Some New Substituted Amides

By Joseph D. Park, Robert D. Englert[1] and John S. Meek

The six compounds reported here were prepared and screened in this Laboratory for their insecticidal value against the roach, *Periplaneta americana*. Five of these possessed no high degree of insecticidal activity, and N-ethylphenoxyacetanilide was too insoluble in the vehicle used to be tested. Melting points were taken on a Fisher–Johns melting point block, and the nitrogen analyses were done by a modification of a semi-micro borate method of Cole and Parks.[2] The infrared absorption spectra of the liquid compounds were obtained by using a Perkin–Elmer Infrared Spectrometer, model 12-B.

N-Ethyl-*p*-ethoxyacetanilide.—*p*-Phenetidine (274 g.), ethyl bromide (109 g.) and benzene (approximately 400 ml.) were refluxed overnight. The mass was cooled and filtered, and the residue washed with several portions of benzene. The filtrate and washings were combined, and the benzene removed. A slight excess of acetic anhydride was used to acetylate the amine. On distillation, 127 g. (61.4%) of a light yellow liquid was collected at 137–149° (1 mm.); $n^{20}\text{D}$ 1.5231; $d^{20}{}_{20}$ 1.0531; *MR* calcd., 60.05; found, 60.03. The compound was redistilled and a middle fraction taken for the infrared spectrogram. The liquid was light yellow with a light green fluorescence.

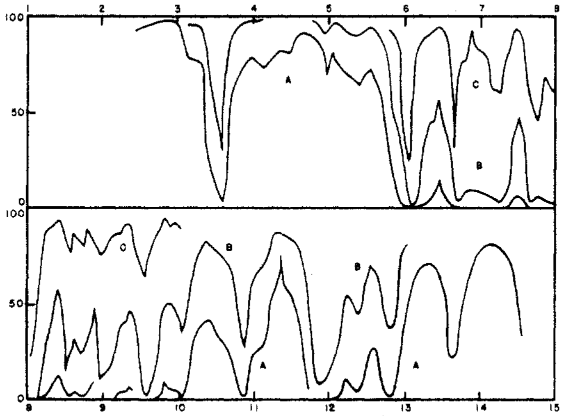

Fig. 1.—Infrared spectrogram of N-ethyl-*p*-ethoxyacetanilide: (A) 0.100-mm. cell thickness, pure liquid; (B) 0.025-mm. cell, pure liquid; (C) 0.025-mm. cell, 10% concentration in *n*-heptane.

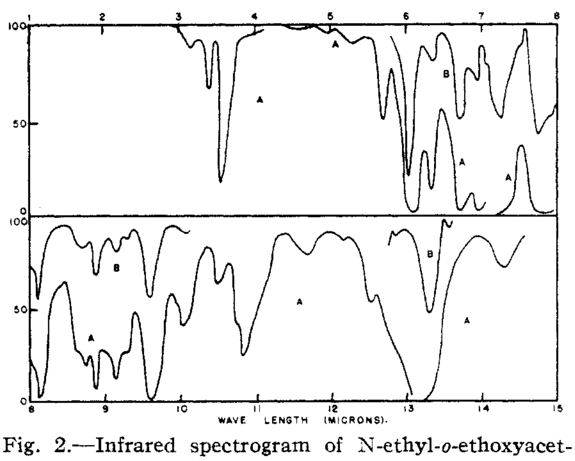

Fig. 2.—Infrared spectrogram of N-ethyl-*o*-ethoxyacetanilide using 0.025-mm. cell: (A) pure liquid and (B) 10% concentration in *n*-heptane.

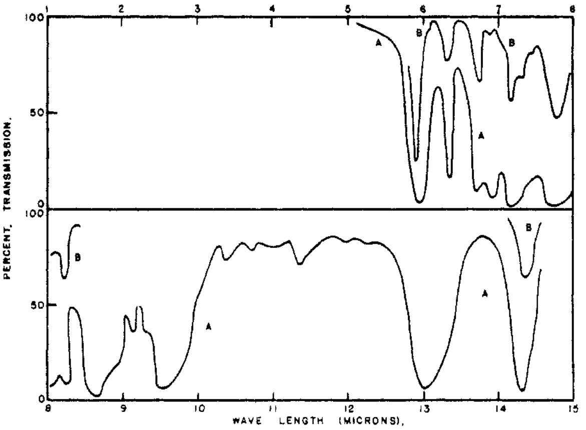

Fig. 3.—Infrared spectrogram of ethyl N,N-isoamyl phenylcarbamate using 0.025-mm. cell: (A) pure liquid and (B) 10% concentration in *n*-heptane.

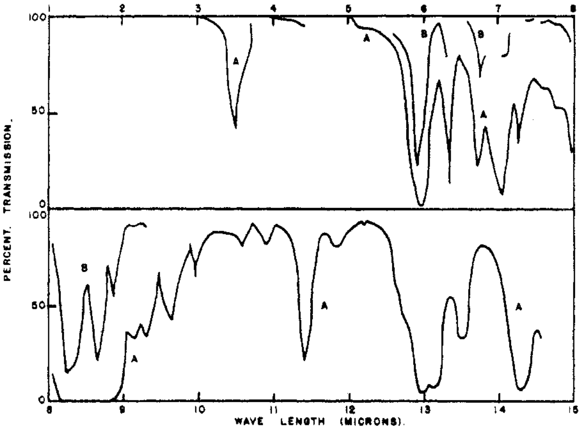

Fig. 4.—Infrared spectrogram of N-ethyl trifluoroacetanilide using 0.025-mm. cell: (A) pure liquid and (B) 10% concentration in *n*-heptane.

Anal. Calcd. for $C_{12}H_{17}NO_2$: N, 6.76. Found: N, 6.61, 6.55.

N-Ethyl-*o*-ethoxyacetanilide.—This compound was prepared in a similar manner and on distillation a 52.5% yield of a light yellow liquid distilling at 134–139° (1 mm.) was obtained; $n^{20}\text{D}$ 1.5193; $d^{20}{}_{20}$ 1.0435; *MR* calcd., 60.05; found, 60.24. The compound was redistilled and a colorless middle fraction taken for the infrared spectrogram.

Anal. Calcd. for $C_{12}H_{17}NO_2$: N, 6.76. Found: N, 6.55, 6.58.

N-Ethylphenoxyacetanilide.—The compound was prepared from N-ethylaniline and phenoxyacetyl chloride in pyridine. A fraction (54.9%) distilling at 180–182° (3 mm.) ($n^{20}\text{D}$ 1.5723) was collected, which solidified on standing in the ice-box. The product was decolorized with charcoal and was recrystallized from an ether–petroleum ether mixture. A white solid was obtained which melted at 58.5°.

Anal. Calcd. for $C_{16}H_{17}NO_2$: N, 5.49. Found: N, 5.62, 5.33.

N-Isoamylphenoxyacetanilide.—This was prepared from the acyl chloride and the secondary amine, and a fraction (52.2%) distilling at 192–194° (1 mm.) ($n^{20}\text{D}$ 1.5519) was collected. This liquid crystallized on standing in the ice-box and was taken up in an ether–petroleum ether solution, decolorized with charcoal, filtered, and crystallized. A white solid was obtained, melting at 66–67°. After further purification the compound melted at 66.5–67.5°.

Anal. Calcd. for $C_{19}H_{23}NO_2$: N, 4.71. Found: N, 4.63, 4.68.

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(1) Chemical Foundation Fellow in Chemistry. Presently at the Stanford Research Institute.

(2) Cole and Parks, *Ind. Eng. Chem., Anal. Ed.*, **18**, 61 (1946).

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.); $n^{20}\text{D}$ 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.); $n^{20}\text{D}$ 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	

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(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.

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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.

"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

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

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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.

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(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).