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SYNTHESIS OF SOME 1-SUBSTITUTED-4-FORMYLPYRIDINIUM OXIMES AND OXIMATES

by

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In connection with a broad study to find new reagents for applications in chemical detection, a number of new pyridinium oximes and oximates were synthesized. 1-Substituted-4-formylpyridinium chloride oximes were synthesized by alkylation of isonicotinaldehyde oxime. Corresponding iodide salts were obtained by treating the chlorides with an excess of methyl iodide. Oximate internal salts were prepared by the reaction of the oxime halides with silver oxide. All the oximates were found to be stable at 100°C for at least 8 hours.

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David W. Reger
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Defense Research Branch

December 1971

Task 1B662710AD2901

DEPARTMENT OF THE ARMY
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FOREWORD

The work described in this report was authorized under Task 1B662710AD2901, Chemical Detection and Identification Technology, Detection and Identification Concepts. The work was performed in February 1970. The results are recorded in notebook 8328.

Acknowledgments

Elemental analyses were performed by the Analytical Chemistry Branch, Chemical Laboratory, Edgewood Arsenal, Maryland 21010.

DIGEST

In connection with a broad study to find new reagents for applications in chemical detection, a number of new pyridinium oximes and oximates were synthesized. 1-Substituted-4-formylpyridinium chloride oximes were synthesized by alkylation of isonicotinaldehyde oxime. Corresponding iodide salts were obtained by treating the chlorides with an excess of methyl iodide. Oximate internal salts were prepared by the reaction of the oxime halides with silver oxide. All the oximates were found to be stable at 100°C for at least 8 hours.

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SYNTHESIS OF SOME 1-SUBSTITUTED-4-FORMYLPYRIDINIUM OXIMES AND OXIMATES

I. INTRODUCTION.

As part of a broad study on the use of pyridinium derivatives in chemical detection, a series of 1-substituted-4-formylpyridinium chloride (and iodide) oximes and 1-substituted-4-formylpyridinium oximates were synthesized and characterized. Analytical data, colors, and melting points for the chloride oximes, the iodide oximes, and the oximates are given in tables I, II, and III. No attempt was made to optimize yields, but they were generally well over 50%.

II. MATERIALS AND METHODS.

A. Chloride Oximes.

The 1-substituted-4-formylpyridinium chloride oximes were prepared by dissolving equimolar quantities of isonicotinaldehyde oxime (mp 132° to 133°C) and the appropriate benzyl chloride in 75 ml of acetone and heating the solutions overnight at 80°C. It was found convenient to use 200-ml heavy walled polymer bottles, which were capped before placing them in the 80° oven. Colorless solids formed during the heating process. The bottles were allowed to cool to room temperature; the reaction mixtures were filtered. One recrystallization was performed from methanol-ether. CAUTION! Because of the lachrymal properties of the alkylating agents, all procedures were carried out in a fume hood. 1-(*n*-Dodecyl)-4-formylpyridinium bromide oxime was prepared in a similar fashion from isonicotinaldehyde oxime and *n*-dodecyl bromide.

B. Iodide Oximes.

The 1-substituted-4-formylpyridinium iodide oximes were prepared by adding an excess of methyl iodide to a methanolic solution of the appropriate chloride oxime and allowing the solution to stand for at least 24 hours. The solutions were protected from light during the reaction period. Addition of ether effected the precipitation of the iodide oximes. One recrystallization was performed from methanol-ether.

C. Oximate Inner Salts.

The 1-substituted-4-formylpyridinium oximate inner salts were prepared by treating a methanolic solution of the appropriate halide oxime with excess silver oxide. (To ensure dryness of the reaction medium, 3 ml of triethylorthoformate were added prior to adding the silver oxide.) The resulting mixture was stirred vigorously for 5 minutes and then filtered. Slow addition of ethyl ether to the filtrate generally caused the oximate to crystallize. When immediate crystallization did not occur (as with the dodecyl and *p*-methoxybenzyl derivatives), the solution was evaporated to dryness. Ethyl ether then was added to the residue, and the mixture was allowed to stand in a refrigerator until solidification occurred. The mixture was filtered, and the product was dried over calcium sulfate in an Abderhalden apparatus at 100°C under vacuum for at least 8 hours.

III. RESULTS.

In contrast to the reported instability of 1-methyl-4-formylpyridinium oximate,* the oximates reported here were stable under the drying conditions of 100°C for at least 8 hours. Also, none of the oximates showed any signs of decomposition after several months at room temperature. Pyridinium oximates are of interest because of their internal charge-transfer properties.

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*Engelhard, N., and Werth, B. Tetrahedron Letters (10), 661 (1963).

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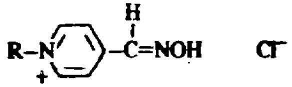
Table I. 1-Substituted-4-Formylpyridinium Chloride Oximes



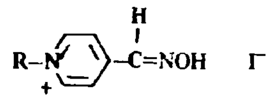
R	mp[a]	Color	Calcd					Found				
			C	H	Cl	N	O	C	H	Cl	N	O
	°C											
n-Dodecyl[b]	132-133	White	58.2	8.4	21.5[b]	7.5	4.3	58.2	8.3	21.2[b]	7.4	4.1
Benzyl[c]	209-211	White	62.8	5.2		11.3	6.4	62.9	5.3		11.3	6.3
p-Chlorobenzyl	174-176.5	White	55.1	4.3		9.9	5.6	55.0	4.2		10.0	5.9
o-Chlorobenzyl	219-221	White	55.1	4.3	25.0	9.9	5.6	55.4	4.3	24.8	9.7	5.8
2,4-Dichlorobenzyl	227-230	White	49.2	3.5	33.5	8.8	5.0	48.9	3.5	33.4	9.0	5.2
3,4-Dichlorobenzyl	216-219	White	49.2	3.5	33.5	8.8	5.0	48.9	3.5	33.7	8.7	5.0
p-Methoxybenzyl	179-181	White	60.3	5.4	12.7	10.1	11.5	60.3	5.6	12.9	10.0	11.5
p-Nitrobenzyl	208-209	Light tan	53.1	4.1	12.0	14.3	16.3	53.0	3.8		14.4	16.2
m-Nitrobenzyl	194-196	White	53.1	4.1	12.0	14.3	16.3	52.8	4.2	11.7	14.1	16.5

[a]Decomposition points except for the *n*-dodecyl derivative. A Thomas Hoover capillary melting point apparatus was used.

[b]The oxime bromide was prepared.

[c]Previously reported *in* Binenfeld, Z., Milojevic, M. M., Milosevic, M. P., and Andel Kovic, D. I. Glas. Hem. Drus., Beograd *31*, 243 (1966); Chem. Abstr. *69*, 59055z (1963).

Table II. 1-Substituted-4-Formylpyridinium Iodide Oximes

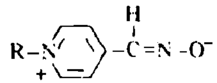


R	mp[a]	Color	Calcd						Found					
			C	H	Cl	I	N	O	C	H	Cl	I	N	O
	°C													
n-Dodecyl[b]	94-96	Yellow	51.7	7.5			6.7	3.8	51.6	7.3			6.9	3.7
Benzyl	113-117	Yellow	45.9	3.9		37.3		4.7	45.6	4.1		37.0		
p-Chlorobenzyl	198-199	Yellow	41.6	3.2	9.5	33.9			41.4	3.0	9.6	33.8		
o-Chlorobenzyl	165-167	Yellow	41.6	3.2			7.5	4.3	41.8	3.3			7.5	4.6
2,4-Dichlorobenzyl	207-208	Yellow	38.2	2.7		31.0	6.9	3.9	38.3	2.8		31.1	6.8	3.8
3,4-Dichlorobenzyl	211-213	Yellow	38.2	2.7		31.0	6.9	3.9	38.3	3.0			7.0	4.2
p-Methoxybenzyl	176-178	Yellow	45.4	4.1			7.6	8.7	45.7	4.3			7.6	8.9
p-Nitrobenzyl	184-187	Yellow	40.5	3.1			10.9	12.5	40.3	3.1			10.7	12.3
m-Nitrobenzyl	192-193	Yellow	40.5	3.1		33.0			40.3	3.4		32.9		

[a]Decomposition points except for the *n*-dodecyl derivative. A Thomas Hoover capillary melting point apparatus was used.

[b]Previously reported in Cohen, W., and Erlanger, B. F. J. Amer. Chem. Soc. 82, 3928 (1960).

Table III. 1-Substituted-4-Formylpyridinium Oximates



R	mp[a]	Color	Calcd					Found				
			C	H	Cl	N	O	C	H	Cl	N	O
	°C											
n-Dodecyl	103-105	Black	74.4	10.4	9.7	5.5		74.1	10.5	9.8	5.7	
Benzyl	121-123	Purple-black	73.6	5.7	13.2			73.3	5.8	13.3		
p-Chlorobenzyl	135-138	Brown	63.3	4.5			14.4	62.9	4.5			14.3
o-Chlorobenzyl	128-131	Black	63.3	4.5			14.4	62.9	4.6			14.1
2,4-Dichlorobenzyl	132-133	Black-brown	55.5	3.6			25.2	55.3	3.8			24.9
3,4-Dichlorobenzyl	152-154	Dark purple	55.5	3.6			25.3	55.6	3.6			25.3
p-Methoxybenzyl	105-109	Black	69.4	5.8			14.5	69.1	5.6			14.6
p-Nitrobenzyl[b]	113-134	Purple-black	59.4	4.3				59.5	4.4			
m-Nitrobenzyl	136-138	Dark brown	60.6	4.3	16.3			60.5	4.3	16.2		

[a]Decomposition points. A Thomas Hoover capillary melting point apparatus was used.
[b]Monohydrate.