action between the siliceous silicate, $Na_2O\cdot 3.3SiO_2$, and sodium hydroxide is slow. Changes in the electrical conductivity of freshly prepared mixtures of siliceous sodium silicates and sodium hydroxide for as long as ten hours were observed in 1893 by Kohlrausch.[4] Apparently there has been no further published study of the rate of this reaction, which probably involves the breaking down of the micelles present in the more siliceous silicates.

Differences in the colors of dyes in silicate solutions of the same composition and concentration may be large enough to be apparent to the unaided eye. For example, a 1.0×10^{-5} M solution of pinacyanol chloride in solutions of crystalline sodium meta- or orthosilicate having the same silica concentration (0.33 M) as 0.1 M $Na_2O\cdot 3.3SiO_2$ is blue whereas the same concentration of dye in a mixture of 0.1 M $Na_2O\cdot 3.3SiO_2$ and sodium hydroxide having exactly the same composition as the meta- or orthosilicate is reddish violet. This difference is due to a different type of silica being present in the solutions rather than to the additional free alkali.[2]

A Klett–Summerson photoelectric colorimeter equipped with an amber filter having maximum transmission at 475 mμ was adjusted to zero density with distilled water in the light path. Density readings were made for 1.0×10^{-5} M pinacyanol chloride in sodium metasilicate and sodium orthosilicate solutions containing 0.33 M SiO_2 and compared with solutions prepared from $Na_2O\cdot 3.3SiO_2$ and sodium hydroxide to give the same final compositions. The results in the following table show that the addition of sodium hydroxide to a siliceous silicate produces a slow gradual change in the type of silica present.

Final solution	Source	Colorimeter reading 0 hr.	5 hr.	24 hr.
0.33 M Na_4SiO_4	Na_4SiO_4	495	...	...
0.33 M Na_4SiO_4	$Na_2O\cdot 3.3SiO_2 + NaOH$	330	405	440
0.33 M Na_2SiO_3	Na_2SiO_3	460	...	...
0.33 M Na_2SiO_3	$Na_2O\cdot 3.3SiO_2 + NaOH$	303	375	395
0.1 M $Na_2O\cdot 3.3SiO_2$	$Na_2O\cdot 3.3SiO_2$	264	...	...

The colorimeter reading of the dye in an exceptionally pure sample of sodium metasilicate obtained through the courtesy of Drs. P. Debye and R. V. Nauman of Cornell University was practically the same as in solutions of commercial grade products. Apparently a small amount of impurities does not significantly affect the results.

This method of studying interactions or reactions of colloidal electrolytes by means of their changing metachromatic effect on dyes can probably be used generally. It should be useful in studying the degradation or depolymerization of other molecular colloidal electrolytes, such as pectinic, alginic, and other polyuronic acids, polyacrylic acids and their salts and similar materials.

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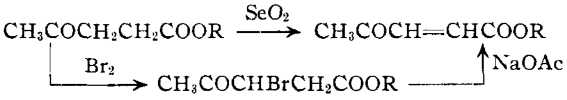
[4] F. Kohlrausch, *Z. physik. Chem.*, **12**, 773 (1893).

The Reaction of Selenium Dioxide with Levulinates

BY SAMUEL RAYMOND

Selenium dioxide has been used to introduce the hydroxyl or carbonyl group into aliphatic compounds at a position adjacent to a keto or other unsaturated group.[1] A second type of selenium dioxide oxidation is the removal of hydrogen forming a double bond.

Levulinic esters are dehydrogenated by selenium dioxide in a reaction of this second type. The products are esters of β-acetylacrylic acid, identical with the esters of this acid synthesized by a known method.[2]



$$\begin{tikzcd} CH_3COCH_2CH_2COOR \arrow[rr, "SeO_2"] \arrow[dr, "Br_2"'] & & CH_3COCH{=}CHCOOR \\ & CH_3COCHBrCH_2COOR \arrow[ur, "NaOAc"'] & \end{tikzcd}$$

Identity was shown by the direct comparison of physical properties, including mixed m. p., and by the preparation of the semicarbazone derivatives. Owing to the low yield and difficulty of separation of the products from the starting materials, this reaction cannot be considered of preparative value for these acetylacrylic esters.

Experimental

One-tenth of a mole of levulinic ester was heated with 0.05 mole of selenium dioxide on a steam-bath. After eighteen hours the precipitated selenium was filtered off and washed with dichloromethane. The filtrate and washings were mixed with 500 ml. of water, saturated with salt, and steam distilled. Two liters of distillate was collected and extracted thoroughly with dichloromethane. The extract was dried and distilled *in vacuo*. The quantity of acetylacrylic ester in the distilled oil was determined from the absorption at 222 mμ. Yields and physical properties are recorded in Table I.

TABLE I

ACETYLACRYLIC ESTERS

Alkyl	Yield, % SeO₂	Yield, % Wolff	B. p., °C., 15 mm.	Molar extinction log ε	at mμ
Methyl[a]	3.2	34	85–86	4.15	222
Ethyl	3.8	38	93–94[b]	4.00	224
Propyl	9.6	46	103–104	4.04	222
Butyl	13.2	39	118–122	3.98	222
Benzyl	0.0	42	116–120[c]	4.12	222

[a] M.p. 59–60°. [b] Adams and Wilkinson (THIS JOURNAL, **65**, 2207 (1945)) give b.p. 65–67° (2 mm.). [c] At 2 mm.

Methyl acetylacrylate was isolated from the reaction with methyl levulinate by cooling the steam-distilled oil to −20°. The crystals which formed were filtered off and washed with ether–ligroin mixture. Their m.p. was 56–60° and was raised to 59–60° by one recrystallization from ether and ligroin. The mixed m.p. with methyl acetylacrylate prepared by the method of Wolff[2] was unchanged.

The semicarbazones were prepared from the steam-distilled oils by the standard procedure and were recrystallized from dilute alcohol. Although this oil contains a large proportion of levulinic ester the semicarbazones of the acetylacrylates could be isolated easily because they

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[1] For a review see Waitkins and Clark, *Chem. Revs.*, **36**, 241 (1948).

[2] Wolff, *Ann.*, **265**, 229 (1891).

are much less soluble than the semicarbazones of the corresponding levulinic esters. The semicarbazones isolated in this way were identical in m.p. and mixed m.p. with those obtained from the products of the Wolff synthesis (Table II).

TABLE II

SEMICARBAZONES OF THE ACETYLACRYLIC ESTERS

Alkyl	M. p., °C.	Nitrogen, % Calcd.	Found
Methyl	193–194[a,b]		
Ethyl	199–200[b]	21.10	21.08
Propyl	161–163[c]	19.71	19.75
Butyl	135–136	18.50	18.39
Benzyl	165–166[c]	16.10	16.22

[a] Rinkes and v. Hasselt, *Chem. Centr.*, **87**, II, 390 (1916); *cf.* **88**, I, 208 (1917), give m.p. 196°. [b] Mixture of methyl and ethyl semicarbazones melted at 188–191°. [c] Mixture of propyl and benzyl semicarbazones melted at 138–150°.

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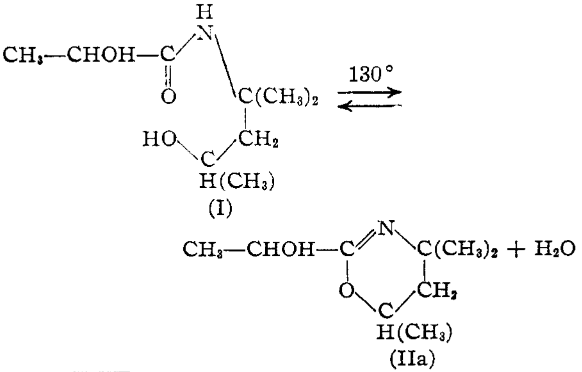
Lactic Acid Derivatives. 4,4,6-Trimethyl-2-(1-hydroxyethyl)-5,6-dihydro-1,3,4H-oxazine[1]

BY WILLIAM P. RATCHFORD

Although hydroxy alkyl amides of lactic acid are generally prepared from methyl lactate without difficulty[2] the attempted preparation of N-(1,1-dimethyl-3-hydroxybutyl)-lactamide (I), from 4-methyl-4-amino-2-pentanol and methyl lactate has led instead to the formation (at 130°) of an anhydro compound of empirical formula $C_9H_{17}O_2N$ (II), which we believe to be 4,4,6-trimethyl-2-(1-hydroxyethyl)-5,6-dihydro-1,3,4H-oxazine (IIa).



(I)

(IIa)

The lactamide (I) was obtained in 12% yield by crystallization from the aminolysis mixture and also by reversal of the above reaction. The evidence on which we assign the structure (IIa) is (1) empirical formula, (2) neutralization equivalent, (3) hydroxyl analysis, (4) conversion of (II) to (I) by an equivalent of water, (5) analysis of the picrate of (II), (6) molecular refraction (the observed molecular refraction, 47.75, agreed more closely with that calculated[3] for (IIa), 47.76, than with that for an N-alkene lactamide, 48.72), and (7) analogy with the work of Smith and Adkins,[4] who attempted to distil N-(1,1-dimethyl-3-hydroxybutyl)-acetamide at 130–140°, and obtained instead 2,4,4,6-tetramethyl-5,6-dihydro-1,3,4H-oxazine.

The two methyl groups on the carbon adjacent to the amide nitrogen promote the dehydration of (I) to (II), for N-(3-hydroxybutyl)-lactamide (which lacks these two methyl groups) was distilled in a tensimeter-still[5] without difficulty.

Experimental[6]

Materials.—The methyl lactate, a commercial material, was redistilled in vacuum. The 4-methyl-4-amino-2-pentanol was distilled in vacuum in an efficient still; b. p. 83° (22 mm.); $n^{20}D$ 1.4362; neut. equiv., 116.4 (calcd., 117.2).

4,4,6-Trimethyl-2-(1-hydroxyethyl)-5,6-dihydro-1,3,-4H-oxazine.—To 128 g. (1.1 moles) of the amine was added 104 g. (1.0 mole) of methyl lactate; after storage at room temperature for seven days, a sample of the mixture showed 97% reaction. Methanol and excess amine (and possibly water) were removed under vacuum (Vigreux column); the pressure was gradually lowered so that the temperature of the liquid did not exceed 130°. The remaining liquid was transferred to the tensimeter-still. It had a higher vapor pressure than expected; it distilled at 92° (14.5 mm.) to 97° (9.5 mm.) in 90% yield (computed as (II)). The temperature of the liquid did not exceed 130°. After redistillation twice in vacuum (Vigreux column), b. p. 97° (18.5 mm.), the following properties were determined: $n^{20}D$ 1.4481; d^{20}_4 0.9679; neut. equiv. (in ice-water), 171.6, 171.1 (basic). *Anal.* Calcd. for $C_9H_{17}O_2N$: C, 63.1; H, 10.0; N, 8.18; neut. equiv., 171.2; OH, 9.9. Found: C, 63.1; H, 10.2; N, 8.08; OH, 10.5.[7]

Base Picrate.—The picrate of (II) was formed in good yield by treatment with picric acid in benzene, and was recrystallized thrice from benzene, m. p. 147°. *Anal.* Calcd. for $C_{15}H_{20}O_9N_4$: C, 45.0; H, 5.04; N, 14.0. Found: C, 45.7; H, 5.18; N, 13.8. A picrate of 4-methyl-4-amino-2-pentanol was prepared, m. p. 146–147°; mixed m. p. with the oxazine picrate 120–125°.

Attempts to characterize (II) through the 3,5-dinitrobenzoate and the *p*-nitrobenzoate were unsuccessful; the former was a gummy mass and the latter an oil. Toward benzenesulfonyl chloride, (II) was unreactive.

Hydrolysis of (II) to (I).—To an 8.0-g. (0.047 mole) sample of (II) was added 0.85 g. (0.047 mole) of water. After ten days, the mixture solidified. It was recrystal-

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[1] Contribution from one of the Laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

[2] Ratchford, *Ind. Eng.Chem.*, in press.

[3] Using 4.10 for the atomic refraction of N in the group C—N=C of (IIa) (von Auwers, *Z. physik. Chem.*, **147**, 436 (1930)); 2.76 for N in the unsaturated lactamide (D'Alelio and Reid, THIS JOURNAL, **59**, 109–111 (1937)), and the customary values for the other atoms (Gilman, "Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 1751).

[4] Smith and Adkins, THIS JOURNAL, **60**, 407 (1938).

[5] Ratchford and Rehberg, *Anal. Chem.*, **21**, 1417 (1949).

[6] All melting points are uncorrected.

[7] Hydroxyl determination by the method of Ogg, Porter and Willits, *Ind. Eng. Chem., Anal. Ed.*, **17**, 394 (1945).