[Contribution from the Department of Chemistry, Industrial Science Division, West Virginia University]

Some β-Alkoxyethyl Esters of *p*-Aminobenzoic Acid

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In view of the fact that an ether linkage usually increases the solubility of organic substances in lipoids, it was thought worth while to prepare and study the physiological properties of a series of compounds of the anesthesine type but containing an ether linkage in the alcohol portion of the molecule.

The starting materials for this work were the mono-ethers of glycol. The methyl, ethyl and butyl ethers were obtained from the Carbide and Carbon Chemicals Corporation. The propyl, isopropyl, isobutyl and secondary butyl ethers were prepared by heating the corresponding alcohols with ethylene oxide in the presence of a small amount of sulfuric acid as a catalyst.[1] The tertiary butyl ether was prepared in the same manner except that acid aluminum fluosilicate was used as the catalyst.[2]

The ethers were purified by fractional distillation, using a distillation column packed with jack chain. Only samples having a boiling range of 0.5° or less were used.

p-Nitrobenzoates

The *p*-nitrobenzoates of these monoglycol ethers were prepared according to the method of Conn, Collett and Lazzell.[3] These esters are viscous, practically odorless liquids having a pale yellow color. They are insoluble in water but soluble in all the common organic solvents.

Table I

p-Nitrobenzoates

R in β-R-ethyl	Yield, %	B. p., °C.	$d^{25}_{\text{abs.}}$	n^{25}_D	γ^{25}	Formula	Nitrogen analyses, % Calcd.	Found	
Propoxy	84	181.6–182.6	1.1763	1.5165	37.8	$C_{12}H_{15}O_5N$	5.53	5.70	5.67
Isopropoxy	86	172.0–172.8	1.1741	1.5148	36.5	$C_{12}H_{15}O_5N$	5.53	5.50	5.55
Isobutoxy	83	184.8–185.6	1.1532	1.5118	35.4	$C_{13}H_{17}O_5N$	5.24	5.28	5.19
s-Butoxy	80	183.5–184.5	1.1560	1.5124	36.1	$C_{13}H_{17}O_5N$	5.24	5.18	5.31
t-Butoxy	97	174.8–175.8	1.1579	1.5123	35.1	$C_{13}H_{17}O_5N$	5.24	5.29	5.30

Table I lists the analyses, physical constants and yields of all the new *p*-nitrobenzoates prepared. The analyses were made by titration with titanous chloride solution. All boiling points were taken under a pressure of 4.0 mm. with a thermometer completely immersed in the vapor. Refractive indices were determined by means of an Abbé refractometer at 25°. Surface tensions were obtained by means of a Du Noüy tensiometer at 25° and Harkins' correction for the ring method was applied. The yields are based upon the amount of glycol ether used.

p-Aminobenzoates

The *p*-aminobenzoates were obtained from the nitro compounds by reduction with hydrogen using Adams platinum–platinum oxide catalyst.[4]

One-tenth mole of the nitro compound was dissolved in 150 cc. of alcohol, 0.2 g. of Adams platinum–platinum oxide catalyst added and the solution shaken with hydrogen under an initial pressure of 45 lb./sq. in. until the theoretical amount of hydrogen was absorbed. The shaking with hydrogen was allowed to continue for an additional half-hour to ensure complete reduction. The catalyst was then filtered off and the alcohol removed by evaporation on the steam-bath. The red colored viscous oil remaining was dissolved in ether. The solution was then dried over anhydrous sodium sulfate, filtered, and dry hydrogen chloride passed in with cooling until precipitation was complete. The hydrochloride was filtered off, washed with dry ether until perfectly white and finally dried. To obtain the free base, the hydrochloride was dissolved in water, the solution cooled to 0–10° and dilute sodium carbonate solution added until the solution was alkaline. The free base was then filtered off and washed with cold water. The isobutyl, secondary butyl and tertiary butyl compounds were distilled under reduced pressure immediately after removing the alcohol.

Table II lists the analyses, physical constants and yields of these compounds. The analyses for nitrogen were made by the Kjeldahl method.

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(1) German Patent 580,075, July 5, 1933; *C. A.*, **27**, 4814 (1933).

(2) French Patent 39,773, Feb. 17, 1931; *C. A.*, **26**, 4826 (1932).

(3) Conn, Collett and Lazzell, This Journal, **54**, 4370 (1932).

(4) Adams, "Organic Syntheses," John Wiley & Sons, Inc., 440 Fourth Ave., New York City, 1928, Vol. VIII, pp. 10–16, 92–99.

TABLE II

p-AMINOBENZOATES

R in β-R-ethyl	Yield, %	M. p., °C. base	M. p., °C. picramide	Formula	Nitrogen analyses, % Calcd.	Found	
Methoxy	94	75.9	132.0	$C_{10}H_{13}O_3N$	7.18	7.15	7.24
Ethoxy	93	79.2	136.7	$C_{11}H_{15}O_3N$	6.69	6.40	6.56
Propoxy	87	44.5	138.4	$C_{12}H_{17}O_3N$	6.27	6.20	6.18
Isopropoxy	86	95.4	156.0	$C_{12}H_{17}O_3N$	6.27	6.23	6.30
Butoxy	79	34.0	123.1	$C_{13}H_{19}O_3N$	5.90	6.07	5.71
Isobutoxy	77	..	150.3	$C_{13}H_{19}O_3N$[a]	5.90	5.88	5.86
s-Butoxy	84	..	132.5	$C_{13}H_{19}O_3N$[b]	5.90	5.87	5.89
t-Butoxy	84	77.4	140.0	$C_{13}H_{19}O_3N$[c]	5.90	5.94	5.88

[a] B. p. 176.5–177.5° at 0.7 mm. [b] B. p. 177.0–178.0° at 0.7 mm. [c] B. p. 173.5–174.5° at 0.3 mm.

The picramides were prepared by the method given by Mulliken.[5]

The melting points of the hydrochlorides are not given since they apparently decompose before melting. The bases were all crystallized from ligroin with the exception of the tertiary butoxy compound which was crystallized from a water–alcohol mixture and the isobutoxy and secondary butoxy compounds which solidified after distillation when placed in a cool place for a few days, but these did not give definite melting points and could not be recrystallized. They apparently melt near room temperature. The yields are based upon the amount of glycol ether used.

Physiological data on these compounds will be reported in a later paper.

Summary

Five new β-alkoxy ethyl *p*-nitrobenzoates and a series of eight *p*-aminobenzoates have been prepared and some of their physical constants determined.

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[5] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., 440 Fourth Ave., New York City (1916), Vol. II, p. 32.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

A Gaseous Discharge Tube Especially Designed as an Intense Source of Continuous Ultraviolet Radiation

BY R. H. MUNCH

In the study of certain gaseous absorption lines, during the course of some research work under the direction of Dr. F. T. Gucker, Jr., the author required an intense source of continuous ultraviolet radiation which was simpler and more efficient than any that could be found described in the literature. This article deals with the development of such a source. Beyond about 3500 Å. there are only three sources of continuous radiation: the so-called Lyman continuum[1] (to 300 Å.), the hydrogen continuum[2] (3657–1216 Å.) and the helium continuum[3] (1125–500 Å.). The hydrogen continuum, which is the most useful, may be excited with considerable intensity if about 1500 v. is applied to an ordinary discharge tube made with a long capillary viewed from the end. Such a tube, dissipating as much as 18 kw., must be made of quartz and water cooled. It is, therefore, expensive and is comparatively inefficient. A more convenient method of exciting the hydrogen continuum without using high voltage and water cooling is by means of thermoelectrons from a hot cathode as in the low voltage arc of Duffendack and Manley.[4] This arc passed between a heated tungsten filament and a disk anode, in a tube containing a palladium tube to admit hydrogen and a quartz window sealed on with wax. We built a tube differing from this only in having an oxide coated

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[1] V. Schumann, "Smithsonian Contributions to Knowledge," **29**, No. 1413, 13 (1903); T. Lyman, *Astrophys. J.*, **60**, 1 (1924); *Nature*, **118**, 156 (1926); G. H. Dieke and J. J. Hopfield, *Z. Physik*, **40**, 299 (1926); *Phys. Rev.*, **30**, 400 (1927); G. Rathenau, *Z. Physik*, **87**, 32 (1933); Collins and Price, *Rev. Sci. Inst.*, **5**, 423 (1934).

[2] V. Schumann, *loc. cit.*, E. Gehrcke and E. Laue, *Ann. Physik*, **76**, 673 (1925); Bay and Steiner, *Z. Physik*, **45**, 337 (1927); Lawrence and Edlefsen, *Rev. Sci. Inst.*, **1**, 45 (1930); Kistiakowsky, *ibid.*, **2**, 549 (1931); Stevens, *ibid.*, **6**, 40 (1935).

[3] J. J. Hopfield, *Astrophys. J.*, **72**, 137 (1930).

[4] Duffendack and Manley, *J. Opt. Soc. Am.*, **24**, 222 (1934); **23**, 101 (1933).