N-Ethyltrifluoroacetanilide.—Trifluoroacetyl chloride[3] was prepared; however, it was not collected but run directly into a pyridine solution of ethylaniline. The amine mixture was cooled in an ice-bath and stirred constantly. When the acyl chloride addition was complete, the reaction mixture was put on a steam-bath for one-half hour, cooled and poured into water. On acidification to litmus, an oily layer developed on the bottom of the container. An ether extract was washed three times with water, once with an aqueous sodium bicarbonate solution, and three times with water. The extract was dried over anhydrous sodium sulfate. On distillation a 48.8% yield of product was collected distilling at 80–82° (3 mm.); $n^{20}D$ 1.4680; d^{20}_{20} 1.2227; MR calcd., 48.29; found, 49.14. The liquid was redistilled and a colorless middle fraction taken for the infrared spectrogram. Nitrogen analyses were checked by Miss Zerwo of the University of Colorado.

Anal. Calcd. for $C_{10}H_{10}F_3NO$: N, 6.45. Found: N, 6.17, 6.22. Found: N, 6.47.

Ethyl N-Isoamyl-N-phenylcarbamate.—This compound was prepared by the method of Hartman and Brethen[4] for ethyl N-methylcarbamate. On distillation a 65.2% yield of a liquid was collected distilling at 130–134° (1.5 mm.); $n^{20}D$ 1.4971; d^{20}_{20} 0.9898; MR calcd., 69.28; found, 69.49. The liquid was redistilled and a yellow-colored middle fraction taken for the infrared spectrogram.

Anal. Calcd. for $C_{14}H_{21}NO_2$: N, 5.96. Found: N, 6.05, 5.96.

Infrared Absorption Spectra.—To resolve all the peaks of complete absorption cell thicknesses of 0.10 and 0.025 mm. were used as well as a 10% concentration of the compounds in *n*-heptane in the 0.025-mm. cell.

Insecticide Investigation.—The candidate insecticides dissolved in deobase (5% w./v.) were aspirated into a Lucite chamber which enclosed the roaches. After a 15-minute contact period, the roaches were removed to clean petri dishes and observed. The results are summarized in Table I.

TABLE I

SUMMARY OF INSECTICIDE TESTING

Compound	Knock-down in 15 min., %	Kill in 24 hr., %	Comment
N-Ethyl-*p*-ethoxyacetanilide	0	0	
N-Ethyl-*o*-ethoxyacetanilide	40	100	Warm day
	0	0	Cool day
N-Ethylphenoxyacetanilide			Insoluble in deobase
N-Isoamylphenoxyacetanilide	0	60	
N-Ethyltrifluoroacetanilide	0	0	
Ethyl N,N-isoamyl phenylcarbamate	0	60	

(3) Henne, Alm and Smook, THIS JOURNAL, **70**, 1968 (1948).

(4) Hartman and Brethen, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 278.

CHEMICAL FOUNDATION LABORATORY AND
CHEMISTRY DEPARTMENT OF THE
UNIVERSITY OF COLORADO
BOULDER, COLORADO

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Ion-Exchange Separation of Hafnium and Zirconium

BY I. E. NEWNHAM

In the course of an investigation on the properties of the cation exchange resin "Dowex 50" Street and Seaborg[1] separated 10 mg. of hafnium oxide from a mixture containing 35 mg. of ZrO_2 and 15 mg. of HfO_2. In the light of their suggestion that gram samples could probably be handled effectively their method was applied to a 2-g. oxide mixture containing 20% HfO_2. This mixture had been prepared from a 30-g. sample of Australian zircon in the course of an investigation on suitable methods for concentration of the low hafnium content of this material.

(1) K. Street and G. T. Seaborg, THIS JOURNAL, **70**, 4268 (1948).

"Dowex 50" of 100–200 mesh, kindly supplied by the Dow Chemical Company, was packed in a column 150 cm. high × 3.5 cm. diameter. In accordance with the technique suggested by Street and Seaborg the oxide mixture was converted to oxychloride crystals (2.8 g.) which were slowly added to 1200 cc. of 2 *M* perchloric acid containing 40 cc. of "Dowex 50." After 30 minutes the supernatant liquid was siphoned off and the resin slurry was added to the top of the exchange column. Elution with 6 *M* hydrochloric acid at the rate of 0.5 cc./min. followed. The hafnium content of successive fractions listed below in their order of collection indicates the possibilities of this separation method.

Fraction no.	Total HfO_2, recovered, %	HfO_2 content of fraction, %
1	42	99.9
2	18	90
3	10	75
4	10	52
5	10	34

DIVISION OF INDUSTRIAL CHEMISTRY
COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION
MELBOURNE, AUSTRALIA

RECEIVED MAY 7, 1951

Quinoxaline Studies. III. The Preparation and Physical Properties of Some 2,3-Dialkoxyquinoxalines

BY ROBERT PATTON[1] AND HARRY P. SCHULTZ

A series of 2,3-dialkoxyquinoxalines have been prepared and their physical properties have been determined. Only two 2,3-dialkoxyquinolines have previously been reported.[2]

The 2,3-dialkoxyquinoxalines were prepared by the reaction of 2,3-dichloroquinoxaline with sodium, or preferably potassium, alkoxides.

Table I lists the physical properties of the compounds. As is also shown in Table I, all compounds of this series show similar ultraviolet absorption characteristics: a maximum absorption at 241 and 312 millimicrons, a small plateau between 300–302 mμ.

Experimental Procedures

2,3-Dichloroquinoxaline.—This material was prepared from 2,3-dihydroxyquinoxaline[3] according to the procedure of Hinsberg and Pollak.[4]

2,3-Dialkoxyquinoxalines, General Procedure.—Two grams (0.01 mole) of 2,3-dichloroquinoxaline was added to a solution of 0.78 g. (0.02 mole) of potassium dissolved in 10 ml. of the requisite dry alcohol. The solution was stirred and heated on a steam-bath until neutral to moist *p*H paper.

(1) Abstracted from a thesis by Robert Patton, presented to the Graduate Faculty of the University of Miami, in partial fulfillment of the requirements for the degree of Master of Science in chemistry, June, 1951.

(2) (a) J. Stevens, K. Pfister, III, and F. Wolf, THIS JOURNAL, **68**, 1035 (1946); (b) A. Gowenlock, G. Newbold and F. Spring, *J. Chem. Soc.*, 622 (1945).

(3) R. Meyer and A. Seelinger, *Ber.*, **29**, 2641 (1896).

(4) O. Hinsberg and J. Pollak, *ibid.*, **29**, 784 (1896).

TABLE I

2,3-DIALKOXYQUINOXALINES

2,3-Disubstituents	M.p., °C., uncor.	Yield, %	Nitrogen, % Calcd.	Nitrogen, % Found	Density d^{25}_4	Refractive index $n^{25}D$	Absorption maxima and molecular extinction coefficients[c] $\epsilon \times 10^{-3}$ (λ, 246 mμ)	$\epsilon \times 10^{-3}$ (λ, 300–302 mμ)	$\epsilon \times 10^{-3}$ (λ, 312 mμ)
OCH_3	92–93[a]	82	14.7	14.6	...	....	13.6	4.9	9.8
OCH_2CH_3	77–78[b]	70	12.8	12.9	...	....	14.5	5.3	9.7
$OCH_2CH_2CH_3$	53–54	71	11.4	11.1	...	....	14.7	5.9	10.1
$OCH(CH_3)_2$	93–94	55	11.4	11.1	...	....	14.7	6.5	12.4
$OCH_2CH_2CH_2CH_3$	50–51	45	10.2	10.2	...	....	15.8	6.5	10.2
$OCH_2CH(CH_3)_2$	liq.	76	10.2	10.4	1.040	1.5370	15.6	6.5	9.9
$OCH_2CH_2CH_2CH_2CH_3$	liq.	68	9.3	9.4	1.022	1.5304	15.8	6.5	10.1
$OCH_2CH_2CH(CH_3)_2$	liq.	79	9.3	9.6	1.014	1.5290	15.7	6.6	10.1
$OCH_2CH_2CH_2CH_2CH_2CH_3$	60–65	60	8.5	8.5	...	....	14.7	7.5	10.8

[a] Stevens, Pfister and Wolf[2a] reported a melting point of 92–93°. [b] Gowenlock, Newbold and Spring[2b] reported a melting point of 78°. [c] Solvent, 95% ethanol.

The time of heating varied from 1 hour for the dimethoxy derivative to 11 hours for the di-*n*-hexoxy derivative of quinoxaline. The yield was then worked up by two different procedures.

If the alkoxy group contained less than four carbon atoms, 20 ml. of water was added to the reaction mixture, and the precipitated 2,3-dialkoxyquinoxaline was filtered off and washed several times with water. One recrystallization from ethanol–water gave pure material.

If the alkoxy group had four or more carbon atoms, the reaction mixture was steam distilled to remove excess alcohol. The residue was then extracted with ethyl ether, treated with decolorizing charcoal, and the ether evaporated. The colorless oils were purified by distillation at 1 mm. from a Hickman vacuum still.[5]

Following this treatment, 2,3-di-*n*-butoxyquinoxaline was recrystallized from ethanol–water; 2,3-diisobutoxy-, 2,3-di-*n*-amoxy- and 2,3-diisoamoxyquinoxaline remained in a liquid state as colorless, very viscous oils that could not be distilled through a conventional distillation apparatus. 2,3-Di-*n*-hexoxyquinoxaline slowly solidified in about 10 days to a wax-like solid that could not be recrystallized from any solvent.

Absorption Spectra.—The ultraviolet absorption spectra, condensed in Table I, were obtained on a Beckman model DU quartz spectrophotometer.

(5) K. Hickman and C. Sanford, *J. Phys. Chem.*, **34**, 637 (1930).

DEPARTMENT OF CHEMISTRY
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RECEIVED JULY 25, 1951

The Preparation of Morphine-N-methyl-C^{14}

BY HENRY RAPOPORT, CALVIN H. LOVELL AND BERT M. TOLBERT

In order to study the metabolic fate and mode of action of morphine and codeine in both the addict and non-addict, a program was initiated for the preparation of these alkaloids labeled at various parts of the molecule with radioactive carbon. The preparation[1] of codeine-3-methoxy-C^{14} and some results on its metabolism[2] in the rat have been reported. The present report is concerned with the preparation of morphine-N-methyl-C^{14}.

Since codeine-N-methyl-C^{14} can be readily prepared in the manner described by von Braun[3] the most attractive path to the corresponding morphine compound would be through cleavage of the 3-methoxyl group. Although this cleavage reaction has been used to convert some codeine derivatives to their morphine analogs, no successful application of this reaction to codeine itself has been reported. The usual ether-cleaving reagents (concentrated hydrogen iodide and hydrogen bromide, in aqueous solution or in glacial acetic acid) appear to be too drastic. However, pyridine hydrochloride, which has been used recently to prepare desoxymorphines from desoxycodeines,[4] under carefully controlled conditions effected the cleavage of codeine to morphine in a reasonable yield (22%), and hence was applied to the preparation of morphine-N-methyl-C^{14} from codeine-N-methyl-C^{14}.

Experimental[5]

Morphine-N-methyl-C^{14}.—Cleavage of 1.00 g. of codeine-N-methyl-C^{14} (specific activity 3.56 μc./mg.) was effected by heating with pyridine hydrochloride in the manner previously described for Δ^7-desoxycodeine.[4b] The reaction mixture was dissolved in 20 ml. of water, basified with 10 ml. of 4 *N* sodium hydroxide, and the non-phenolic material was removed by extraction with four 15-ml. portions of chloroform. The combined chloroform extracts were washed with 10 ml. of 0.5 *N* sodium hydroxide and 10 ml. of water, and the aqueous phase, after adding the washings, was adjusted to *p*H 9 and cooled thoroughly to precipitate phenolic material. After filtering and drying, this phenolic material was digested with 75 ml. of methanol, the mixture was filtered hot, and the filtrate was chromatographed on an alumina (Merck and Co., Inc.) column (120 × 11 mm.) using 700 ml. of methanol as eluent. The residue after evaporation of the methanol was dissolved in 10 ml. of 0.2 *N* sodium hydroxide, filtered, and the filtrate was adjusted to *p*H 9, precipitating the crude morphine. After drying, this crude morphine was sublimed (180–190° (0.1 mm.)), and the sublimate was crystallized from absolute ethanol. There was thus obtained a total of 210 mg. (22%) of morphine-N-methyl-C^{14}, m.p. 254–255°, specific activity, 3.75 μc./mg.

(1) F. N. Chang, J. F. Oneto, P. T. Sah, B. M. Tolbert and H. Rapoport, *J. Org. Chem.*, **15**, 634 (1950).

(2) T. K. Adler and M. E. Latham, *Proc. Soc. Expti. Biol. Med.*, **73**, 401 (1950); M. E. Latham and H. W. Elliott, *J. Pharmacol. Expti. Therap.*, **101**, 259 (1951).

(3) J. von Braun, *Ber.*, **47**, 2312 (1914).

(4) (a) H. Rapoport and R. M. Bonner, THIS JOURNAL, **73**, 2872 (1951); (b) H. Rapoport and R. M. Bonner, *ibid.*, **73**, 5485 (1951).

(5) All melting points are corrected.

DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY
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Preparation of 1,4-Dihydroxy-2-naphthyl Hydroxymethyl Ketone

BY DEAN R. REXFORD

Previous to the appearance of Spruit's excellent work in the preparation of a series of substituted