

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

Investigations in the Retene Field. III. Some New Nitroretenols, Nitrofluorenones and Related Compounds

BY MARSTON T. BOGERT AND TORSTEN HASSELSTRÖM

Attempts by various investigators¹ to obtain crystalline nitro derivatives by the direct nitration of retene itself have not been very successful, the results in most cases having been either tars or oxidation products.

Ekstrand^{1c} obtained a yellow flocculent precipitate when he diluted the acid mixture upon the completion of the nitration of retene, but it resinified when crystallization was attempted. Arnot^{1e} obtained a similar product, which he stated to be a dinitroretene, for he reduced it to a base^{1f} from which azo dyes were prepared by the usual reactions. He claimed also the production of a nitroretene sulfonic acid by nitration of retene dissolved in a 20% oleum, and of a dinitroretenequinone from the quinone, but none of these products appear to have been either crystalline or analytically pure.

Heiduschka and Scheller² have reported a nitrotribromoretenequinone, and Bogert and Hasselström³ a crystalline dinitroacetylretene.

To this scanty list, we can now add a mononitro derivative of 6-acetoxyretene (I), prepared by direct nitration of the latter.^{1h,4} On reduction, this gave us an unstable amino derivative, acetylation of which yielded a stable crystalline compound. Fieser and Young⁴ found that 5-amino-6-hydroxyretene was similarly unstable and also resorted to acetylation, to obtain a crystalline pure product.

Experiments were carried out on the nitration of the closely related so-called "retene ketone" (1-methyl-7-isopropylfluorenone) (II).^{1d,5} Bamberger and Hooker⁶ have shown that the 1-methyl-7-isopropylfluorene yields without difficulty a dinitro derivative. It was to be expected, therefore, that the retene ketone likewise

(1) (a) Fehling, *Ann.*, **106**, 390 (1858); (b) Fritzsche, *ibid.*, **109**, 251 (1859); (c) Ekstrand, *ibid.*, **185**, 79 (1877); (d) Bamberger and Hooker, *ibid.*, **229**, 116, 144 (1885); (e) Arnot, German Patent 315,623 (1919); *Chem. Zentr.*, II, 188 (1920); (f) Arnot, British Patent 149,354 (1920); *Chem. Zentr.*, II, 37 (1921); (g) Wahlforss, Thesis, Helsingfors, 1924, p. 24; (h) Komppa and Wahlforss, *THIS JOURNAL*, **52**, 5009 (1930).

(2) Heiduschka and Scheller, *Arch. Pharm.*, **248**, 89 (1909).

(3) Bogert and Hasselström, *THIS JOURNAL*, **53**, 3465 (1931).

(4) Fieser and Young, *ibid.*, **53**, 4120 (1931).

(5) Komppa and Fogelberg, *ibid.*, **54**, 2900 (1932).

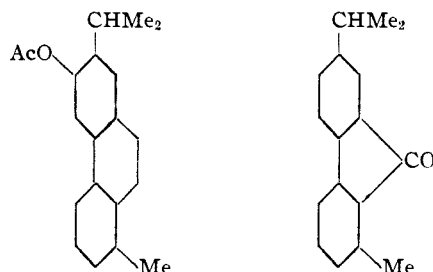
(6) Ref. 1d, p. 144. See also Schmidt and Bauer, *Ber.*, **38**, 3758 (1905).

could be smoothly nitrated, and this proved to be the case. The mononitro derivative so prepared was reduced to the amine and the latter acetylated.

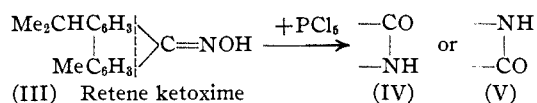
Bamberger and Hooker⁷ were unsuccessful in their attempts to obtain the retene ketoxime (III). Our experiments have now shown that the oxime can be prepared from the ketone if the reaction be conducted in anhydrous media. By treatment with phosphorus pentachloride, this oxime underwent the usual Beckmann rearrangement, with formation of the corresponding phenanthridone (IV or V).⁸

As is well known,⁹ phenanthraquinones may be converted into fluorenones by treatment with caustic alkalies, and this is occasionally of service in determining the constitution of the original phenanthraquinone; but when this reaction was applied to 6-acetoxyretenequinone, the rearrangement failed and only 6-hydroxyretenequinone was formed. This agrees with the experience of Fieser and Young.⁴

When 6-hydroxyretenequinone was reduced in alkali solution with sodium hydrosulfite, a vat resulted which dyed cotton a peach red.



(I) 6-Acetoxyretene (II) Retene ketone



(III) Retene ketoxime

(IV) (V)

The constitutions of the new nitro derivatives and of the phenanthridone mentioned above have not been determined as yet.

(7) Ref. 1d, p. 139.

(8) (a) Wegerhof, *Ann.*, **252**, 38 (1889); (b) Pictet and Gosset, *Arch. sci. phys. nat.*, [4] **3**, 37 (1897); (c) Moore and Huntress, *THIS JOURNAL*, **49**, 2618 (1927).

(9) Schmidt and Bauer, *Ber.*, **38**, 3755 (1905).

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Experimental

Nitro-6-acetoxyretene.—To a solution of 5 g. of 6-acetoxyretene (m. p. 133–134°, corr.) in 20 cc. of glacial acetic acid, there was added dropwise a solution of 15 cc. of fuming (sp. gr. 1.52) nitric acid in 15 cc. of glacial acetic acid, maintaining the temperature of the mixture at 15–20°. Upon the completion of the nitration, the mixture was poured upon ice, the orange-brown precipitate was collected, washed with water, then with a dilute sodium bicarbonate solution, with water again and dried. Some tarry impurities were removed by extraction with petroleum ether. The insoluble residue was crystallized first from glacial acetic acid (yield, 3.5 g.) then from benzene and finally from alcohol, in which last solvent it dissolved but sparingly. The purified product formed pale yellow rectangular plates, m. p. 194.5–195.5° (corr.).

Anal. Calcd. for $C_{20}H_{19}O_4N$: C, 71.2; H, 5.6. Found: C, 71.2; H, 5.7.

Amino-6-acetoxyretene.—A solution of 30 g. of stannous chloride in 250 cc. of alcohol, saturated with dry hydrogen chloride, was added to a suspension of 5 g. of the nitro-acetylretene in 200 cc. of hot alcohol and the mixture was refluxed for two hours and then cooled. Water was added, followed by sodium bicarbonate. The precipitate, consisting of the amine and tin salts, was removed, dried at room temperature under diminished pressure and the greenish solid extracted with ether. Evaporation of the ether left 4.2 g. of nearly colorless residue, which was dissolved in hot benzene. As the benzene solution cooled, there separated a jelly which yielded on filtering an amorphous solid, which rapidly turned greenish in the light and air. An attempted recrystallization from alcohol likewise gave a jelly, which in the dry unstable amorphous condition melted at about 215–217° (corr.).

Acetyl Derivative.—In view of the instability of the above amine it was acetylated by digestion with acetic anhydride and sodium acetate; yield, nearly that calculated; colorless fine crystals (from alcohol), m. p. 203.5–204.5° (corr.).

Anal. Calcd. for $C_{22}H_{23}O_3N$: C, 75.6; H, 6.6. Found: C, 75.4; H, 6.7.

Nitroretene Ketone (Nitro-1-methyl-7-isopropylfluorenone).—Retene ketone (1.5 g.) (m. p. 88–89°) was nitrated in glacial acetic acid solution with fuming nitric acid (10 cc.), essentially as described for the nitration of acetoxyretene above, and the crude product was crystallized first from alcohol and then from acetone. The purified compound appeared as bright yellow needles, m. p. 165.5° (corr.); yield, 1.3 g.

Anal. Calcd. for $C_{17}H_{16}O_3N$: C, 72.6; H, 5.4. Found: C, 72.3; H, 5.5.

Aminoretene Ketone (Amino-1-methyl-7-isopropylfluorenone).—The nitro ketone was reduced with stannous chloride in an alcoholic solution saturated with dry hydrogen chloride. After boiling the mixture for a few minutes, it became colorless and the tin salt of the amine separated. When the mixture was cold, this precipitate was removed and digested with a 5% sodium hydroxide solution, which liberated the dark red amine. This was extracted first with acetone, to free it from some tin oxide, and the residue which remained after the evaporation of the filtered acetone extract was crystallized from alcohol. The product so obtained formed dark red needles, m. p. 146° (corr.); yield, nearly that calculated.

Anal. Calcd. for $C_{17}H_{17}ON$: C, 81.3; H, 6.8. Found: C, 81.1; H, 7.4.

Acetyl Derivative.—Bright yellow needles (from alcohol), m. p. 197.5–198.5° (corr.).

Anal. Calcd. for $C_{19}H_{19}O_2N$: C, 77.8; H, 6.5. Found: C, 77.4; H, 6.9.

Oxime of Acetyl Derivative.—A mixture of 0.3 g. of the above acetaminoretene ketone, 5 g. of hydroxylamine hydrochloride, 5 g. of barium carbonate and 30 cc. of absolute alcohol, was refluxed for twelve hours. When cold, the mixture was filtered and the filtrate diluted with water. This precipitated the oxime in nearly theoretical yield. Recrystallized from alcohol, it appeared in pale yellowish plates, which began to decompose at about 250° and liquefied at about 254–255.5° (corr.).

Anal. Calcd. for $C_{19}H_{20}O_2N_2$: C, 74.0; H, 6.5. Found: C, 74.3; H, 6.9.

Retene ketoxime (1-methyl-7-isopropylfluorenon-oxime) was prepared similarly, by refluxing for eight hours a mixture of 0.5 g. of retene ketone, 0.5 g. of hydroxylamine hydrochloride, 0.7 g. of barium carbonate, in 20 cc. of methanol; yield, 0.5 g. Recrystallized from dilute alcohol, it formed colorless needles, m. p. 174.5° (corr.).

Anal. Calcd. for $C_{17}H_{17}ON$: C, 81.3; H, 6.8. Found: C, 81.0; H, 6.7.

Methyl-isopropylphenanthridone (IV or V).—To a solution of 5 g. of retene ketoxime in 40 cc. of dry ether, there was added in small portions 7.5 g. of phosphorus pentachloride. Upon the conclusion of the reaction, the ether was evaporated. The residue was treated with ice water, washed with a sodium bicarbonate solution and extracted with ether. The ether extract was evaporated and the solid residue (2 g.) was crystallized first from alcohol and then from benzene, when it appeared in colorless prismatic needles, m. p. 219.5–220.5° (corr.).

Anal. Calcd. for $C_{17}H_{17}ON$: C, 81.3; H, 6.8; N, 5.6. Found: C, 80.9; H, 7.2; N, 6.2.

Action of Alkali upon 6-Acetoxyretenequinone.—When this quinone was refluxed for four hours with a strong (50%) potassium hydroxide solution, the only product isolated from the mixture crystallized from alcohol in dark orange prisms, which decomposed when heated and appeared to be identical with the 6-hydroxyretenequinone described by Fieser and Young.⁴

A Vat Dye from 6-Hydroxyretenequinone.—When a solution of 1 g. of 6-hydroxyretenequinone in 100 cc. of

dilute (10%) sodium hydroxide was reduced by the addition of 0.5 g. of sodium hydrosulfite, there resulted a pale yellow vat, which dyed cotton a peach red, fairly stable to laundering but fugitive to light.

Summary

1. 6-Acetoxyretene is readily nitrated to a crystalline mononitro derivative, which can be reduced to the corresponding amine.

2. Retene ketone (1-methyl-7-isopropylfluorenone) likewise yields a mononitro derivative by direct nitration, and this nitro derivative also is easily reduced to the amine.

3. Retene ketone, in anhydrous media, gives the oxime which, by phosphorus pentachloride, is rearranged to a phenanthridone.

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The Free Aldehyde Form of Fucose Tetraacetate

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The methods previously employed in this Laboratory for the synthesis of non-cyclic sugar acetates¹ have now been extended to the methylpentose *l*-fucose. This substance has the configuration of *l*-galactose and may be named *l*-galactomethyllose. The open chain or aldehydgalactose pentaacetate (CH₂OAc(CHOAc)₄CHO) differed from the other open chain acetates in that it formed well-defined carbonyl addition compounds.² The same property has been found for the corresponding fucose compound (CH₂(CHOAc)₄CHO). Aldehydo-*l*-fucose tetraacetate shows an unusually low solubility in all solvents. This same property is shown by the corresponding open chain tetraacetate of galactose, recently prepared by Micheel and Suckfuell,³ in which the terminal methyl group of fucose is replaced by a primary alcohol group. This low solubility of the fucose acetate made its isolation quite a different problem from that of the other open chain sugar acetates.

For comparative purposes, one of the ring acetates of fucose (CH₂CH(CHOAc)₃CHOAc) was also synthesized.

Experimental

***l*-Fucose Ethyl Mercaptal Tetraacetate.**—The fucose used in this work was prepared from seaweed by the excellent method of Clark.⁴ Twenty-five grams of fucose ethyl mercaptal⁵ was dissolved in 150 cc. of pyridine and 225 cc. of acetic anhydride added. The mixture was held

at 0° for one hour and then at room temperature for eighteen hours. The solution was then poured into five liters of ice water, whereupon the acetate crystallized immediately. This was filtered and washed with cold water. Pure material was obtained by dissolving the product in 150 cc. of hot methanol and adding water to opalescence; yield, 35 g. or 87%; lustrous plates soluble in warm water and warm petroleum ether, and very soluble in other common organic solvents.

Anal. Calcd. for C₈H₈O₄(SC₂H₅)₂(COCH₃)₄: S, 14.62; acetyl, 9.13 cc. 0.1 N NaOH per 100 mg. Found: S, 14.56; acetyl, 9.13 cc.

Aldehydo-*l*-fucose Tetraacetate.—Fifteen grams of fucose ethyl mercaptal tetraacetate was dissolved in 60 cc. of acetone in a three-necked flask equipped with a mechanical stirrer, a condenser and a dropping funnel. Thirty grams of finely powdered cadmium carbonate and 7.5 cc. of water were added, and under vigorous stirring a solution of 30 g. of mercuric chloride in 60 cc. of acetone was added drop by drop. After twenty hours of constant stirring the reaction mixture was heated at a bath temperature of 50° for fifteen minutes and finally refluxed at 60° for the same length of time. The mixture was then rapidly filtered while still warm. White crystals of aldehydo-*l*-fucose tetraacetate separated almost immediately. The crystallization was completed by standing overnight in the ice box and the product filtered and washed with cold acetone; yield, 9.6 g. of crude material.

Pure material was obtained by dissolving the crude product in acetylene tetrachloride, adding carboraffin and filtering. Petroleum ether was added to the filtrate to incipient crystallization, and the solution placed in the ice box overnight to complete the crystallization. The white crystals produced by this procedure were filtered under suction and washed with petroleum ether; yield, 7.8 g.

The substance showed a constant rotation in acetylene tetrachloride solution but mutarotated slowly in methanol, changing from a specific rotation of +22 to +9° in about four days at room temperature. It is sparingly soluble in methanol, ethyl acetate and in acetone; almost insoluble in ether, ethanol and chloroform, and is insoluble in water, petroleum ether, benzene and carbon tetrachloride. It dissolves quite readily in pyridine and warm acetylene

(1) M. L. Wolfrom, *THIS JOURNAL*, **51**, 2188 (1929); **52**, 2464 (1930); M. L. Wolfrom and Mildred R. Newlin, *ibid.*, **52**, 3619 (1930); **53**, 4379 (1931).

(2) M. L. Wolfrom, *ibid.*, **53**, 2275 (1931); M. L. Wolfrom and W. M. Morgan, *ibid.*, **54**, 3390 (1932).

(3) F. Micheel and F. Suckfuell, *Ann.*, **502**, 85 (1933).

(4) E. P. Clark, *J. Biol. Chem.*, **54**, 65 (1922).

(5) E. Votěček and V. Veselý, *Z. Zuckerind. Böhmen*, **40**, 207 (1916).