tional 2 ml. of concentrated nitric acid. The trimetaphosphate portion was similarly converted to orthophosphate. The two solutions were neutralized with ammonium hydroxide until just acid to methyl red. Two ml. of the ammonium molybdate reagent was added to each portion to precipitate ammonium phosphomolybdate. These precipitates were separated by centrifuging, slurried with distilled water, and quantitatively transferred to aluminum pans (1 inch diameter, 1/8 inch deep). They were carefully evaporated to smooth surfaces with an infrared lamp and coated with 3 drops of the 3% collodion solution. The activities of the samples were determined by using a thin-walled self-quenching Geiger–Müller counter and a scale of 64 scaling unit. The samples were counted for ten minutes and the resulting activities corrected for background and decay of the $P^{32}$. The background was consistently 0.29 ± 0.01 count per second for a counting time of 100 minutes. The activity of the trimetaphosphate portion was within 10% of $8.0 \times 10^5$ counts per second per mole. The exchange data are given in Table I.

TABLE I

EXCHANGE DATA OF 0.005 *M* SODIUM TRIMETA- AND 0.03 *F* SODIUM HEXAMETAPHOSPHATE

| Temp., °C. | Initial *p*H | Time, hours | Activity hexameta, counts/sec. |
|---|---|---|---|
| 0 | 2.0 | 25 | 0.02 ± 0.04 |
| | 5.0 | 2 | 0.04 |
| | | 20 | .05 |
| | | 40 | .02 |
| | | 90 | .01 |
| | 10.0 | 26 | .05 |
| 25 | 2.0 | 25 | .00 |
| | 5.0 | 20 | .02 |
| | 10.0 | 26 | .05 |
| 100 | 2.0 | 0.17[a] | |
| | 5.0 | 0.17 | .08 |
| | 10.0 | 0.25 | .02 |

[a] Hexametaphosphate completely hydrolyzed—no precipitate.

## Discussion of Results

It is known that the various metaphosphates hydrolyze through a number of phosphate species ultimately to orthophosphate. Kinetic studies[8] indicate that sodium hexametaphosphate hydrolyzes to ortho and trimetaphosphate. The latter hydrolyzes to ortho and triphosphate, triphosphate going to pyro which then hydrolyzes to orthophosphate. Under the conditions of our experiments the trimetaphosphate was not appreciably hydrolyzed. However, the hexametaphosphate was slowly hydrolyzing to trimetaphosphate as the experiment proceeded, and thus one could not make the hexametaphosphate radioactive. When the trimetaphosphate is radioactive and the hexametaphosphate not, the latter will become radioactive only if an exchange mechanism is operating.

The 0.9 statistical error of the activities of the hexametaphosphate precipitates was about ±0.04 count per second. Thus, the observed activities of the hexametaphosphate precipitate are of the order of magnitude of this error. If complete exchange had occurred the activity of the precipitate would be about 13 counts per second.

(8) R. N. Bell, *Ind. Eng. Chem.*, **39**, 136 (1947).

In one further experiment a solution was made 0.03 *F* $(NaPO_3)_6$, 0.005 *M* $(NaP^*O_3)_3$ and 0.015 *M* $NaH_2P^*O_4$. After twenty-five hours at 25° the activity of the barium hexametaphosphate precipitate was 0.07 count per second.

Thus, we may conclude that the phosphorus of trimetaphosphate or orthophosphate will not exchange with that of hexametaphosphate under these experimental conditions. The reaction in which trimetaphosphate is formed from hexametaphosphate is therefore irreversible. These experiments also show that barium hexametaphosphate may be precipitated by the method of Jones[7] without appreciable co-precipitation of ortho and trimetaphosphate.

DEPARTMENT OF CHEMISTRY
ILLINOIS INSTITUTE OF TECHNOLOGY
CHICAGO, ILLINOIS
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## The Identity of β-Longilobine with Retrorsine

BY FRANK LOUIS WARREN, MEYER KROPMAN,[1] ROGER ADAMS, T. R. GOVINDACHARI AND J. H. LOOKER

In a recent paper Adams and Govindachari[1a] have described the separation of longilobine, obtained by Manske[2,3] from *Senecio longilobus*, into α-longilobine, $C_{18}H_{23}O_5N$, and β-longilobine, $C_{18}H_{25}O_6N$.

In two publications[4] it has been shown that both retrorsine and isatidine give on hydrolysis either retronecic or isatinecic acids according to the method employed. In fact, following the designation by Leisegang and Warren[5] of the structure of isatinecine as retreonecine N-oxide, it has been shown that isatidine is retrorsine N-oxide. Retronecic and isatinecic acids are geometrical isomers and their structures have been elucidated.[4a]

β-Longilobine has the characters of retrorsine[3,6] and gives on hydrolysis retronecine and β-longinecic acid, $C_{10}H_{16}O_6$, which seemed to be identical with the known isatinecic acid, $C_{10}H_{16}O_6$.[7]

| | M. p., °C. | $[\alpha]_D$ | $CH_3I$ Cpd. |
|---|---|---|---|
| β-Longilobine[1] | 207–208 | −48.6° | 256° |
| Retrorsine[6] | 212 | | 260° |
| Retrorsine[3] | 214–215 | −17.6° | 266° |
| β-Longinecic acid[1] | 146–147 | − 9.06° | |
| Isatinecic acid[7] | 148.5 | | |

Furthermore, β-longilobine on reduction[1] takes up two moles of hydrogen to give the tetrahydro compound as an amorphous powder which, hydrolyzed with barium hydroxide, gave retronecanol

(1) C. S. I. R. Bursar.
(1a) Adams and Govindachari, THIS JOURNAL, **71**, 1180 (1949).
(2) Manske, *Can. J. Res.*, **17B**, 1 (1939).
(3) Manske, *ibid.*, **5**, 651 (1931).
(4) Christie, Kropman, Leisegang and Warren, *J. Chem. Soc.*, 1700 (1949); (a) Christie, Kropman, Novellie and Warren, *ibid.*, 1708 (1949).
(5) Leisegang and Warren, *ibid.*, 486 (1949).
(6) Barger, Seshadri, Watt and Yabuta, *ibid.*, 11 (1935).
(7) de Waal, *Onderstepoort J. Vet. Sci. Animal Husb.*, **14**, 443 (1940).

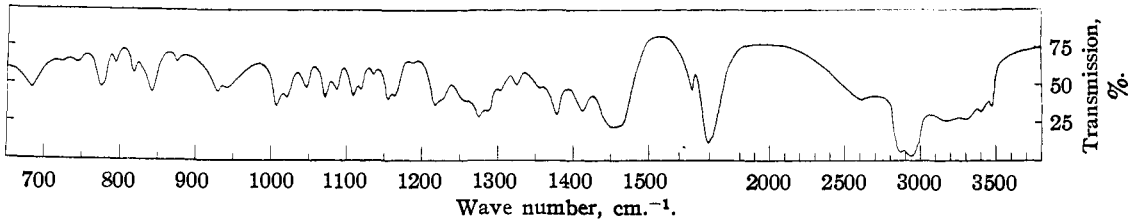


Fig. 1.—Infrared spectrum of β-longinecic acid (isatinecic acid) determined in Nujol mull.

and β-longinecic acid (isatinecic acid). Barger, *et al.*,[6] gave a similar description of the reduction and reduction product of retrorsine, but they hydrolyzed with sodium hydroxide and obtained retronecanol and retronecic acid which is the stable geometrical form.

We have now determined the infrared spectra of specimens of retrorsine and isatinecic acid and found them to be identical with those of β-longilobine and β-longinecic acid (*cf.* Adams and Govindachari[1]). Furthermore, a mixture of isatinecic acid, m. p. 148–148.5° (cor.) and β-longinecic acid, m. p. 148–149° (cor.) gave no depression. These results establish unequivocally the identity of the two alkaloids.

The sample of β-longinecic acid used for the infrared absorption reported in a previous paper[1] was found to contain small amounts of impurity, probably retronecic acid lactone. The infrared spectrum of a perfectly pure sample of β-longinecic acid which is identical with that of isatinecic acid is given in Fig. 1.

The melting points of the various *Senecio* alkaloids and the acid moieties from them deserve comment. Rather marked differences in values are reported in the literature for the same products even in those cases where the products can be assumed to be essentially pure. The values recorded above for the acids were obtained by starting in a cold bath and heating at about 2° a minute. Using a preheated bath at 136° and heating 1° a minute lowers the m. p. by about 5°. The alkaloids themselves decompose gradually upon heating so that the only satisfactory procedure is to use a preheated bath (180°).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NATAL
PIETERMARITZBURG, S. AFRICA
NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS RECEIVED DECEMBER 27, 1949

## The Use of N-Methylformanilide in the Preparation of Thiophenecarboxaldehydes

BY ARTHUR W. WESTON AND R. J. MICHAELS, JR.

The formation of 2-thiophenecarboxaldehydes by the direct formylation of the thiophene nucleus, employing N-methylformanilide and phosphorus oxychloride, has recently been disclosed.[1] This note presents some of our observations regarding this thiophenecarboxaldehyde preparation which we had also investigated[2] in connection with an alternate synthesis of N,N-dimethyl-N′-(2-pyridyl)-N′-(2-thenyl)-ethylenediamine (Thenylene.)[3]

With thiophene, we found that N-ethylformanilide gave yields of 2-thiophenecarboxaldehyde comparable to those obtained with N-methylformanilide. On the other hand, substitution of formamide for N-methylformanilide proved detrimental as only a trace of aldehyde was formed. Phosphorus oxychloride was the preferred condensing agent because of its solvent properties. Although phosphorus oxybromide gave similar results, a solvent such as chlorobenzene was usually necessary to ensure a homogeneous reaction mixture.

In contrast to the reported conditions,[1] in which the reaction mixture is heated on the steam-bath and then quickly removed as the exothermic reaction progresses, we found that the reaction proceeded equally well at room temperature, thereby increasing its utility. Under our conditions, an appreciable increase in the reaction temperature usually resulted in a decrease in the amount of aldehyde formed. This depended somewhat upon the nature of the group attached to the thiophene nucleus, the halogenated thiophenes being less affected than the alkylthiophenes or thiophene itself. Equimolar amounts of the reactants or a slight excess of the thiophene gave the best results.

With 2-bromothiophene, an impure 5-bromo-2-thiophenecarboxaldehyde was formed, due apparently to halogen interchange with the phosphorus oxychloride. The material obtained, however, could be purified by careful fractionation. King and Nord[1] obtained only the 5-chloro derivative from this reaction. This difficulty can be overcome by employing phosphorus oxybromide.[4] 2-Nitro- and 2,5-dichlorothiophene gave no isolable amounts of aldehyde. An attempt to formylate 2-thiophenecarboxaldehyde further resulted in tar formation.

It has been found possible to introduce a 3-formyl group into a thiophene derivative by this reaction. 2,5-Dimethylthiophene gave the corresponding 3-carboxaldehyde although the yield was much lower than in the other cases. With

(1) King and Nord, *J. Org. Chem.*, **14**, 635 (1948).

(2) British Patent Specification No. 27,882 (1947).

(3) Weston, THIS JOURNAL, **69**, 980 (1947).

(4) After this manuscript was submitted, King and Nord, *J. Org. Chem.*, **14**, 405 (1949), reported a similar preparation of the 5-bromo-2-thiophenecarboxaldehyde.