sium hydroxide solution, cooled, diluted with water and extracted with ether (discarded). The aqueous layer was acidified, extracted with ether and the residue from the washed and dried ether extract was dissolved in methanol containing a few drops of concd. sulfuric acid. After heating for 24 hr., water was added and the **lactone VII** was extracted with ether and recrystallized several times from chloroform–ligroin; m.p. 184–186°, $[\alpha]^{25}D$ −31° (*c* 0.47 in $CHCl_3$), λ_{max}^{KBr} 5.76 μ (no hydroxyl band).

Anal. Calcd. for $C_{19}H_{28}O_3$: C, 74.96; H, 9.27; O, 15.97. Found: C, 74.78; H, 9.01; O, 15.80.

Conversion of Lactone VII to Keto Ester IX.—The above lactone VII (0.6 g.) was heated under reflux for 12 hr. with 15 cc. of methanol, 10 cc. of water and 2.0 g. of potassium hydroxide, cooled, diluted with water and extracted with ether. The aqueous layer was cooled in ice[21] and over a period of 1 hr. there was added slowly with stirring 36 cc. of 1 *N* sulfuric acid. Extraction with chloroform, drying and evaporation afforded 0.51 g. of the **hydroxy acid VIIIa**, m.p. 150–153° after one recrystallization. Three recrystallizations from chloroform–ligroin led to 0.17 g. of the analytical specimen, m.p. 157–161°,[22] λ_{max}^{KBr} 2.87 and 5.76 μ (as well as typical broad "acid" absorption in 3.6 μ region).

Anal. Calcd. for $C_{19}H_{30}O_4$: C, 70.77; H, 9.38; O, 19.85. Found: C, 70.37; H, 9.27; O, 20.04.

Methylation of 89 mg. of the hydroxy acid (m.p. 150–153°) with excess ethereal diazomethane solution afforded the **hydroxy ester VIIIb** as a colorless resin. Chromatography on 10 g. of Woelm neutral alumina (activity III) and elution with benzene and benzene–ether (9:1) led after recrystallization from chloroform–ligroin to 62 mg. of the lactone VII, m.p. 176–179°.

Consequently in a second experiment, the methyl ester from 140 mg. of hydroxy acid VIIIa was not chromatographed, but the crude oily ester ($\lambda_{max}^{capill.}$ 2.80 and 5.77 μ) obtained on washing the ether solution with sodium bicarbonate, was treated directly at 0° with 100 mg. of chromium trioxide in 10 cc. of pyridine. The mixture was allowed to warm to room temperature and was then stirred for 9 hr. before dilution with water. After cooling in ice and acidifying slowly with 25% sulfuric acid, the product was extracted with ether, washed with sodium bicarbonate and water, dried and evaporated. The residue was chromatographed on 12 g. of Merck acid-washed alumina and the pooled benzene–ether (1:1) eluates were evaporated (80 mg., m.p. 55–64° after one recrystallization) and recrystallized eight times from chloroform—hexane to afford 37 mg. of the **keto ester IX**, m.p. 78–80°, λ_{max}^{KBr} 5.73 and 5.79 μ; R.D. in methanol (*c* 0.095): $[\alpha]_{700}$ +13°, $[\alpha]_{589}$ +29°, $[\alpha]_{312.5}$ +643°, $[\alpha]_{270}$ −357°, $[\alpha]_{255}$ −155°.

Anal. Calcd. for $C_{20}H_{30}O_4$: C, 71.82; H, 9.04; O, 19.14. Found: C, 71.92; H, 9.15; O, 19.35.

(21) When the acidification was conducted rapidly at room temperature, a mixture of lactone VII and hydroxy acid VIIIa was obtained.

(22) The melting point of the hydroxy acid varied with the rate of heating. When heated very slowly, melting commenced at 154° with gas evolution, the melt resolidifying partially and then showing m.p. 178–187°, presumably due to lactonization. Rapid heating of a specimen placed on a preheated block of 140° showed m.p. 160–164°.

[CONTRIBUTED FROM THE NATIONAL RESEARCH CENTER, CAIRO, EGYPT]

The 4-Pyrones. Part I. Reactions of Some 4-Pyrones and 4-Thiopyrones Involving the Ring Oxygen

BY MOHAMED ABDEL-FATTAH ELKASCHEF AND MICHAEL H. NOSSEIR

RECEIVED JUNE 15, 1959

4-Pyrones and 4-thiopyrones react with N-alkylamines to give N-alkylpyridones and N-alkylthiopyridones, respectively. The N-alkylpyridones do not react with carbonyl or Grignard reagents. When brominated they give the dibromo derivatives, the bromine of which could not be removed by alkali and did not react as aromatic bromine when treated with magnesium. N-Alkyl-2,6-diphenyl-4-pyridone is not hydrolyzed with hydrochloric acid but can be converted to the corresponding thione by the action of phosphorus pentasulfide. The N-alkyl-4-thiopyridones, when oxidized with perhydrol, give the corresponding anhydrosulfonic acids.

The 4-pyrones react with hydrazines to form pyrazoles,[1,2] with hydroxylamine to give hydroxypyridones[3] and with ammonia to give pyridones.[4]

We have found that methylamine or ethylamine react with the pyrones (Ia, IIa and IIIa) to give the N-methyl- or N-ethylpyridones (VI, VII and VIIa or b).

The thiopyrones (Ib, IIb, IIIb and IVb) were found to react with the same reagents to give the corresponding thiopyridones (VI, VII, VIII and IXc or d).

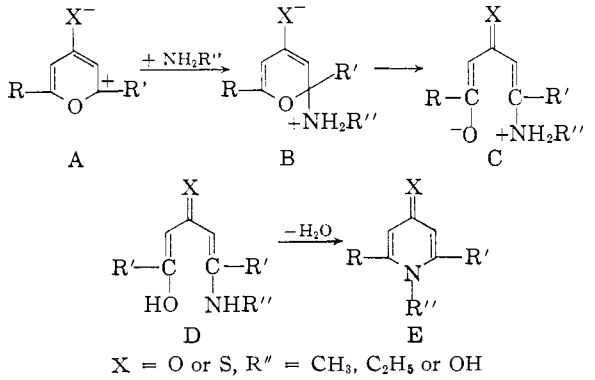
The formation of the N-hydroxy- or N-alkylpyridones as well as the N-alkylthiopyridones may be represented by the scheme A–E.

The non-reactivity of 2,6-di-*p*-methoxyphenyl-4-pyrone (IVa) may be attributed to the partial compensation of the positive charge in structure A by the +T effect of the two methoxyl groups in the *p*-positions, 2-*p*-methoxyphenyl-6-phenyl-4-pyrone (IIIa) being less readily convertible to the pyridone than the 2,6-diphenyl-4-pyrone. Conversely, the

a, A = X = O
b, A = O, X = S
c, A = O, X = NOH
a, X = O, R'' = CH_3
b, X = O, R'' = C_2H_5
c, X = S, R'' = CH_3
d, X = S, R'' = C_2H_5
e, X = O, R'' = OH
I, R = R' = CH_3
II, R = R' = C_6H_5
III, R = C_6H_5; R' = $C_6H_4OCH_3(p)$
IV, R = R' = $C_6H_4OCH_3(p)$
V, R = C_6H_5; R' = $C_6H_4Br(p)$
VI, R = R' = CH_3
VII, R = R' = C_6H_5
VIII, R = C_6H_5; R' = $C_6H_4OCH_3(p)$
IX, R = R' = $C_6H_4OCH_3(p)$
X, R = C_6H_5; R' = $C_6H_4Br(p)$

reactivity of the 2,6-di-*p*-methoxyphenyl-4-thiopyrone may be attributed to the stronger −T effect of the C=S group as compared to that of the C=O

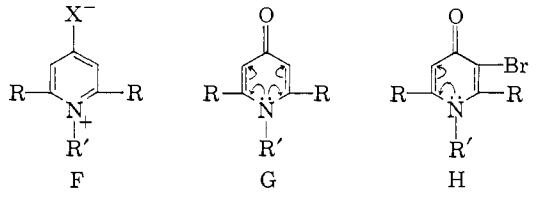
(1) R. G. Jones and M. J. Mann, THIS JOURNAL, **75**, 4048 (1953).
(2) C. Ainsworth and R. G. Jones, *ibid.*, **76**, 3172 (1954).
(3) G. Soliman and I. E-S. El-Kholy, *J. Chem. Soc.*, 1755 (1954).
(4) L. Neelakantan, *J. Org. Chem.*, **23**, 741 (1958).



X = O or S, R″ = CH_3, C_2H_5 or OH

group. Also the pyrone oxime does not react with alkylamines owing to the −T effect of the C=NOH group being weaker than that of the C=O group.

Moreover, the N-alkylpyridones and the N-alkylthiopyridones do not react with Grignard or carbonyl reagents. This may be due to the fact that the N-alkyl group is a stronger electron donor than the ring oxygen; the positive charge (*cf.* structure A) is largely compensated by the +T effect of the N-alkyl group and, as a result, the molecule exists predominantly in the zwitterion structure (structure F). The N-alkylpyridones could not be reduced by hydrogen in the presence of nickel catalyst under ordinary pressure. The N-methyl-2,6-diphenyl-4-pyridone (VIIa), contrary to 2,6-diphenyl-4-pyridone,[4] could not be hydrolyzed even with 10% hydrochloric acid solution. Nevertheless, it was converted to the corresponding thione by the action of phosphorus pentasulfide in dry benzene.



While the 4-pyrones on bromination give both the mono- and dibromo derivatives, the N-alkylpyridones give only the dibromo derivatives even when the reagents are used in equimolecular proportions. This may be attributed to the distribution of the negative charge on the 3- and 5-positions liable to be attacked by the bromonium ions (*cf.* structure G). Then, a higher concentration of electrons is established at position 5 due to the +E effect being directed one way only (*cf.* structure H). This renders the progress of bromination to a second position easier than to a fresh molecule. The bromine in the dibromopyridones could not be removed by alkalies. It did not react as aromatic bromine with magnesium in ethyl ether or anisole even on boiling or upon activation with bromine, iodine or dimethylaniline to form compounds analogous to Grignard reagents.

With perhydrol in hot glacial acetic acid the N-alkylthiopyridones (VI and VIIc and d) we find furnished the anhydro-2,6-disubstituted N-hydroxy,N-alkylpyridine-4-sulfonic acids.[5]

(5) A. Michaelis and A. Hölken, *Ann.*, **331**, 245 (1904).

For the preparation of the pyrones, the procedure of Soliman and El-Kholy[3] was modified as follows: after the passage of carbon dioxide the alkaline solution was left overnight, acidifying with 20% sulfuric acid solution and extracting with ether. The pyrone was extracted by concentrated hydrochloric acid from the oil remaining after the evaporation of the ether.

Experimental

The light petroleum used had b.p. 70–80°.

Preparation of 2-*p*-Methoxyphenyl-6-phenyl-4-pyrone (IIIa).—*p*-Methoxyacetophenone (13.0 g.) and ethyl phenylpropiolate (15.0 g.) were condensed in an ice-cold suspension of sodium ethoxide (from 2.0 g. of sodium) in ether. After standing for 2 days in the ice-chest, the mixture was poured into water and the ethereal layer was removed, washed with water, and the washings added to the alkaline aqueous layer. After passing carbon dioxide in the solution, it was left overnight. The solution is acidified with sulfuric acid solution (20% solution) and then extracted with ether. The oil obtained on evaporation of the solvent was extracted (boiling for 6 hours with 250 ml. and decantation 3 times) with concentrated hydrochloric acid. The acid solution, diluted with thrice its volume of crushed ice, gave a yellowish precipitate of crude pyrone (*ca.* 0.7 g.); crystallized from benzene, the pure pyrone had m.p. and mixed m.p.[3] 162°. In the ultraviolet light this pyrone gave a greenish fluorescence.

2-*p*-Bromophenyl-6-phenyl-4-pyrone (Va), prepared in the same way as the previous one (IIIa), pale yellowish crystals having m.p. and mixed m.p.[3] 172°, gave a sky-blue fluorescence in the ultraviolet light.

2-*p*-Methoxyphenyl-6-phenyl-4-thiopyrone (IIIb).—To a solution of IIIa (0.5 g.) in dry benzene (25 ml.), pure phosphorus pentasulfide (1.5 g.) was added. The reaction mixture was refluxed for 1 hour and filtered hot. The residue was washed with concentrated ammonium sulfide solution and added to the reddish-brown solid obtained on evaporation of the filtrate to dryness. The whole crop crystallized from ethanol to give IIIb as reddish-brown crystals, m.p. 180°. It gives an orange color with green fluorescence in concentrated sulfuric acid; yield *ca.* 0.35 g.

Anal. Calcd. for $C_{18}H_{14}O_2S$: C, 73.5; H, 4.8; S, 10.9. Found: C, 73.9; H, 4.8; S, 11.1.

2-*p*-Bromophenyl-6-phenyl-4-thiopyrone (Vb).—The treatment of Va (0.5 g.) with pure phosphorus pentasulfide (1.5 g.) as in IIIb afforded a solid that crystallized from ethanol and recrystallized from light petroleum in dark reddish-brown crystals, yield *ca.* 0.2 g., m.p. 173°, which gave a yellow color with concentrated sulfuric acid. *Anal.* Calcd. for $C_{17}H_{11}OSBr$: C, 59.4; H, 3.2; S, 9.3. Found: C, 59.3; H, 3.3; S, 9.4.

1-N-Alkyl-4-pyridones or Thiopyridones.—A solution of the pyrone or thiopyrone (0.5 g.) in ethanol (25 ml.) and the N-alkylamines (10 ml. of 40% aqueous solution) were refluxed for 7 hours. The alcohol was evaporated and the resulting pyridones (*cf.* Table Ia and Ib) or thiopyridones (*cf.* Table IIa and IIb) were recrystallized from ethanol. The oily pyridones were identified as picrates.

Pyridone Picrates.—When a saturated ethanolic solution of picric acid was added to a saturated alcoholic solution of the pyridone derivatives, crystals of the picrate were separated. These recrystallized from ethanol as yellow crystals (*cf.* Table III).

TABLE Ia

N-METHYL-4-PYRIDONES

Pyrone derivs.	Pyridone derivs.	M.p., °C.	Yield, g.	Formula	—Analyses, %— Calcd.	Found
Ia	VIA colorless	110[6]	0.37	$C_8H_{11}NO$	C, 70.0	69.6
					H, 8.1	8.5
					N, 10.2	10.1
IIa	VIIa colorless cryst.[a]	187[7]	0.20	$C_{18}H_{15}NO$	C, 82.7	83.1
					H, 5.8	5.8
					N, 5.4	5.4
IIIa	VIIIa, oily[c]	...	...	...	...	...
IVa	No pyridnoe	..	...	...	...	...

TABLE Ib

N-ETHYL-4-PYRIDONES

Pyrone derivs.	Pyridone derivs.	M.p., °C.	Yield, g.	Formula	Analyses, % Calcd.	Found
Ia	VIb colorless cryst.[b]	72	0.4	$C_9H_{13}ON$	C, 71.5	71.4
					H, 8.6	8.6
					N, 9.3	9.4
IIa	VIIb, oily	..	...	...	...	...
IIIa	VIIIb, oily[c]	..	...	...	...	...
IVa	No pyridone	..	...	...	...	...

[a] From light petroleum. [b] From benzene–light petroleum. [c] These compounds (0.3 g.) were separated together with starting pyrone (0.2 g.). Increasing reflux time to 10 hr. gave pyridones (0.4 g.) and starting material (0.05 g.).

TABLE IIa

N-METHYL-4-THIOPYRIDONES

Thiopyrone derivs.	Thiopyridone derivs.	M.p., °C.	Yield, g.	Formula	Analyses, % Calcd.	Found
Ib	VIc pale yellow cryst.	268[5]	0.41	$C_8H_{11}NS$	C, 62.7	62.7
					H, 7.2	7.4
					N, 9.1	9.0
					S, 20.9	20.5
IIb	VIIc pale yellow cryst.	248	.4	$C_{18}H_{15}NS$	C, 78.0	77.6
					H, 5.4	5.5
					N, 5.1	5.2
					S, 11.5	11.3
IIIb	VIIIc orange cryst.	200	.37	$C_{19}H_{17}ONS$	C, 74.3	74.0
					H, 5.6	6.0
					N, 4.6	4.3
					S, 10.4	10.3
IVb	IXc brown cryst.	225	.43	$C_{20}H_{19}O_2NS$	C, 71.2	70.8
					H, 5.7	5.6
					N, 4.2	3.8
					S, 9.4	9.4

TABLE IIb

N-ETHYL-4-THIOPYRIDONES

Thiopyrone derivs.	Thiopyridone derivs.	M.p., °C.	Yield, g.	Formula	Analyses, % Calcd.	Found
Ib	VId yellow cryst.	248[5]	0.4	$C_9H_{13}NS$	C, 64.7	64.6
					H, 7.8	7.8
					N, 8.4	8.3
					S, 19.1	19.2
IIb	VIId yellow cryst.	210	.34	$C_{19}H_{17}NS$	C, 78.3	78.2
					H, 5.9	5.7
					N, 4.8	5.1
					S, 11.0	10.8
IIIb	VIIId reddish-brown cryst.	162	.24	$C_{20}H_{19}ONS$	N, 4.4	4.1
IVb	IXd yellow cryst.	220	.41	$C_{21}H_{21}O_2NS$	C, 71.8	71.3
					H, 6.1	6.2
					N, 4.0	3.9
					S, 9.1	8.8

TABLE III

PYRIDONE PICRATES

Pyridone derivs.	Picrate m.p., °C.	Formula	Analyses, % Calcd.	Found
VIa	196	$C_{14}H_{14}O_8N_4$	N, 15.3	15.1
VIb	191	$C_{15}H_{16}O_8N_4$	N, 14.7	14.4
VIIa	220	$C_{21}H_{18}O_8N_4$	N, 11.4	11.3
VIIb	200	$C_{25}H_{20}O_8N_4$	C, 59.5	59.5
			H, 4.0	3.8
			N, 11.1	11.3
VIIIa	164	$C_{25}H_{20}O_9N_4$	C, 57.7	57.9
			H, 3.9	4.1
			N, 10.8	10.7
VIIIb	199	$C_{26}H_{22}O_9N_4$	N, 10.5	10.3

Treatment of N-Alkylpyridones with Hydrochloric Acid.—(a) N-Methyllutidone (VIa) (0.5 g.) dissolved in water (10 ml.) was refluxed with hydrochloric acid (10 ml. of 20% solution) for 1.5 hour. The crystals that remained after the evaporation of the water were dissolved in ethanol and precipitated with ether as colorless crystals, m.p. 270° of N-methyllutidone hydrochloride. *Anal.* Calcd. for $C_8H_{11}ON\cdot HCl$: N, 8.0; Cl, 20.2. Found: N, 7.5; Cl, 19.9. This when treated with aqueous sodium carbonate solution afforded the N-methyllutidone, m.p. and mixed m.p.[6] 110°.

(b) N-Methyl-2,6-diphenyl-4-pyridone (VIa) (0.2 g.) in hydrochloric acid solution (20 ml. of 10% hydrochloric acid) in a reaction as above afforded the hydrochloride of the starting substance, m.p. and mixed m.p. 245°.[7]

Treatment of the N-alkylpyridones with hydroxylamine or hydrazine hydrate gave only starting material.

TABLE IV

N-ALKYLPYRIDONE DIBROMIDES

Pyridone derivs.	Dibromide m.p., °C.	Formula	Analyses, % Calcd.	Found
VIa	308	$C_8H_9NOBr_2$	C, 32.5	32.4
			H, 3.1	3.1
			N, 4.7	4.7
			Br, 54.2	54.3
VIb	248	$C_9H_{11}NOBr_2$	C, 35.0	35.1
			H, 3.6	3.4
			N, 4.5	4.4
			Br, 51.8	51.5
VIIa	313	$C_{18}H_{13}NOBr_2$	C, 51.6	51.6
			H, 3.1	2.9
			N, 3.3	3.3
			Br, 38.2	37.7
VIIb	285	$C_{19}H_{15}NOBr_2$	C, 52.7	52.5
			H, 3.5	3.4
			N, 3.2	3.3
			Br, 37.0	37.1

TABLE V

ANHYDRO-PYRIDINESULFONIC ACIDS

Thiopyridone derivs.	Sulfonic acid m.p., °C.	Formula	Analyses, % Calcd.	Found
VIc	270[5]	$C_8H_{11}O_3NS$	C, 47.8	47.6
			H, 5.5	5.1
			N, 6.9	6.5
			S, 15.9	15.6
VId	248	$C_9H_{13}O_3NS$	C, 50.2	50.3
			H, 6.0	6.1
			N, 6.5	6.0
			S, 14.9	14.4
VIIc	>360	$C_{18}H_{15}O_3NS$	C, 66.5	66.1
			H, 4.6	4.6
			N, 4.3	3.7
			S, 9.8	9.7
VIId	310	$C_{19}H_{17}O_3NS$	C, 67.3	66.8
			H, 5.0	5.1
			N, 4.1	3.9
			S, 9.4	9.4

Treatment of N-alkylthiopyridones with hydroxylamine gave only starting material.

Treatment of N-methyllutidone with phenylmagnesium bromide yielded only the starting pyridone.

Action of Phosphorus Pentasulfide on N-Methyl-2,6-diphenyl-4-pyridone (VIIa).—N-Methyl-2,6-diphenyl-4-pyridone (0.2 g.) in dry benzene (20 ml.) and pure phosphorus pentasulfide (0.5 g.) were refluxed for 2 hours. The benzene was evaporated and the residue was washed with a concentrated solution of ammonium sulfide and then crystallized from ethanol as yellow crystals, m.p. and mixed m.p. with the thione derivative 248°; yield *ca.* 0.1 g.

(6) M. Conrad and F. Eckhardt, *Ber.*, **22**, 73 (1889).

(7) P. Petrenko-Kritschenko, *ibid.*, **42**, 3683 (1909).

Bromination of the N-Alkylpyridone Derivatives.—To a solution of the N-alkylpyridone derivative (1 mol.) in glacial acetic acid, bromine (2 mols.) in glacial acetic acid was added while stirring at room temperature. The solid pyridone dibromide that is formed was filtered, and then boiled with an alcoholic solution (50%) of sodium bicarbonate and the solution filtered while hot. On cooling, crystals of the pyridone dibromide separated and were recrystallized from ethanol in quantitative yield. Using one mol. only of bromine led to the formation of only half of the quantity of the dibromide derivative and half of the pyridone was recovered unchanged (*cf.* Table IV).

Treatment of N-methyl-3,5-dibromo-2,6-dimethyl-4-pyridone with sodium hydroxide gave only unchanged starting material.

N-Methyl-3,5-dibromolutidone did not react with activated magnesium on long boiling in ether or anisole even on activation with dimethylaniline.

Oxidation of the 4-Thiopyridone Derivatives.—To a hot solution of the thiopyridone derivative (0.5 g.) in glacial acetic acid (20 ml.) hydrogen peroxide (30% solution, 5 ml.) was added and heating was continued for half an hour on the water-bath. The solid residue that remained after the evaporation of the solvent crystallized from ethanol. Yields were quantitative and were identified as anhydro-pyridinesulfonic acids (*cf.* Table V).

2,6-Di-*p*-methoxyphenyl-4-pyrone[8] (IVa) did not react with hydroxylamine.

Treatment of 2,6-Diphenyl-4-pyrone Oxime with Methylamine.—Methylamine (7 ml.) of 40% solution and 2,6-diphenyl-4-pyrone oxime (0.2 g.) in ethanol (40 ml.) were refluxed for 7 hours. The crystals that separated on cooling were recrystallized from ethanol; m.p. and mixed m.p. with the starting oxime[9] 196°, yield *ca.* 0.18 g. With a saturated solution of picric acid, this oxime gave a picrate that recrystallized from ethanol in yellow crystals, m.p. 200°. *Anal.* Calcd. for $C_{23}H_{16}O_9N_4$: C, 56.3; H, 3.0; N, 11.4. Found: C, 56.1; H, 3.1; N, 11.6.

Treatment of 2,6-diphenyl-4-pyrone oxime (IIc) **with phenylmagnesium bromide** gave only starting material.

(8) A. Schönberg, M. Elkaschef, M. Nosseir and M. M. Sidky, THIS JOURNAL, **80**, 6312 (1958).

(9) F. Arndt, E. Scholz and P. Nachtwey, *ibid.*, **57**, 1903 (1924).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY, AND THE TEXTILE RESEARCH INSTITUTE AT PRINCETON, N. J.]

New Method of Removing Xanthate Groups from Carbohydrates. Chemical Structure of Methyl α-D-Glucopyranoside Monoxanthate[1]

BY JOHN J. WILLARD[2] AND EUGENE PACSU

RECEIVED JANUARY 22, 1960

A method of locating the xanthate groups in carbohydrates by classical means has been established. Methyl α-D-glucopyranoside xanthate in aqueous barium hydroxide solution forms carbon-6 xanthate in 20% yield, isolated as the crystalline S-benzyl ester I. The action of mercuric acetate on the crystalline tribenzoate III of I yields the crystalline tribenzoyl monothiolcarbonate IV which is quantitatively decomposed by oxidation with hydrogen peroxide in glacial acetic acid to give the known crystalline methyl 2,3,4-O-tribenzoyl-α-D-glucopyranoside (V) in high yield. That no benzoyl migration occurred during dexanthation is proved by synthesis of the identical monothiolcarbonate IV from the dexanthated tribenzoate V and benzyl chlorothiolformate.

The position of xanthate groups in viscose, or sodium cellulose xanthate, has posed a problem of considerable theoretical and commercial interest for many decades. When extensive investigations on this subject failed to result in a method by which the problem could be solved, we were led to study the reactions of a xanthate ester of methyl α-D-glucopyranoside as a model compound.

Methyl α-D-glucopyranoside was xanthated according to a procedure of Lieser[3] using aqueous barium hydroxide. Although Lieser converted the barium xanthate salt to the difficultly crystalline methyl xanthate ester *via* the silver salt, it was discovered in our laboratory that the action of benzyl bromide directly on the barium salt gives rapid conversion to the benzyl ester I. The benzyl xanthate ester, readily crystallized from benzene, was obtained in 20% yield, based on methyl α-D-glucopyranoside, and had m.p. 89–92° and $[\alpha]^{20}D$ 79.4° ($CHCl_3$). Analysis of the purified solution of xanthate barium salt for barium showed that under the optimum conditions as reported by Lieser, only 20% conversion of methyl α-D-glucopyranoside to a monoxanthate salt was obtained.

The crystalline triacetate II and tribenzoate III derivatives of the xanthate benzyl ester were prepared and had m.p. 105–107° and 123–124°, and $[\alpha]^{20}D$ 106.3° ($CHCl_3$) and $[\alpha]^{20}D$ 56.8° ($CHCl_3$), respectively.

Lieser speculated that the xanthate ester group was located at carbon-2, although his evidence was by no means conclusive.

Methyl α-D-glucopyranoside-(S-benzyl) xanthate (I) readily decomposed at 190° in high vacuum, giving nearly the theoretical yield of benzyl mercaptan, collected as a distillate. This observation was surprising in view of the fact that Freudenberg[4] reported that the diacetone derivative of glucose-3-(S-methyl) xanthate failed to undergo a Tschugaev reaction but rearranged at 300° to give the dithiol methyl carbonate derivative. A crystalline derivative could not be obtained from the residue of our reaction, and it was finally concluded that caramelization had probably occurred. The triacetate of the xanthate ester gave back only unchanged starting material after heating for one hour at 250°.

Methyl α-D-glucopyranoside-(S-benzyl) xanthate (I) failed to give a tosyl derivative or trityl derivative under conditions known to give those derivatives with compounds not substituted at the carbon-6-position.

The tribenzoyl derivative III of methyl α-D-

(1) This paper was taken in part from the Ph.D. dissertation of John J. Willard, Princeton University, 1959, and was presented at the 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

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(3) Th. Lieser and A. Hackl, *Ann.*, **511**, 121 (1934).

(4) K. Freudenberg and A. Wolf, *Ber.*, **60**, 232 (1927).