Summary

1. Hydrolysis of the product obtained in the Reformatsky reaction between 6-acetylretene and ethyl bromoacetate yields β-hydroxy-β-6-retylbutanoic acid.

2. Dehydration of this acid followed by reduc-tion gives β-6-retylbutanoic acid whose acid chloride yields upon cyclization 1'-keto-3'-methyl-5,6-cyclopentenoretene.

3. The Clemmensen reduction of this cyclic ketone yields 3'-methyl-5,6-cyclopentenoretene.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

A Series of Aliphatic Dimethyl Amides[1]

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Dimethyl amides have been prepared by several investigators,[3] but the data on them are incomplete and not correlated. It seemed desirable to make a complete series of them so that comparisons can be made, not only between individual compounds, but also between this and other series. The eight dimethyl amides of the normal acids from formic to caprylic have been prepared and characterized. An unexpected discovery was that the acids except formic and their dimethyl amides give azeotropes boiling 4–5° *above* the amides. The data are in Table I and II. All of these dimethyl amides are mobile liquids which mix in all proportions with carbon disulfide, chloroform, carbon tetrachloride, benzene, ether, acetone and alcohol. The first two have limited solubility in petroleum ether, while the others mix with it. The lower members mix with water, but the higher homologs become increasingly insoluble; the solubility of VIII in water is less than 1%. In these respects dimethyl amides resemble esters, except that they are much more soluble in water and boil at substantially higher temperatures than esters of the same carbon content.

Another object was to investigate further the method of preparation of dimethyl amides recently proposed by Mitchell and Reid.[4] Repetition of their work showed that dimethyl amides are formed in liberal amounts by their procedure, but that the reactions are not complete, except

with formic acid. Fractionation, taking very close cuts, gave what appeared to be pure compounds, but these proved to be azeotropic mixtures of the dimethyl amides and the acids. These azeotropes caused Mitchell and Reid to overestimate their yields and troubled van der Zande.[5] The data on these constant boiling mixtures are brought together in Table II.

Experimental

Two equivalents of gaseous dimethylamine was passed into an acid which was heated under a reflux condenser from the top of which the excess of amine passed to a water trap. The water in the condenser jacket was kept warm enough to permit water vapor to escape. When there seemed to be no further reaction, the product was fractionated through a six-foot (2 meter) precision still,[6] a narrow cut being taken at what appeared to be the boiling point. The products were found to contain free acid which was titrated with the results given in Table II. Several experiments were made with acetic acid, noting the temperature of the boiling mixture, and titrating samples of it after successive portions of amine had been added. No matter how much amine was passed in the liquid in the flask never became neutral.

Dimethyl acetamide was obtained in 78% yield by heating 360 g. of acetic acid, saturated with gaseous dimethylamine at 35°, for five hours at 200° in a steel bomb. Solid caustic potash was added to the product to take up water and acetic acid. The liquid thus purified was distilled at 162–165°; it was then dried and fractionated taking the cut 164.8–164.9° at 759 mm. Analysis showed this to be 99.25% pure. The dimethyl amides of butyric, heptoic and caprylic acids were made similarly. With the higher acids a new difficulty was encountered; the potassium salt of the acid is soluble in the dimethyl amide. In such cases the reaction product was taken up in a large volume of benzene and this solution shaken with potassium hydroxide solution, dried and distilled. Franchimont and Klobbie prepared heptoic dimethyl amide by this method.

Other dimethyl amides were obtained in good yields by adding the acid chloride dropwise during three hours to a

(1) From a part of the Ph.D. dissertation of John R. Ruhoff, 1932.

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(3) (a) A. P. N. Franchimont, *Rec. trav. chim.*, **2**, 332 (1883); (b) A. P. N. Franchimont and E. A. Klobbie, *ibid.*, **6**, 247 (1887); (c) A. P. N. Franchimont and H. A. Rouffaer, *ibid.*, **13**, 336 (1894); (d) A. Verley. *Bull. soc. chim.*, [3] **9**, 690 (1893); (f) *J. Russ. Phys.-Chem. Soc.*, **29**, 227 (1897); (e) M. Tiffeneau and K. Fuhrer, *Bull. soc. chim.*, [4] **15**, 169–170 (1914).

(4) Mitchell and Reid, THIS JOURNAL, **53**, 1879 (1931).

(5) Van der Zande, *Rec. trav. chim.*, **8**, 233 (1889).

(6) Peters and Baker, *Ind. Eng. Chem.*, **18**, 69 (1926).

TABLE I

PHYSICAL PROPERTIES OF THE DIMETHYL AMIDES

Amide	M. p.,[a] °C.	B. p., °C.	Press., mm.	$d^0{}_4$	$d^{25}{}_4$	n^{25}D	M_D, obsd.	At. ref.[b] of N
I[c]	−61	153.0	760	0.9683	0.9445	1.4269	19.84	2.60
II[d]	−20	165.0	758	.9599	.9366	1.4351	24.24	2.49
III	−45	175.5	765	.9429	.9203	1.4371	28.75	2.40
IV[e]	−40	124.5	100	.9279	.9064	1.4391	33.39	2.43
V	−51	141.0	100	.9178	.8962	1.4419	38.08	2.52
VI	−42	158.0	100	.9099	.8896	1.4430	42.62	2.46
VII[f]	−19	172.5	100	.9051	.8854	1.4450	47.19	2.43
VIII	−21	187.0	100	.9002	.8810	1.4471	51.87	2.50
							Average	2.49

[a] The freezing points were determined with a copper–constantan thermocouple and potentiometer. [b] Obtained by subtracting the sum of the atomic refractions of all the atoms except nitrogen (Getman and Daniels, "Outlines of Theoretical Chemistry," p. 93) from the observed M_D. [c] Verley (ref. 3d) gives b. p. 155° and d^{20} 0.968; Franchimont and Rouffaer (ref. 3c) give b. p. 153° and sp. gr. 0.9525 at 15°; Bruhl [*Ph. Ch.*, **22**, 375 (1897)] gives b. p. 76° at 39 mm., $d^{22.4}{}_4$ 0.9484, and $n^{22.4}$D 1.42938. By interpolation our densities are 0.9493$^{20}{}_4$, 0.9540$^{15}{}_4$, and 0.9469$^{22.4}{}_4$. [d] Franchimont (ref. 3a) gives b. p. 165.5° at 754 mm. and d^{20} 0.9405; Bruhl (*Ph. Ch.*, **22**, 376 (1897)) gives b. p. 83–84° at 32 mm., $d^{20}{}_4$ 0.9434, and $n^{22.5}$D 1.43708. Our (calcd.) value is $d^{20}{}_4$ 0.9413. [e] Tiffeneau and Fuhrer (ref. 3e) give b. p. 186–196°. Franchimont and Klobbie (ref. 3b) give b. p. 242.5–243.5° at 758 mm., and sp. gr. 0.894^{15}, our $d^{15}{}_4$ 0.893.

TABLE II

AZEOTROPIC MIXTURES OF ACIDS AND THEIR DIMETHYL AMIDES

Amide	Boiling range, °C.	Pressure, mm.	Amide, %	Acid, %	Sum
I	153.2	757	97.4	1.2	98.6
II	170.8–170.9	761	77.2	21.1	98.3
III	179.2–179.4	767	75.8	23.4	99.2
IV	129.9–130.0	100	66.1	32.0	98.1
V	145.7–145.9	100	68.0	30.8	98.8
VIII	189.9–190.0	100	71.9	26.0	97.9

TABLE III

ANALYTICAL DATA

Amide	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found
III	59.35	59.40	10.97	11.35
V	65.05	65.67	11.71	11.65
VI	67.07	67.61	11.97	11.76
VIII	70.10	69.73	12.37	12.26

concentrated aqueous solution of three moles of the amine kept at −20 to −10°. The resulting mixture was saturated with potassium hydroxide in the cold, and the dimethyl amide separated and distilled.

The analyses of the new dimethyl amides, propionic, n-valeric, caproic and caprylic are given in Table III.

Summary

The first eight members of the series of normal aliphatic dimethyl amides have been prepared and their more common physical properties measured.

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