

TABLE I
 SOME ANHYDRO-*p*-ALKYLAMINOBENZYL ALCOHOLS

Compound R $\begin{array}{l} \diagup \\ \diagdown \end{array} \text{NC}_6\text{H}_4\text{CH}_2\text{—} \\ \text{R}$	M. p. (corr.) °C.	Molecular weights			Analyses					
		In benzene found ^a	Calcd. trimer	In camphor	Carbon, %		Hydrogen, %		Nitrogen, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
Methyl	209–12 ^b	351 ^c	357	2070					11.8	11.4 ^g
Ethyl	84–6 ^d	396	399	1500					10.5	10.4 ^g
<i>n</i> -Propyl	106–8	447	441	1350	81.6	81.6	8.84	8.83	9.5	9.35 ^g
<i>n</i> -Butyl	52–3	484	483	1670	82.0	81.8	9.32	9.25	8.7	8.7 ^h
<i>i</i> -Amyl	46–8	508	525	1470	82.3	82.2	9.71	9.73	8.0	8.3 ^h
Benzyl	162–3 ^e	579	585	1570	86.2	86.1	6.67	6.56	7.2	7.1 ^f

^a Averages of from two to five values. ^b Previously reported^{2,3}: 210°, 205–210°. ^c Friedländer⁴ found 224. ^d Previously reported^{2,4}: 86°, 79–80°. ^e Previously reported²: 161°. ^f Semi-micro method. Analyses by Wm. McClellan. ^g Semi-micro Kjeldahl method. Analyses by F. W. Landau. ^h Micro Dumas method. Analyses by Edw. D'Ouille.

continued some minutes longer, and any lumps of base were broken up. The mixture was treated with several volumes of ice water, and the precipitated base was filtered off and washed with cold 50% alcohol. It was dried in a vacuum desiccator and then crystallized. The methyl compound was satisfactorily crystallizable from benzene, and the other compounds from ligroin (70–90°). The *n*-butyl and isoamyl compounds were very soluble in ligroin, and their recovery necessitated evaporation of part of the solvent; the isoamyl compound required considerable manipulation to induce crystallization.

The bases were crystalline and white, but became discolored on standing. Melting points were not in all cases sharp; it is possible that melting was accompanied by incipient decomposition or by change in polymeric state. The melting points of homologous bases showed "alternation."

Reduction of Anhydro-*p*-alkylaminobenzyl Alcohols to Alkyl-*p*-toluidines.—Reduction was effected using zinc dust and hot dilute sulfuric acid as previously described.³ The alkyl-*p*-toluidines from new bases were identified by their boiling points and by melting points of their hydrochlorides. The values obtained were as follows: (1) *n*-propyl-*p*-toluidine, b. p. 237–240°; hydrochloride, m. p. 154–155°, (2) *n*-butyl-*p*-toluidine, b. p. 251–252°; hydro-

chloride, m. p. 148–149°, (3) isoamyl-*p*-toluidine, b. p. 266–267°; hydrochloride, m. p. 139–142°, (4) benzyl-*p*-toluidine, b. p. 318–320°; hydrochloride, m. p. 180–181°. The hydrochlorides of *n*-butyl- and isoamyl-*p*-toluidines were identified also by mixed melting point tests.

Summary

1. Three new bases of the anhydro-*p*-alkylaminobenzyl alcohol series have been prepared, and together with three bases previously known, have been characterized with respect to polymeric state and structure.

2. The six bases were found to be trimeric in benzene solution, a finding at variance with Friedländer's conclusion that anhydro-*p*-methylaminobenzyl alcohol is dimeric. In molten camphor polymerization was found to be extensive. Strong reduction split the bases into the corresponding alkyl-*p*-toluidines, showing them to have the structure $\left[\begin{array}{l} \text{R} \\ \diagup \\ \diagdown \end{array} \text{NC}_6\text{H}_4\text{CH}_2\text{—} \right]_3$.

PHILADELPHIA, PENNA. RECEIVED FEBRUARY 16, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME]

Reactions of Alkenyl Esters Derived from Alkylacetylenes¹

BY STEFAN J. SLANINA AND G. F. HENNION

Introduction

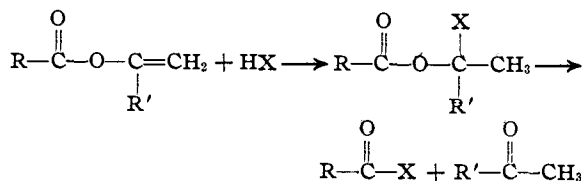
It was reported in a previous paper² that addition of bromine to the 2-acyloxy-1-alkenes derived from alkylacetylenes was followed by spontaneous cleavage yielding an acyl bromide and a mono-

(1) Paper XX on the chemistry of the alkylacetylenes and their addition compounds; previous paper, *J. Org. Chem.*, **1**, in press (1937).

(2) Slanina, Hennion and Nieuwland, *This Journal*, **58**, 891 (1936).

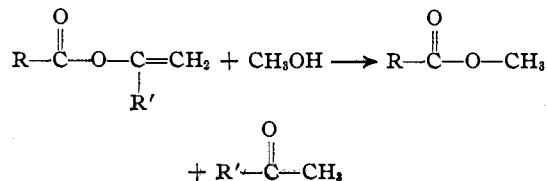
bromomethyl alkyl ketone. Further study has revealed that a number of other agents effect similar cleavage.

As in the case of bromination these esters react readily with hydrogen bromide and chloride. The addition compounds are unstable and cleave to yield the acyl halide and corresponding methyl alkyl ketone. The reactions may be represented as



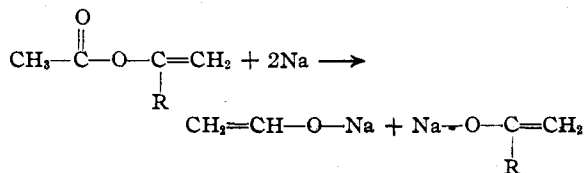
The intermediate halogen esters were not isolated. When hydrogen bromide was used, however, there was obtained, in addition to the two products indicated in the above equation, a small quantity of unidentified high-boiling material. Tests for bromine were negative. A corresponding substance was not obtained when 2-(chloroacetoxy)-1-hexene was treated with hydrogen chloride.

The alkenyl esters alcoholize readily when either *p*-toluene sulfonic acid or sodium methylate are employed as catalysts.



When such an ester and sodium methylate were mixed in molar proportions the reaction was extremely violent and apparently yielded the sodium ketone enol in addition to the methyl ester.

The 2-acetoxy-1-alkenes do not decompose when kept in contact with liquid ammonia at -34° for one hour. They do, however, react rapidly with sodium in liquid ammonia in the ratio of one mole of ester to two atoms of sodium, probably as follows



Addition of 2-acetoxy-1-hexene to a solution of iodine in liquid ammonia also effected ester cleavage. Iodoform was the only identified product and the reaction was not further investigated.

Experimental

Reagents.—The alkenyl esters were prepared from the appropriate alkylacetylene and acid as previously described by Hennion and Nieuwland.³ Hydrogen bromide was generated by the action of bromine on hot tetralin and was purified by passage over naphthalene followed by phosphorus pentoxide. Hydrogen chloride was obtained from

sodium chloride and sulfuric acid and was dried by bubbling through sulfuric acid.

Action of Hydrogen Bromide on 2-Acetoxy-1-heptene.—A one-liter three-necked flask was equipped with a reflux condenser, a motor-driven mercury-sealed stirrer and a gas inlet tube extending to the bottom. Into the flask there was placed 117 g. (0.75 mole) of acetoxyheptene. The flask was cooled with ice and water and hydrogen bromide passed in with stirring until saturated which required about thirty minutes. The crude product was transferred to a 500-ml. round-bottomed flask provided with a 40-cm. Vigreux column and distilled. Three fractions were collected at atmospheric pressure: up to 100° , $100-140^\circ$ and $140-160^\circ$. The pressure was then reduced to 23 mm. and a fraction boiling between $135-150^\circ$ was collected. There was 14 g. of residue. Repeated distillation of the first three fractions yielded 38 g. (41% yield) of acetyl bromide, b. p. $80-81^\circ$, 10 g. of acetic acid, and 42 g. (49% yield) of methyl amyl ketone,⁴ b. p. $145-150^\circ$. The vacuum distilled material was redistilled *in vacuo* and 15 g. of product collected between $140-150^\circ$ at 23 mm. This unidentified material had the following characteristics: n_D^{27} 1.4511; d_4^{27} 0.8421.

The identity of the acetyl bromide was confirmed by its action on anhydrous methanol. Methyl acetate was formed with rapid evolution of hydrogen bromide. The methyl amyl ketone yielded a semicarbazone, m. p. 122° .

Action of Hydrogen Bromide on 2-Acetoxy-1-hexene.—Hydrogen bromide was passed into 106.5 g. (0.75 mole) of acetoxyhexene at $30-32^\circ$ as described above. Distillation gave 40 g. (43% yield) of acetyl bromide, 34 g. (45% yield) of methyl butyl ketone,⁴ b. p. $124-127^\circ$, and 12 g. of a fraction, unidentified, b. p. $130-140^\circ$ at 23 mm.; n_D^{27} 1.4491; d_4^{27} 0.8465. There was 23 g. of non-distilled residue.

Action of Hydrogen Chloride on 2-(Chloroacetoxy)-1-hexene.—Hydrogen chloride was passed into 106 g. (0.6 mole) of chloroacetoxyhexene at approximately 10° as described above. Distillation to 124° at atmospheric pressure gave 40 g. of distillate. The pressure was then reduced to 20 mm. and distillation continued yielding 35 g. boiling to 90° and 35 g. boiling between $90-102^\circ$. The residue weighed 9 g. Repeated distillation yielded 25 g. of chloroacetyl chloride, b. p. $108-112^\circ$, 33 g. of methyl butyl ketone, b. p. $124-127^\circ$ and 35 g. of recovered chloroacetoxyhexene, b. p. $97-102^\circ$ at 20 mm.

Alcoholysis of 2-Acetoxy-1-heptene.—A solution of 0.5 g. of sodium in 12 g. of absolute methanol was treated with 47 g. (0.3 mole) of acetoxyheptene at 0° . The mixture was refluxed on a water-bath for thirty minutes and distilled. There was obtained 18 g. (81% yield) of methyl acetate, b. p. $54-57^\circ$ and 28 g. (81% yield) of methyl amyl ketone, b. p. $148-155^\circ$.

A second sample of acetoxyheptene weighing 41 g. (0.263 mole) was treated with 40 g. of absolute methanol in which 1 g. of *p*-toluene sulfonic acid had been dissolved. The mixture was heated for three hours on the water-bath and distilled, yielding 15 g. of methyl acetate and 25 g. of methyl amyl ketone.

Cleavage of 2-Acetoxy-1-heptene with Sodium in Liquid Ammonia.—A mixture of 41 g. (0.263 mole) of acetoxy-

(3) Hennion and Nieuwland, *THIS JOURNAL*, **56**, 1802 (1934).

(4) The product darkened upon standing unless thoroughly washed with sodium carbonate and water prior to final distillation.

heptene in 200 ml. of liquid ammonia was treated with 11.5 g. (0.5 mole) of sodium dissolved in 200 ml. of liquid ammonia. It was necessary to add 1 ml. more of the ester to effect complete decolorization of sodium. The mixture was hydrolyzed by careful addition of 250 ml. of water. The organic layer was washed twice with water, dried over calcium chloride, and distilled. Distillation was complete between 146–151° to give 23 g. (77% yield) of methyl amyl ketone. The semicarbazone melted at 122°.

Summary

Cleavage of alkenyl esters $R-COO-C(R)=CH_2$ with hydrogen bromide, hydrogen chloride, methanol, sodium in liquid ammonia and iodine in liquid ammonia is reported and the products described.

NOTRE DAME, INDIANA

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

Anthranol-beta-d-glucoside¹

BY JOHN H. GARDNER² AND THOMAS F. McDONNELL

In view of the suggestion of Hauser³ that barbaloin is a *d*-arabinoside of aloë-emodin anthranol, since it yields aloë-emodin anthrone on hydrolysis with borax solution, we have prepared anthranol- β -*d*-glucoside as the most readily obtained analogous compound and have studied its hydrolysis under a variety of conditions by the methods used previously in the study of glycosides of various mono- and dihydroxyanthraquinones.⁴ It was found that anthranol- β -*d*-glucoside is hydrolyzed completely by 0.05 *N* hydrochloric acid in one hour and by 0.05 *N* potassium hydroxide in thirty minutes. Hydrolysis was 62.4% complete in one hour with 9% borax. All hydrolyses were carried out at 100°. In the acid hydrolysis, pure anthrone was recovered, but with potassium hydroxide a part of the product was oxidized to dianthrone. The hydrolysis product formed with borax was not separated from unchanged glucoside and consequently was not identified.

These results differ markedly from the behavior of barbaloin in several ways. Notably, aloin is hydrolyzed extremely slowly by hydrochloric acid yielding chiefly a red, resinous material with a small amount of aloë-emodin, an anthraquinone derivative. No evidence of the formation of aloë-emodin anthrone under these conditions has ever been found. Reasoning by analogy, it seems extremely improbable that aloin could be an arabinoside of aloë-emodin anthranol.

(1) Anthracene Series. XI1.

(2) This investigation was made possible by a grant to the senior author from a fund given to Washington University by the Rockefeller Foundation for research in science.

(3) Hauser, *Pharm. Acta Helv.*, **6**, 79 (1931).

(4) Gardner, McDonnell and Wiegand, *THIS JOURNAL*, **57**, 1074 (1935); Foster and Gardner, *ibid.*, **58**, 597 (1936); Gardner and Demaree, *ibid.*, **58**, 737 (1936).

Experimental

Anthranol-tetraacetyl- β -*d*-glucoside.—To a solution of 0.25 g. of potassium hydroxide in 50 cc. of acetone and 25 cc. of water there were added 0.8 g. of anthrone and 1.7 g. of acetobromoglucose. The flask was closed quickly with a stopper provided with a stopcock and evacuated until the solvent boiled. The evacuated flask was swirled vigorously until an orange solution had formed and it was then allowed to stand at room temperature for five hours with occasional shaking. During this time, the solution became lemon yellow and a magma of fine needles precipitated. The reaction mixture was then diluted to 150 cc. with water and filtered. The cream colored solid was stirred into 15 cc. of methyl alcohol and filtered, leaving 0.6 g. (28%) of nearly pure anthranol-tetraacetyl- β -*d*-glucoside. After recrystallizing four times from ethyl alcohol, it formed long colorless needles, m. p. 205–205.2°.

Anal. Calcd. for $C_{28}H_{28}O_{10}$: C, 64.1; H, 5.38. Found: C, 64.0, 64.4; H, 5.54, 5.33.

Anthranol- β -*d*-glucoside.—A suspension of 0.6 g. of anthranol-tetraacetyl- β -*d*-glucoside in 75 cc. of 50% ethyl alcohol was heated to 60° and treated with 1 g. of barium hydroxide in 20 cc. of water. The mixture was maintained at 60° for fifteen minutes, with mechanical stirring. It was then cooled in ice and made slightly acid with dilute sulfuric acid. The precipitated barium sulfate was filtered out and the filtrate was concentrated under reduced pressure to 20–25 cc. The cream colored solid which separated was filtered out, crystallized from 25% ethyl alcohol and dried over sulfuric acid in a vacuum; m. p. 204–206°. Mixed with an equal quantity of the tetraacetyl glucoside, it melted at 175–187°. Its solutions in alcohol and other common solvents showed a brilliant blue fluorescence.

Anal. Calcd. for $C_{20}H_{20}O_6 \cdot H_2O$: C, 64.1; H, 5.92. Found: C, 63.7; H, 5.33.

A sample was dried in a Pregl microdesiccator for thirty minutes at 110° in a current of dry air.

Anal. Calcd. for $C_{20}H_{20}O_6$: C, 67.4; H, 5.62. Found: C, 66.7; H, 5.41.

Hydrolysis Experiments.—As our supply of the glucoside was limited because of the poor yields, no attempt was