reduction has the same composition and molecular weight as 2-aminomethyl-3-aminoquinoline.

The above fact has shown that the active methyl was converted into a cyano group. The possible mechanism of this reaction may be proposed as follows : The first step should be the action of nitrous acid at the active methyl group of quinoline; in the second step, this nitroso derivative would change into oxime acylate, and the final step is the elimination of acetic acid from aldoxime acylate. The experiments described below were carried out in order to prove this mechanism.

When the chloroform solution of quinaldine 1-oxide with suspended silver nitrite was treated with acetyl chloride under cooling, slightly yellow needles (V), $C_{12}H_{10}O_3N_2$, m.p. 135.5°, were obtained. Its ultraviolet absorption spectrum was like that of 2-cyanoquinoline 1-oxide and showed the solvent effect, and its infrared spectrum exhibited characteristic peaks at 1771 and 1196 cm^{-1} which were respectively assigned to C=O(R-CO-O-C=C type) and C-O-N=. In addition to these spectral data, the crystals were quantitatively converted into (III) under heating in polar solvents. From a consideration of these data, (V) was concluded to be quinoline 1-oxide 2-aldoxime acetate.

The presence of an intermediate product proved the reliability of the above reaction mechanism. The improvement and application of this reaction is being studied at present.

The writer expresses his deep gratitude to Prof. E. Ochiai of the University of Tokyo for his unfailing guidance.

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May 26, 1959

UDC 543.864 : 547.457 : 547.584

Microdetection of Reducing Sugars with 3,6-Dinitrophthalic Acid*

Several nitro compounds are widely used in the detection and estimation of reducing sugars, giving a specific coloration when heated with the sugar in alkaline medium. These involve picric acid,[1] 3,5-dinitrosalicylic acid,[2] and 3,4-dinitrobenzoic acid.[3]

In the writers' laboratory, 3,6-dinitrophthalic acid proved to give a more sensitive color reaction with reducing sugars than the reagents mentioned above. When the new reagent dissolved in aqueous sodium carbonate solution is heated with a small amount of a reducing sugar, an orange-red color appears in several minutes. This color changes rapidly to yellow, but if sodium thiosulfate is added to the reaction mixture, the color is stable for several days, and is easily distinguished from a blank test color which is only a faint yellow. In sodium hydroxide solution of the reagent, the color develops more rapidly but it is less stable, and the blank test gives a deeper color. Therefore, it is preferable to carry out this reaction in sodium carbonate solution.

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* cf. Part XVII on Organic Analysis, This Bulletin, in press (1959).
1) C.D. Braun : J. prakt. Chem., **96**, 411(1865).
2) J.B. Sumner, V.A. Graham : J. Biol. Chem., **47**, 5(1921).
3) E. Borel, H. Deuel : Helv. Chim. Acta, **36**, 801(1953).

3,6-Dinitrophthalic acid, which was previously prepared by one of the writers,[4] was dissolved in ether and passed through a short column of activated carbon. The ethereal solution was concentrated, separated crystals were collected, washed with ether, and dried in a desiccator.

The reagent solution was prepared by dissolving 250 mg. of the purified acid in 100 cc. of 5% Na_2CO_3, to which 5 g. of $Na_2S_2O_3 \cdot 5H_2O$ was added. This almost colorless solution was stored in a light-resistant container.

Procedure : To one drop of aqueous solution of a reducing sugar, one drop of the reagent solution is added and the mixture is heated on a boiling water bath for 5~10 minutes. An orange to red color develops according to the concentration of the sugar.

TABLE I. Limit of Detection of Reducing Sugars (in one drop of water)

	γ		γ
Glucose	0.2	Maltose	0.4
Fructose	0.2	Lactose	0.2
Galactose	0.8	Ascorbic acid	0.8
Arabinose	0.4	Glucuronic acid	0.4
Xylose	0.2	Galacturonic acid	0.4

The limit of the quantity of reducing sugars in one drop of water (about 0.05 cc.) detected by this method is shown in Table I. This reaction gives negative result with sucrose, alcohols, and polyhydric alcohols. It is interfered by inorganic and organic reducing agents.

Estimation of reducing sugars with the reagent is in progress.

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[4] T. Momose, M. Torigoe : Yakugaku Zasshi, **71**, 977(1951).

UDC 547.677.2 : 547.94.02

Über die Konstitution des Alkylphenanthrens (Schmp. 79~81°), eines Dehydrierungsprodukts des Songorins

Bei der Selen-Dehydrierung des Songorins erhielt Kuzovkov[1] ein Alkylphenanthren, $C_{18}H_{18}$, vom Schmp. 80.5~81.5° (Trinitrobenzolat, Schmp. 154.5°; Pikrat, Schmp. 134~134.5°), welches mit dem von ihm hergestellten 1,10-Dimethyl-7-äthylphenathren identifiziert wurde.[2] Hierbei haben Wiesner und seine Forschungsgruppe[2] darauf hingewiesen, dass 1,9-Dimethyl-7-äthylphenanthren auch in Frage käme, was auf die bei der letzten Aromatisierungsstufe der Synthese bestehende Umlagerunsmöglichkeit der Methylgruppe auf der 9-Stellung in die 10-Stellung zurückzuführen ist.

Neulich hat einer von uns[3] durch Selen-Dehydrierung von Isodesoxosongorin-Hydrochlorid,[*1] das aus Songorin durch Reduktion nach Huang-Minlon und anschliessende

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[*1] Da die Shimoburobase-I mit dem Songorin identifiziert wurde,[2] wollen wir die Isoshimoburobase-I bzw. Desoxoshimoburobase-I Isosongorin bzw. Desoxosongorin nennen.

[1] A.D. Kuzovkov : J. Gen. Chem. U.S.S.R.(Eng. Transl.), **25**, 1955(1955).

[2] K. Wiesner, S. Ito, Z. Valenta : Experientia, **14**, 167(1958).

[3] T. Sugasawa : Eine noch unpublizierte Arbeit, die bald veröffentlicht werden wird.