* yield 5.0 g.; m.p. 121.6–122°. The silver salt was prepared, dried *in vacuo* and thermally decarboxylated in an evacuated Y tube (see Fig. 2 of ref. 8). The O^{18} concentration was 0.64 atom per cent. excess.

Exchange of Benzoic Acid-O^{18}.—Two hundred and fifty mg. of the benzoic acid-O^{18} and 20 ml. of acetic anhydride were refluxed for 1 hour. The acetic anhydride was removed by vacuum distillation, the residue dissolved in 1 *N* NaOH and 30 minutes later the benzoic acid precipitated by addition of nitric acid. The benzoic acid was immediately removed by filtration, washed with cold water and dried *in vacuo;* yield 85 mg. Forty-five mg. of this benzoic acid was neutralized and dissolved with 1 *N* NaOH. $AgNO_3$ was added and the precipitated silver benzoate filtered, washed and dried *in vacuo* at 90°. The silver salt was thermally decarboxylated in an evacuated Y tube. It contained 0.01 atom per cent. excess O^{18}.

Repetition of the above experiment with the addition of 1 ml. of acetic acid to the acetic anhydride gave a benzoic acid containing 0.00 atom per cent. excess O^{18}.

When benzoic acid-O^{18} was dissolved in acetic anhydride and kept at room temperature for 90 minutes the O^{18} concentration in the benzoic acid was reduced to 0.52 atom per cent. excess. In this experiment the isolation was so conducted that all operations took place at room temperature or lower.

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The Reaction of Raney Nickel with Organoselenium Compounds

BY GEORGE E. WISEMAN AND EDWIN S. GOULD

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As part of our work in determining the orientation of substitution reactions of dibenzoselenophene, we have tested the applicability of a reaction analogous to the Mozingo desulfurization reaction.[1] Mozingo used Raney nickel to remove sulfur from organosulfur compounds with a variety of sulfur-containing functional groups. Our modification of the desulfurization reaction applies to the removal of selenium from at least one member of each of the following classes of compounds: diarylselenides, arylheterocyclic selenides, diaryldiselenides, diarylselenium dichlorides, diarylselenones, arylselenocyanates and arylseleninic acids. The yields are generally fair except in cases where separations of the products are difficult. The weight of Raney nickel used was approximately 20 times the weight of sample. The usual desulfurization solvent, dilute ethanol, gave low yields. However, a mixture of alcohol and benzene greatly improved the process. Consequently, all other experiments were carried out in 10–20% by volume solution of ethanol in benzene. It is conceivable that better yields would result from variations of refluxing time, weight of nickel used, and solvent composition; but extended search for optimum conditions in this reaction was not carried out.

The compounds undergoing deselenization are listed in Table I. Most of our substances were chosen to yield biphenyl in view of the ease of iso-

TABLE I

COMPOUNDS UNDERGOING DESELENIZATION

Compounds deselenized	Reflux time, hr.	Product	Yield, %
Dibenzoselenophene[2]	2.5	Diphenyl	87
p,p'-Diethoxydiphenylselenium	5	Phenetole	79
Di-(*o*-biphenylyl) diselenide	3	Diphenyl	76
p,p'-Diethoxydiphenylselenium dichloride	4	Phenetole	43
2-Selenocyanobiphenyl	7	Diphenyl	84
Dibenzoselenophene oxide[2]	5	Diphenyl	72
Dibenzoselenophene dichloride	5	Diphenyl	72
p-Selenocyanoaniline	5.5	Aniline	79
o-Biphenylylseleninic acid[3]	5.5	Diphenyl	62
p,p'-Dimethoxydiphenylselenone	5.5	Anisole	25
p-Selenocyano-N,N-dimethylaniline	4.5	Dimethylaniline (as picrate)	14
Diphenyl diselenide	4	Benzene	0[a]
Dibenzothiophene	3	Diphenyl	66[a,4,5]

[a] Solvent was ethanol.

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lating this compound, and because future experiments with substituted dibenzoselenophenes are expected to yield substituted biphenyls.

Experimental

Raney Nickel.—The Raney nickel was prepared according to the directions of Pavlic and Adkins.[6]

Deselenization.—A typical experiment follows: In a 3-necked r.b. flask equipped with a mechanical stirrer and reflux condenser, was placed 100 ml. of benzene, 20 ml. of ethanol, 35 g. of Raney nickel and 1.5 g. of dibenzoselenophene oxide. Refluxed in oil-bath for 5 hr. The unreacted solid was filtered and washed with 40 ml. of benzene (nickel burst into flames on drying). Combined solvents were washed twice with 30 ml. of concentrated H_2SO_4 and twice with water. Benzene was removed, and residue recrystallized from ethanol–water; yield 0.67 g. of biphenyl (72%), m.p. 67–68°. One further recrystallization brought m.p. to 71° (reported 70°[7]); no depression on admixture with authentic sample.

Acknowledgment.—It is a pleasure to acknowledge the assistance of Dr. J. R. McCormick who suggested the method some years ago.

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The Isolation of Bufotenine from *Piptadenia peregrina*

BY VERNER L. STROMBERG

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The inhalation of a narcotic snuff by the natives of Haiti was a common practice at the time of the discovery of the West Indies. This snuff, called cohoba, was used by the necromancers or priests in their ceremonies and was supposed to enable them to communicate with unseen powers.

The ceremonial use of cohoba was described as early as 1496 by Ramon Pane who was with Columbus on his second voyage, but in later years cohoba was confused with tobacco.

The chemistry of this snuff has never been studied although the leguminous shrub *Piptadenia peregrina* is now known to be its source.[1]

In the present work there was isolated from the seeds of this plant a crystalline organic base, m.p. 146–147°, with empirical formula $C_{12}H_{16}N_2O$ in 0.94% yield.

The ultraviolet absorption spectrum in 0.1 *N* hydrochloric acid showed a maximum at 277 mμ, a shoulder with a second maximum at 295 mμ and a minimum at 247 mμ. In 0.1 *N* sodium hydroxide the absorption spectrum shows a shift of the second maximum to 322 mμ. This shift is similar to that observed for the vasoconstrictor 5-hydroxytryptamine (serotonin).[2]

A methiodide, picrate, oxalate and *m*-nitrobenzoate were prepared. The melting points were in good agreement with the literature values for bufotenine

	Bufotenine m.p., °C.	Piptadenia alkaloid m.p., °C.
Base	147[3]	146–147
Red picrate	178[3]	176–177
Methiodide	210[3]	213–214
Oxalate	84–88[4]	82–84
m-Nitrobenzoate	258[3]	255–257

The infrared absorption spectrum of the picrate was identical with that of a picrate of a synthetic sample kindly supplied by Dr. M. E. Speeter of the Upjohn Company.

The seeds of *Piptadenia peregrina* evidently constitute an excellent source of bufotenine. The leaves and branches do not give an alkaloid test with Meyer's or silicotungstic acid reagents. The seed pods give only a slight positive test.

Experimental

Isolation of Bufotenine.—*Piptadenia peregrina* seeds, 891 g., secured from Las Mesas, Puerto Rico,[5] were ground in a Waring blendor and extracted twice with 4 l. of 1% ethanolic tartaric acid solution for 2 hours at 55°. The resulting 8 l. of solution was filtered, concentrated to a volume of 1 l. and diluted with 2.5 l. of water. It was acidified with 200 ml. of 2 *N* hydrochloric acid. The solution was filtered and extracted six times with 200-ml. portions of chloroform. The chloroform solution was discarded. The acid solution was neutralized with solid sodium carbonate. This was divided into two parts and each part was extracted seven times with 200-ml. portions of chloroform. The combined chloroform solutions were extracted with 2 *N* hydrochloric acid. This acid solution was made basic with solid sodium carbonate and the base was re-extracted with chloroform. After drying, the solvent was removed to provide 20.95 g. (2.45%) of mixed organic bases.

A crude alkaloid fraction, 10.11 g., was subjected to chromatographic separation on alumina (Merck Reagent). An ethyl acetate fraction contained 0.12 g. of a brown oil. The bufotenine fraction was eluted with 3:1 ethyl acetate–ethanol to give 7.66 g. of material. Several recrystallizations from ethyl acetate gave 4.09 g. (40% of the alkaloid fraction), m.p. 146–147°. Bufotenine represents 0.94% of the Piptadenia seed. The material remaining on the column was eluted with ethanol to give 2.31 g. of residue.

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(3) H. Wieland, W. Kanz and H. Mittasch, *Ann.*, **513**, 1 (1934).

(4) T. Wieland and W. Motzel, *ibid.*, **581**, 10 (1953). The oxalate as originally prepared by H. Wieland had a melting point of 96.5° and was a monohydrate. The oxalate prepared here is a half-hydrate (*Anal.* Calcd. for $2C_{12}H_{16}N_2O \cdot 2C_2H_2O_4 \cdot H_2O$: C, 55.44; H, 6.31; N, 9.24. Found: C, 55.58; H, 6.41; N, 9.05) and is apparently the same as the material reported by T. Wieland without analytical data.

(5) Through the Agricultural Research Service, Plant Exploration and Introduction, United States Department of Agriculture

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The Specific Rotation of Isocolchicine[1]

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During the course of our work on the chemistry of colchicine derivatives we observed that the specific rotation of solutions of isocolchicine changed with time. To our knowledge, this is the first recorded instance of this phenomenon in the col-

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