alcohol. The ethylidene acetals $RCH(OR')_2$ could not be split in this way.

The α-unsaturated ethers prepared, along with their physical properties and analyses, are reported in Tables I, II and III.

TABLE II

PROPERTIES OF α-UNSATURATED ETHERS

No.	B. p. °C.,	mm.	Density	n_D	MR_D Calcd.	MR_D Found
1	119–120	740	0.813^{19}	1.4179^{19}	35.71	35.38
2	132–133	745	$.797^{23}$	1.4170^{23}	40.33	40.38
3	155–156	748	$.798^{23}$	1.4215^{23}	44.94	45.21
4	177–178	745	$.802^{25}$	1.4250^{25}	49.56	49.47
5	166–168	745	$.798^{23}$	1.4228^{23}	49.56	49.78
6	142–143	745	$.806^{24}$	1.4198^{24}	40.33	40.23
7	181–183	745	$.807^{23}$	1.4260^{24}	49.56	49.55
8	191–193	745	$.994^{23}$	1.5395^{23}	41.34	41.62

TABLE III

ANALYSES OF α-UNSATURATED ETHERS

No.	Empirical formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H
1	$C_7H_{14}O$	73.61	12.37	72.9	12.2
2	$C_8H_{16}O$	74.90	12.59	74.4	12.60
3	$C_9H_{18}O$	75.99	12.77	75.68	12.79
4	$C_{10}H_{20}O$	76.84	12.91	76.65	12.99
5	$C_{10}H_{20}O$	76.84	12.91	76.40	12.91

Experimental

Reagents.—The *p*-toluenesulfonic acid required as a catalyst was Eastman C. P. grade. The 2,2-dimethoxyalkanes were prepared as previously described by the authors.[13] The alcohols were purified by drying over lime and distilling before use.

Preparation of 2-Methoxyhexene-1.—To 123 g. of 2,2-dimethoxyhexane in a 250-ml. wide-mouthed flask was added approximately 0.05 g. of *p*-toluenesulfonic acid. The flask was provided with an efficient fractionating column (8 mm. i. d., 110 cm. long), packed with a single nichrome spiral and equipped with a controllable dephlegmator. The flask contents was heated to boiling and the methyl alcohol removed as formed. When nearly the theoretical quantity had been removed, the residue was distilled through a short Vigreux column; yield 95 g., boiling between 117–121°. Upon redistillation it boiled at 119–120° at 740 mm.; yield of pure product 92%.

Preparation of 2-Propoxyhexene-1.—To 73 g. (0.5 mole) of 2,2-dimethoxyhexane was added 60 g. (1 mole) of propanol and about 0.05 g. of *p*-toluenesulfonic acid. The mixture was treated as described above and the excess propyl alcohol removed after all of the methyl alcohol had distilled. The yield of pure 2-propoxyhexene-1, b. p. 155–156° at 748 mm., was 58 g. (82% of the theoretical).

Ethylidene Acetals.—Upon treating diethyl acetal or dipropyl acetal in a similar manner, most of the ethylidene acetal distilled unchanged with the exception of a small amount of polymerized residue. No α-unsaturated ethers were isolated by this method.

Summary

1. α-Unsaturated ethers may be obtained in high yield by distilling 2,2-dimethoxyalkanes with *p*-toluenesulfonic acid.

2. A method is described for the preparation of α-unsaturated ethers from a 2,2-dimethoxyalkane or a 2-methoxyalkene-1.

3. Ethylidene acetals were not able to be split in this way.

NOTRE DAME, INDIANA RECEIVED DECEMBER 19, 1934

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[13] Killian, Hennion and Nieuwland, THIS JOURNAL, **56**, 1384 (1934).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ARKANSAS]

Ethoxybenzyl Ureas

BY E. WERTHEIM

This paper reports further work on the problem of structure *vs.* taste of Dulcin (I). The previously reported preparation of *d*-ethoxybutylurea apparently shows that the aromatic character of dulcin is essentially connected with its sweet taste.[1]

This point has been tested further in the preparation of *p*-ethoxybenzylurea (II), in which the carbamido group is removed from the ring. The compound is practically tasteless in contrast with *a*-methyldulcin (III) which is sweet.[2]

In *m*-ethoxybenzylurea (IV) and *o*-ethoxymethylbenzylurea (V) (having, respectively, one and two aliphatic attachments for the taste groups) the sequence of four carbons between taste groups as found in dulcin has been retained. In addition the latter has a space orientation of these groups similar to that found in dulcin.[3] Both compounds are practically tasteless. The removal of the carbamido group from the ring destroys sweetness despite the spatial similarity of these compounds to dulcin.

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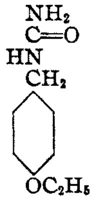
[1] Wertheim, THIS JOURNAL, **56**, 735 (1934).

[2] Lorang, *Rec. trav. chim.*, **47**, 183 (1928).

[3] *Cf.* discussion in a previous paper of this series, THIS JOURNAL, **55**, 2540 (1933).


(I)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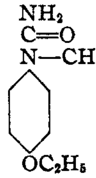
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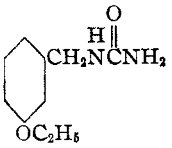
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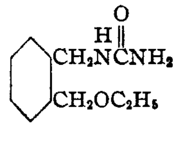
(V)

Further work on the problem of taste *vs.* structure of dulcin will be carried out in this Laboratory.

Experimental Part

p-Ethoxybenzonitrile, $C_2H_5OC_6H_4CN$.—A solution of 27 g. of p-phenetidine in 200 cc. of water and 33 cc. of concd. hydrochloric acid was diazotized with a solution of 14 g. of sodium nitrite in 75 cc. of water. The diazonium salt solution was added to a hot solution of 50 g. of copper sulfate and 55 g. of potassium cyanide in 260 cc. of water. Purification was by steam distillation, etc.; yield, about 17 g.; m. p. 63–65°; m. p. 69 and 57° quoted in the literature.

p-Ethoxybenzylamine, $C_2H_5OC_6H_4CH_2NH_2$.—A solution of 15.8 g. of the nitrile in 240 cc. of absolute methanol was treated with 30 g. of sodium. The methanol was removed by steam distillation, etc.; yield, about 2 g. of light yellow, mobile liquid, strongly basic; b. p. (3 mm.) 97–102°. *Anal.* Calcd. for $C_9H_{13}NO$: C, 71.51; H, 8.61; N, 9.27. Found: C, 71.66; H, 8.69; N, 9.32, 9.28.

p-Ethoxybenzylurea, $C_2H_5OC_6H_4CH_2NHCONH_2$.—A solution of 1.62 g. of potassium cyanate in 8 cc. of water was added dropwise to a solution of 3 g. of p-ethoxybenzylamine in 10 cc. of water and 1.8 cc. of concd. hydrochloric acid. The precipitated urea was recrystallized from hot water or dilute ethanol as white needles of m. p. 163–164°; solid tasteless, dilute alcoholic solution very faintly sweet. *Anal.* Calcd. for $C_{10}H_{14}N_2O_2$: C, 61.86; H, 7.22; N, 14.43. Found: C, 61.84; H, 7.74; N, 14.33, 14.52.

m-Ethoxybenzonitrile, $C_2H_5OC_6H_4CN$.—A yield of about 42% was obtained by following with slight changes the procedure used for the p-nitrile. An adaptation of a recently reported technique for the preparation of benzonitrile gave a 50% yield;[4] light yellow oil, b. p. 241–244°. *Anal.* Calcd. for C_9H_9NO: C, 73.46; H, 6.12; N, 9.52. Found: C, 73.56, 73.73; H, 6.53, 6.11; N, 9.64.

m-Ethoxythiobenzamide, $C_2H_5OC_6H_4CSNH_2$.—A solution of 10 g. of m-ethoxybenzonitrile in 35 cc. of ethanol was saturated with dry ammonia. Another 35 cc. of ethanol was added and the resulting solution, after being saturated with hydrogen sulfide, was heated in sealed tubes for ten hours at 100–105°. The ethanol was evaporated, giving a yellow solid, weight 11 g.; crystallization from dilute acetic acid; m. p. 75–77°. *Anal.* Calcd. for $C_9H_{11}NOS$: N, 7.73; S, 17.70. Found: N, 7.77, 7.83; S, 17.68, 17.85.

m-Ethoxybenzylamine, $C_2H_5OC_6H_4CH_2NH_2$.—A solution of 5 g. of the thiobenzamide in 35 cc. of ethanol was reduced by the gradual addition of 6 g. of zinc dust and 14 cc. of concd. hydrochloric acid. The solution was decanted from the remaining zinc, which was washed with additional alcohol. After evaporation of the alcohol the residue was treated successively with hydrochloric acid (ether) and sodium hydroxide (ether) to isolate the amine; b. p. (5 mm.) 107–110°. *Anal.* Calcd. for $C_9H_{13}NO$: N, 9.27. Found: N, 9.33.

m-Ethoxybenzylurea, $C_2H_5OC_6H_4CH_2NHCONH_2$.—The urea was made by interaction of 1.2 g. of the amine (with 5 cc. of water and 0.85 cc. of concd. hydrochloric acid) and 0.88 g. of potassium cyanate in 4 cc. of water; recrystallization from benzene; yield, about 1 g.; m. p. 121–123°. The compound is colorless and tasteless. *Anal.* Calcd. for $C_{10}H_{14}N_2O_2$: C, 61.85; H, 7.22; N, 14.43. Found: C, 61.75; H, 7.15; N, 14.59, 14.48.

o-Ethoxymethylbenzylamine, $C_2H_5OCH_2C_6H_4CH_2NH_2$.—This compound was made in 2.5 g. yield by the reduction of 7.5 g. of o-ethoxymethylthiobenzamide. Cassirer has reported that the amine cannot be made in this way.[5] As a check the compound was also made by the catalytic reduction of o-ethoxymethylbenzonitrile by the Adams method. The reduction of 8 g. of the nitrile was completed in ten hours at room temperature using hydrogen at 3.3 atmospheres pressure. Acetic acid (8 cc.) was employed as solvent, with a total of 0.150 g. of platinum oxide (added in three portions); b. p. (8 mm.) 118–120°; (10 mm.) 122–125°; picrate, m. p. 155–157°; HCl compound, m. p. 151–153°.[6] *Anal.* Calcd. for $C_{10}H_{15}NO$: N, 8.49. Found: N, 8.53, 8.41.

o-Ethoxymethylbenzylurea, $C_2H_5OCH_2C_6H_4CH_2NHCONH_2$.—A solution of 3.3 g. of the above amine with 5 cc. of water and 1.6 cc. of concd. hydrochloric acid was treated with 1.7 g. of potassium cyanate dissolved in 5 cc. of water. The compound was crystallized from dilute ethanol; m. p. 116–118°. The solid is tasteless, its water and dilute alcohol solutions slightly bitter. *Anal.* Calcd. for $C_{11}H_{16}N_2O_2$: C, 63.46; H, 7.69; N, 13.46. Found: C, 63.50, 63.40; H, 7.22, 7.34; N, 13.80, 13.75.

Summary

The preparation of p- and m-ethoxybenzylureas and o-ethoxymethylbenzylurea shows that the removal of the carbamido group from the benzene ring of the dulcin molecule destroys the sweet taste. Sweet taste is not secured by an arrangement of carbon atoms like that in dulcin so long as this part of the molecule has an aliphatic attachment.

FAYETTEVILLE, ARKANSAS RECEIVED DECEMBER 20, 1934

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[4] Rozhdestvenskii and Zepalova-Mikhailova, *J. Applied Chem.* (U. S. S. R.), **6**, 274–277 (1933); *C. A.*, **28**, 2698^6 (1934).

[5] Cassirer, *Ber.*, **25**, 3020 (1892).

[6] Von Braun and Zobel, *ibid.*, **56**, 2145 (1923), made the amine by catalytic reduction of the nitrile over nickel salt (?). They report the preparation of the picrate, m. p. 148°, hydrochloride, m. p. 152°.