3-Acylacetamidobenzaldehyde Ethylene Glycol Acetals

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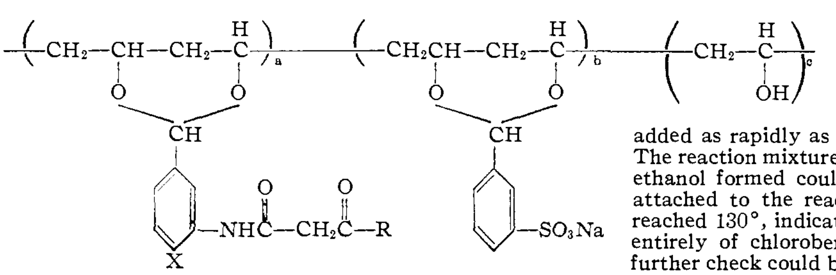
In a previous communication[1] from these laboratories, a series of hydrophilic polymers was described which are capable of use as photographic colloids with silver halide to form colored photographic images. These polymers were polyvinyl acetals made from polyvinyl alcohol, a solubilizing aldehyde and aromatic aldehydes or acetals containing a color-forming group suitable for coupling with oxidized color developer (*p*-aminodiethylaniline hydrochloride) to yield a cyan (minus red) dye.

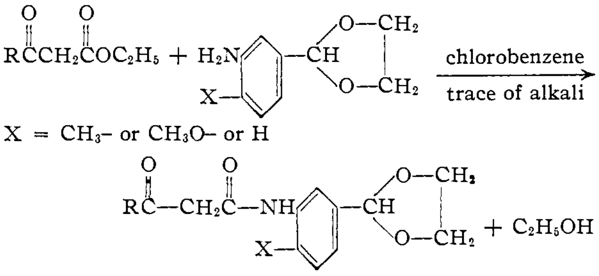
This paper describes a series of acylacetarylides which have been converted to polyvinyl acetals which can couple with oxidized developer to yield yellow (minus blue) dyes. Sodium benzaldehyde-*o*-sulfonate was added as a solubilizing aldehyde[1] to the acetalization reaction. The general structure of the yellow color-forming polymers is



where a, b and c are controlled to contribute the desired properties for photographic use.

The color-formers cited here were prepared in a search for improved spectral characteristics in the color developed dyes. The ideal minus blue dye absorbs all the light in the 400–500 mμ region of the visible spectrum and transmits all the light in the 500–700 mμ (green and red) region. All of the spectral curves showed some absorption in the green portion of the spectrum, and since all the curves were of nearly the same shape, the amount of green absorption was dictated by the position of the curve as indicated by the position of the absorption maximum. This was changed appreciably by certain substituents in the *ortho* position of the benzoyl group in the 3-benzoylacetamidobenzaldehyde polyvinyl acetals. Thus the lowest value obtained was 422 mμ for the dye from 3-(2-methoxybenzoylacetamido)-benzaldehyde polyvinyl acetal and the next lowest value was 430 mμ for the corresponding phenoxy compound (see Table I). The presence of a chlorine atom in this position had no effect. All the other photographic dyes measured had absorption maxima in the range of 440–443 mμ. Those containing chlorine absorbed more strongly in the 500–600 mμ region than did the dyes containing no chlorine and therefore were less desirable as minus blue dyes for color photography.

The acylacetarylides were prepared from ethyl acylacetates and aromatic aminoacetals[2] according to the equation[3,4]



The acylacetarylides thus obtained are shown in Table I. They were converted to polyvinyl acetals by transacetalization with polyvinyl alcohol in aqueous ethanol or were hydrolyzed to the free aldehydes which could also be converted to polyvinyl acetals.

Experimental

Preparation of 3-Acylacetamidobenzaldehyde Ethylene Glycol Acetals. Method I.—Condensation of a β-keto ester with a *m*-aminobenzaldehyde ethylene glycol acetal: A mixture of β-keto ester (2.75 moles), 2 ml. of 50% potassium hydroxide solution and 1 l. of chlorobenzene was heated to boiling and a small amount of chlorobenzene was distilled to remove water. To the solution was added as rapidly as possible 2.5 moles of the aminoacetal. The reaction mixture was then heated at such a rate that the ethanol formed could be distilled through a short column attached to the reaction vessel. When the boiling point reached 130°, indicating that the distillate consisted almost entirely of chlorobenzene, the reaction was stopped. A further check could be obtained by measuring the amount of ethanol distilled. This was done by extracting the distillate with water and noting the decrease in volume of the chlorobenzene. The reaction usually was complete in 1 to 3 hours. The reaction mixture was then cooled and extracted with an excess of 3% potassium hydroxide solution.

It was sometimes necessary to add 100 ml. of chloroform to facilitate a clean separation of the layers. The aqueous layer was washed once with ether and diluted with an equal volume of ethanol. Carbon dioxide was passed into the solution until precipitation was complete. The product was collected on a filter, washed several times with water, and finally with cold ethanol. Recrystallization from ethanol gave products of high purity.

In certain cases, the product separated in the form of an oil. After being washed by decantation, the oil was dissolved in acetone containing a small amount of dilute hydrochloric acid. After a short period of standing at 25–35°, the free aldehyde usually crystallized out and could be recrystallized from methylene chloride and ether or acetone and water.

A summary of the various 3-acylacetamidobenzaldehyde ethylene glycol acetals and the free aldehydes made by this procedure is given in Table I.

Method II.—Reaction of carbethoxyacetyl chloride with a *m*-aminobenzaldehyde ethylene glycol acetal.

A mixture of 0.2 mole of the aminoacetal, 65 ml. of acetone, 65 ml. of water and 0.2 mole of potassium carbonate was cooled to 0°. To this was added dropwise with stirring a solution of 0.2 mole of carbethoxyacetyl chloride in 25 ml. of dry acetone, keeping the temperature at 0 ± 2°. After all the acid chloride had been added, the reaction mixture was stirred for 30 minutes longer and then diluted with 150 ml. of water. The oil which separated as fine droplets soon solidified and was collected and washed with water. Recrystallization from ethanol gave pure products. The results of these experiments are also found in Table I.

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(1) D. M. McQueen and D. W. Woodward, THIS JOURNAL, 73, 4930 (1951).

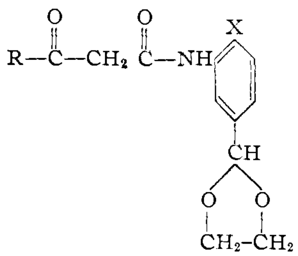
(2) D. M. McQueen and D. W. Woodward, U. S. Patent 2,481,434 (September 6, 1949).

(3) D. M. McQueen, U. S. Patent 2,464,597 (March 15, 1949).

(4) J. O. Corner, U. S. Patent 2,562,628 (July 31, 1951).

TABLE I

3-ACYLACETAMIDOBENZALDEHYDE ETHYLENE GLYCOL ACETALS



R	X	M.p., °C.	Empirical formula	Analyses, %						Max. absorption,[a] mμ
				Carbon		Hydrogen		Nitrogen		
				Calcd.	Found	Calcd.	Found	Calcd.	Found	
C_6H_5	H	91–92	$C_{18}H_{17}O_4N$	69.45	69.37	5.47	5.59	4.50	4.64	443
C_6H_5 (aldehyde)	H	101–102.5	$C_{16}H_{13}O_3N$	71.91	...	4.87	..	5.24	...	
2-$CH_3OC_6H_4$	H	116–118	$C_{19}H_{19}O_5N$	66.82	66.91	5.61	5.81	4.11	4.37	422
4-$CH_3OC_6H_4$	H	.....	$C_{19}H_{19}O_5N \cdot H_2O$	63.47	63.49	6.03	5.95	3.90	3.91	443
2-$C_6H_5OC_6H_4$	H	101–103	$C_{24}H_{21}O_5N$	71.43	70.95	5.25	5.59	3.47	3.86	430
4-$C_6H_5OC_6H_4$	H	Oil	$C_{24}H_{21}O_5N$	71.43	...	5.25	..	3.47	...	
2-ClC_6H_4	H	Oil	$C_{18}H_{16}O_4NCl$	62.50	...	4.67	..	10.24	...	
2-ClC_6H_4 (aldehyde)	H	99–101	$C_{16}H_{12}O_3NCl$	63.66	63.57	4.01	4.14	11.75	11.98	440
4-ClC_6H_4	H	142–144	$C_{18}H_{16}O_4NCl$	62.50	62.33	4.67	4.75	10.24	10.39	441
2,4-$Cl_2C_6H_3$	H	Oil	$C_{18}H_{15}O_4NCl_2$	56.84	...	3.95	..	3.68	...	
2,4-$Cl_2C_6H_3$ (aldehyde)	H	146–147	$C_{16}H_{11}O_3NCl_2$	57.14	57.34	3.30	3.39	21.10	21.11	440
4-$C_2H_5OCOC_6H_4$	H	141.5–142	$C_{21}H_{21}O_6N$	65.80	65.86	5.48	5.57	3.66	3.64	440
4-$C_2H_5OCOC_6H_4$ (aldehyde)	H	152.5–153	$C_{19}H_{17}O_5N$	67.26	67.10	5.01	5.07	4.13	4.10	
4-$HOOCC_6H_4$	H	184–185	$C_{19}H_{17}O_6N$	64.23	...	4.79	..	3.94	...	
C_6H_5	CH_3	155.5–156	$C_{19}H_{19}O_4N$	70.15	70.48	5.85	6.16	4.31	4.32	440
C_6H_5 (aldehyde)	CH_3	151.5–152	$C_{17}H_{15}O_3N$	72.60	72.56	5.34	5.68	4.98	4.95	
C_6H_5	CH_3O	97–98	$C_{19}H_{19}O_5N$	66.86	66.75	5.57	5.69	4.11	4.16	442
CH_3	H	86–86.5	$C_{13}H_{15}O_4N$	62.65	62.79	6.02	6.47	5.62	5.35	441
CH_3 (aldehyde)	H	96.5–97.5	$C_{11}H_{11}O_3N$	64.39	64.25	5.37	5.33	6.83	6.84	
CH_3	CH_3	86–89	$C_{14}H_{17}O_4N$	63.88	...	6.46	..	5.32	...	
CH_3	CH_3O	101–101.5	$C_{14}H_{17}O_5N$	60.21	60.36	6.09	6.24	5.02	5.00	
C_2H_5O	H	Oil	$C_{14}H_{17}O_5N$	60.21	...	6.09	..	5.02	...	
C_2H_5O	CH_3	99–99.5	$C_{15}H_{19}O_5N$	61.43	61.21	6.48	6.73	4.78	4.80	440
C_2H_5O	CH_3O	79.5–80.5	$C_{16}H_{19}O_6N$	58.25	...	6.15	..	4.53	4.2	440
C_2H_5O (aldehyde)	CH_3O	119.5–120.5	$C_{13}H_{15}O_5N$	58.87	58.83	5.66	5.78	5.28	5.31	

[a] Of the yellow photographic dye from oxidized *p*-aminodiethylaniline.

Preparation of Polyvinyl Acetals.—A mixture of 0.034 mole of the 3-acylacetamidobenzaldehyde ethylene glycol acetal, 0.009 mole of sodium benzaldehyde-*o*-sulfonate monohydrate, 50 ml. of water, 250 ml. of ethanol, 3 ml. of 85% phosphoric acid and 50 g. (0.57 mole) of polyvinyl alcohol was stirred at 75–80° for one hour, cooled and diluted with 300 ml. of acetone. The polymer was collected on a filter. It was then suspended in methanol and neutralized with triethylamine, filtered and then resuspended in methanol and finally twice in acetone. After drying, the product usually weighed about 55 g. and contained 8 to 10% of color-forming acetal groups by weight and 3% of solubilizing acetal groups.

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Steam-Volatile Fatty Acids from a Marine Tube Worm

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The unique five-carbon fatty acids, α-methylbutyric and tiglic, have been isolated along with acetic, propionic, butyric and *n*-valeric acids from parasitic hog worms.[1-3] The method of formation and metabolic pathways of these acids in worms is unknown. Intestinal worms are heavily contaminated with bacteria but it has been shown that after these worms have been rendered "bacteria free" the acids are still produced.[1,3,4]

The marine tube worm *Eudistylia vancouveri* grows abundantly on the shore of Brockton Point at Vancouver, British Columbia, and at a few other west coast locations. Recently *n*-octyl alcohol was isolated from this worm in comparatively large amounts and the presence of octanoic acid was suggested at that time.[5] Bacteriological investigation demonstrated the absence of anaerobic bacteria. Thus the marine tube worm appeared to be a suitable species for a study to determine if the acids found in the parasitic hog worm could be synthesized by this "anaerobic-bacteria-free" worm.

No five-carbon acids were found but the tube

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(1) E. Bueding and H. W. Yale, *J. Biol. Chem.*, **193**, 411 (1951).
(2) V. Moyle and E. Baldwin, *Biochem. J.*, **51**, 504 (1952).
(3) E. Bueding, *J. Biol. Chem.*, **202**, 505 (1953).
(4) W. Epps, M. Weiner and E. Bueding, *J. Infect. Dis.*, **87**, 149 (1950).
(5) D. R. Idler and U. H. M. Fagerlund, THIS JOURNAL, **75**, 6312 (1953).