Determination of the position of the reducing carbonyl radical necessitates the preparation of larger quantities of ketolevoglucosan.

Molecular Weights of the Anhydro Derivatives.—The ordinary cryoscopic method for determination of molecular weight could not be employed due to the slight solubility of ketolevoglucosan in ordinary solvents and the limited quantities of *d*-chitoketuronic acid available. Barger's method as modified by Rast[7] gave satisfactory results in control determinations of the molecular weight of glucose but it proved entirely inapplicable to the anhydro derivatives under investigation. A series of dilutions lost water to an intermediate glucose standard, probably because of gradual association or polymerization of the anhydro derivatives. Rast's camphor method[8] gave the following molecular weight values: 330 for ketolevoglucosan, 1100 for brucine *d*-chitoketuronate and 350 for pure levoglucosan. These values are approximately dimolecular but levoglucosan has been shown by the ordinary cryoscopic method to be monomolecular. A common interpretation would imply that the anhydro derivatives reported here are also monomolecular.

Summary

1. *l*-Xyloketuronic acid and *d*-chitoketuronic acid have been isolated as crystalline brucine salts.

2. The keturonic acid similarly isolated from oxidized *l*-arabinose solutions resembles *d*-xyloketuronic acid closely but complete identity of these acids has not been proven.

3. An anhydride of a dicarbonyl sugar has been isolated from oxidized levoglucosan solutions.

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and one potential ketone radical be *keturoses* and that their configurations be referred to the parent ketoses, as in the suggested nomenclature for keturonic acids.[4] Examples: *l-sorbo-6-urose* for the identical structures, *d*-gluconose and *l*-idonose; and *d-fructo-1-urose* for *d*-glucosone.

This terminology avoids multiple naming, is generally applicable and suggests functional relations of these sugars to their uronic acid oxidation products. Present indications are that the dicarbonyl sugar anhydride isolated by the authors is 1,6-anhydro-*l*-sorbo-6-urose (1,6-anhydro-gluconose) but the temporary designation as ketolevoglucosan is preferred until the position of the second carbonyl radical is proven.

(7) Abderhalden, "Handbuch der biologischen Arbeitsmethoden," 1928, Abt. III, Teil AI, p. 751.

(8) Kamm, "Qualitative Analysis," John Wiley and Sons, New York, N. Y., 1932, p. 131.

[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

The Action of Aromatic Amines on 3-Nitro-6-iodonitrostyrene

BY DAVID E. WORRALL AND FREDERICK BENINGTON

Whereas nitration of 2-chloro- and 2-bromonitrostyrene does not entirely inhibit its addition capacity for certain aromatic amines,[1] the halogenated derivatives are not as reactive as nitrostyrene itself. We now find that the analogous iodo derivative closely parallels nitrostyrene in all its reactions with nitrogen bases.

Experimental

α - Nitro - β-(2 - iodophenyl) - ethylene.—Iodobenzaldehyde prepared through the diazo reaction[2] from *o*-aminobenzaldehyde[3] was condensed with nitromethane in the presence of triethylamine; yield, after steam distillation, 65–70%. It separated from alcohol as pale yellow needles, m. p. 113–114°. On oxidation with potassium permanganate it gave 6-iodo-3-nitrobenzoic acid[4] which recrystallized from alcohol in long yellow needles, m. p. approx. 190°.

Anal. Calcd. for $C_8H_6INO_2$: C, 34.8; H, 2.2. Found: C, 35.2; H, 2.5.

α-Nitro-β-(6-iodo-3-nitrophenyl)-ethylene.—Prepared by nitration of the above compound using fuming acid, it was obtained from alcohol as tiny pale yellow needles, m. p. 145–146°.

Anal. Calcd. for $C_8H_5IN_2O_4$: C, 30.0; H, 1.5. Found: C, 30.2; H, 1.3.

The product from bromination of the iodo compound separated as an oil on treatment with a warm alcoholic solution of potassium acetate. On mixing with fuming nitric acid, it solidified and was recrystallized from alcohol in yellow prismatic needles, m. p. 136–137°.

Anal. Calcd. for $C_8H_4BrIN_2O_4$: C, 24.0; H, 1.0. Found: C, 24.4; H, 1.2.

It was observed to form an addition compound with *p*-toluidine, but was not further investigated.

The same procedure previously developed[1] was used for the preparation of the addition compounds. The products, yellow or orange-yellow and deeper in color than the parent nitrostyrene, were recrystallized from alcohol, separating as narrow plates or prismatic needles. The melting points frequently were not sharp and were always accompanied by decomposition so that they varied with the rate of heating. Difficulty was experienced in preparing the *o*-toluidino compound as it did not always separate even on long standing. The anilino derivative formed only after several days. The *o*- and *m*-anisidine derivatives formed more readily than the corresponding toluidine. The hydroxylamino and semicarbazido products were colorless.

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(1) Worrall, THIS JOURNAL, **60**, 2845 (1938).

(2) Patterson, *J. Chem. Soc.*, **69**, 1006 (1896).

(3) Bamberger, *Ber.*, **60**, 319 (1927).

(4) Goldstein and Grampoloff, *Helv. Chim. Acta*, **13**, 310 (1930).

TABLE I

β-DERIVATIVES OF α-NITRO-β-(6-IODO-3-NITROPHENYL)-ETHANE

Substance	M. p., °C.	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
Anilino	115–116	$C_{14}H_{12}IN_3O_4$	40.7	2.9	41.3	2.8
o-Toluidino	168–170	$C_{15}H_{14}IN_3O_4$	42.2	3.3	42.5	3.5
m-Toluidino	113–114	$C_{15}H_{14}IN_3O_4$	42.2	3.3	42.7	3.4
p-Toluidino	130–132	$C_{15}H_{14}IN_3O_4$	42.2	3.3	42.7	3.5
o-Anisidino[a]	146–148	$C_{15}H_{14}IN_3O_5$	40.6	3.2	40.9	3.2
m-Anisidino	140–142	$C_{15}H_{14}IN_3O_5$	40.6	3.2	41.1	3.2
p-Anisidino	123–124	$C_{15}H_{14}IN_3O_5$	40.6	3.2	40.9	3.4
Phenylhydrazine	142–144	$C_{14}H_{13}IN_4O_4$	39.3	3.0	40.2	3.0
β-Naphthylhydrazine	143–144	$C_{18}H_{15}IN_4O_4$	45.2	3.1	. .	3.3
Hydroxylamine	103–105	$C_8H_8IN_3O_5$	27.2	2.3	27.6	2.5
Semicarbazide	187–188	$C_9H_{10}IN_5O_5$	27.3	2.5	27.8	2.5

[a] Both *o*- and *m*-anisidine also react readily with nitrochloronitrostyrene.

α,α′-Di-(6-iodo-3-nitrophenyl)-β,β′-dinitro-diethylamine.—A dry benzene solution of the iodostyrene saturated with ammonia was allowed to evaporate spontaneously to a small bulk. The product, recrystallized from benzene, separated in clusters of nearly colorless needles, m. p. 113–114° with foaming.

Anal. Calcd. for $C_{16}H_{13}I_2N_5O_8$: C, 29.2; H, 2.0. Found: C, 29.7; H, 2.1.

Summary

3-Nitro-6-iodonitrostyrene has been prepared and its additive capacity examined with certain organic bases. It is in this respect the most active nitrostyrene so far studied.

MEDFORD, MASS. RECEIVED OCTOBER 9, 1939

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

The Condensation of Butyraldehyde and Aniline

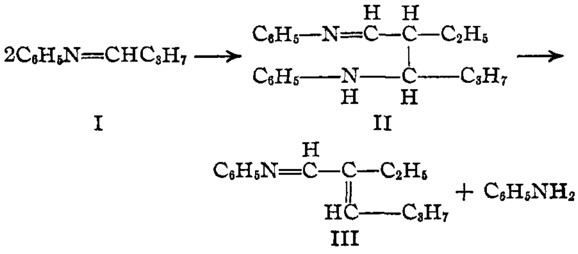
BY M. S. KHARASCH, ISADORE RICHLIN AND FRANK R. MAYO

Introduction

Two general types of structure have been suggested for the dimeric Schiff bases, the cyclic structure by Ingold and Piggott,[1] and the aldol-type structure by Miller and Plöchl.[2] The weight of chemical evidence is in favor of the latter. The work of Eibner is particularly convincing.[3] Our research has been concerned with the determination of the structure of the compounds formed by the condensation of *n*-butyraldehyde and aniline in neutral and in acid media.

Discussion of Results

Two products have thus far been isolated from the reaction of aniline and *n*-butyraldehyde in neutral media: one, a monomeric Schiff base (as the hydrogen cyanide addition product), by Rampini, and the other, its dimer, by Williams.[4] We have found that in the presence of even small amounts of acid, a yellow oil is formed during the condensation. The same oil is formed by treating the crystalline dimer with small amounts of organic acids or by allowing the dimer preparation to stand for several days. In the latter case, the catalyst is the butyric acid formed by atmospheric oxidation, since a similar preparation, carried out in an evacuated bomb-tube, will not produce the oil unless acid had been previously added. Rampini noted this oil but did not investigate it; his failure to obtain the dimer was due to his using aldehyde containing acid. It has been shown by us that this oil is the anil of α-ethyl-β-propylacrolein, formed as follows



$$2C_6H_5N{=}CHC_3H_7 \longrightarrow \begin{array}{l} C_6H_5{-}N{=}\overset{H}{C}{-}\overset{H}{C}{-}C_2H_5 \\ \qquad\qquad\quad | \\ C_6H_5{-}\underset{H}{N}{-}\underset{H}{C}{-}C_3H_7 \end{array} \longrightarrow \begin{array}{l} C_6H_5N{=}\overset{H}{C}{-}C{-}C_2H_5 \\ \qquad\qquad \| \\ \qquad\quad HC{-}C_3H_7 \end{array} + C_6H_5NH_2$$

I II III

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[1] Ingold and Piggott, *J. Chem. Soc.*, **121**, 2793 (1922); **123**, 2745 (1923).

[2] Miller and Plöchl, *Ber.*, **25**, 2020 (1892).

[3] Eibner, *Ann.*, **318**, 58 (1901); **328**, 121 (1903); **329**, 210 (1903).

[4] Rampini, *Ber.*, **25**, 2038 (1892); Williams, U. S. Patent 1,908,093, May 9, 1933; *C. A.*, **27**, 3854 (1933).