Anal. Calcd. for $C_{21}H_{36}O_2$: C, 78.8; H, 11.3. Found: C, 78.6; H, 11.2.

Upon refluxing with acetic anhydride it gave a diacetate melting at 168° which gave no depression in melting point when mixed with the diacetate of *allo*-pregnanediol-$3(\beta),20(\alpha)$. This compound was present in bull urine to the extent of 12 mg. per gallon.

The benzene was removed from the filtrate of the *allo*-pregnanediol-$3(\beta),20(\alpha)$ and the residue sublimed in high vacuum collecting a fraction distilling at 120–150°. This was crystallized from ethyl alcohol and methyl alcohol to a melting point of 137°. The product was saturated to bromine and when mixed with β-equistanol isolated from stallion, cow pregnancy, and mare pregnancy urine it gave no depression in melting point.

Upon refluxing with acetic anhydride it gave an acetate melting at 126° which did not depress the melting point of β-equistanol acetate. Equistanol was present in bull's urine to the extent of 8 mg. per gallon. As in the case of stallions, mares and cows pregnancy urine, the amount of cholesterol present was very small when compared to that in human urine. An investigation of the other steroid fractions will be reported in THIS JOURNAL in the near future.

Summary

Pregnanediol - $3(\alpha),20(\alpha)$, *allo*-pregnanediol - $3(\alpha),20(\alpha)$, *allo*-pregnanediol-$3(\beta),20(\alpha)$ were isolated from bull's urine in quantities about twice or more than that of human pregnancy urine. Equistanol also was isolated but very little cholesterol was found.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WEST VIRGINIA UNIVERSITY]

β-Alkoxy Ethyl Esters of Chlorocarbonic and Carbamic Acids

BY H. G. ASHBURN, A. R. COLLETT AND C. L. LAZZELL

In order to study the relative narcotic powers of a series of carbamic acid esters containing an ethereal oxygen in the alcohol group, we have prepared a series of twelve esters of chlorocarbonic acid, ten of which are new, and from them their corresponding carbamic acid esters, eleven of which are new.

β-Alkoxyethanols.—The β-alkoxyethanols were prepared by treating ethylene oxide with the desired alcohol in the presence of a small amount of sulfuric acid as a catalyst,[1,2] except in the cases of the tertiary butoxy and tertiary amoxy ethanols for which aluminum fluosilicate was used as a catalyst.[3,4]

β-Alkoxyethyl Chlorocarbonates.—The chlorocarbonates were prepared by the action of phosgene upon the various β-alkoxyethanols.[5] A calculated excess of liquid phosgene was placed in a 500-cc. round-bottomed flask clamped in a freezing mixture. A reflux condenser, through which a freezing mixture was passed, was then attached. The alcohol was added drop by drop, the mixture being stirred mechanically, until all was added, and the reaction mixture allowed to come to room temperature gradually. The flask was opened and allowed to remain open for a day, at room temperature, in order to evaporate the excess phosgene. The mixture was poured into ice water, the ester separated and dried over anhydrous calcium chloride. It was then distilled *in vacuo* at 1–20 mm. pressure. The tertiary butoxy and tertiary amoxy chlorocarbonates could not be prepared by this reaction. *bis*-Ethylene chlorocarbonate was obtained in both cases.

The analyses were made in a few cases by digesting the sample with 10% sodium hydroxide, then titrating against standard silver nitrate, using potassium chromate as an indicator. In all cases the chlorocarbonates were converted into their respective carbamates and analyzed for nitrogen by the Kjeldahl method. Refractive indices were determined by means of an Abbe refractometer and surface tension values obtained by means of a du Nouy tensiometer at 25°. The Harkins correction for the ring method was applied. The yields are based upon the amount of the glycol ether used. Table I shows the boiling points, under reduced pressure, the refractive indices, surface tensions (corrected), yields, and the densities of the chlorocarbonates.

β-Alkoxyethyl Carbamates.—The carbamates were prepared from the corresponding chlorocarbonates by treating them with aqueous ammonia. The carbamates, with the exception of the β-methoxy, β-ethoxy- and β-isopropoxyethyl carbamates were purified by distillation *in vacuo*. These three were purified by crystallization from propylene chloride. The yield is based on the chlorocarbonate used. In Table II the yield, melting point or boiling point, and the analyses for the carbamates are given.

Narcotic Properties

Emerson and Abreu[6] have found that the β-ethoxyethyl carbamate is less active and less toxic than urethan. They also found that the propoxy and isopropoxy derivatives are roughly equivalent to urethan in narcotic activity and toxicity and

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[1] Ashburn, Collett and Lazzell, THIS JOURNAL, **57**, 1862 (1935).

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

[3] Ashburn, Collett and Lazzell, THIS JOURNAL, **58**, 1549 (1936).

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

[5] Dumas and Péligot, *Ann. chim.*, [2] **58**, 52 (1835); *Ann.*, **15**, *1–60 (1835)*; *Ann.*, **10**, *284 (1834)*; Hentschel, *Ber.*, **18**, 1177 (1885).

[6] From a report by Emerson and Abreu working in the Pharmacological Laboratory of the University of California Medical School, San Francisco, California.

TABLE I

β-ALKOXYCHLOROCARBONATES ($ROCH_2CH_2OCOCl$)

Alkyl group	Yield, %	B. p. °C.	Mm.	$d^{25}_{abs.}$	n^{25}_D	γ_{25}	Chlorine, %		
							Calcd.	Found	
CH_3—[a]	93	58.7	13.0	1.1905	1.4163	30.86	...	...	...
C_2H_5—[a]	77	67.2	14.0	1.1341	1.4169	29.45	...	...	...
$CH_3(CH_2)_2$—	81	78.3	13.0	1.0879	1.4193	28.55	21.32	20.77	20.48
$(CH_3)_2CH$—	85	71.5	12.0	1.0820	1.4156	27.09	...	...	...
$(CH_3)(CH_2)_3$—	91	93.0–93.5	14.0	1.0696	1.4241	28.64	19.66	19.78	19.80
$(CH_3)_2CHCH_2$—	59	84.0–85.0	12.0	1.0657	1.4205	27.18	...	...	...
$(C_2H_5)(CH_3)CH$—	83	83.0–84.0	14.0	1.0404	1.4180	25.73	...	...	...
$(CH_3)(CH_2)_4$—	83	104.3	12.0	1.0508	1.4275	28.67	18.44	18.74	18.59
$(CH_3)_2CH(CH_2)_2$—	91	95.0–96.0	10.0	1.0565	1.4268	27.63	...	...	...
$(C_2H_5)(CH_3)CHCH_2$—	87	102.0	14.0	1.0700	1.4272	29.00	...	...	...
$(C_2H_5)_2CH$—	72	87.0–87.5	8.5	1.0619	1.4261	27.54	...	...	...
$(n\text{-}C_3H_7)(CH_3)CH$—	90	91.8	9.5	1.0750	1.4262	27.90	...	...	...

[a] The β-methoxy and β-ethoxy ethyl chlorocarbonates are marketed by the Eastman Kodak Company, which gives their boiling points as 54–60° at 13 mm., and 55–65° at 15 mm., respectively.

TABLE II

β-ALKOXYETHYL CARBAMATES ($ROCH_2CH_2OCONH_2$)

Alkyl groups	Yield, %	M. p. °C.	B. p. °C.	Mm.	Nitrogen, %		
					Calcd.	Obtained	
CH_3—	13.3	46.8	...	...	11.86	11.65	11.81
C_2H_5—[a]	39.0	62.2	...	...	10.52	10.21	10.46
$CH_3(CH_2)_2$—	12.7	..	132.2–132.5	7.0	9.65	9.94	9.54
$(CH_3)_2CH$—	66.6	53.0	...	...	9.65	9.55	9.83
$CH_3(CH_2)_3$—	63.5	..	132.2–132.4	2.5	8.69	8.57	8.59
$(CH_3)_2CHCH_2$—	23.2	..	133.0–134.0	5.0	8.69	8.85	8.85
$(C_2H_5)(CH_3)CH$—	34.0	..	135.4	3.0	8.69	8.33	8.32
$(CH_3)(CH_2)_4$—	43.0	..	142.2	3.0	8.00	7.96	7.88
$(CH_3)_2CH(CH_2)_2$—	29.8	..	131.4	1.5	8.00	7.47	7.79
$(C_2H_5)(CH_3)CHCH_2$—	11.9	..	129.0–130.0	2.0	8.00	7.87	8.28
$(C_2H_5)_2CH$—	63.5	..	133.0–134.0	2.5	8.00	8.06	7.73
$(n\text{-}C_3H_7)(CH_3)CH$—	26.6	..	137.0–138.0	3.5	8.00	8.31	7.75

[a] Recorded in the literature as 62° (I. G. Farbenind. S. G. E. P. 309,108 (1928); *Chem. Zentr.*, **100**, II, 650 (1929), and is marketed by the Eastman Kodak Company which gives the melting point of its product as 61–62°.

that the isomers of butoxy and amoxy derivatives are more active and more toxic than urethan.

Summary

Ten new β-alkoxyethyl esters of chlorocarbonic acid and eleven new β-alkoxyethyl esters of carbamic acid have been prepared and some of their physical constants determined.

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