From the reaction mixture it was found that the volatile amine fraction accounted for 85% or more of the total nitrogen of the proteins and model compounds subjected to hydrogenolysis with copper chromite at 250°. The exception was the case of acetyl zein in which the linkages appear to be partly protected. Less was produced from zein II upon Raney nickel hydrogenolysis at 185°. In every instance of hydrogenolysis the volatile amine fraction gave a negative Nessler test for ammonia; instead the reagent produced a white, chalky precipitate. All of this base in each case was identified as tri-*n*-butylamine which was isolated and purified as the picrate. All samples melted from 103–105° with no depression when mixed with authentic sample. The nitrogen content by modified micro-Kjeldahl was 12.9%, the calculated value is 13.5%. However, a value of 12.9% was also obtained on an authentic sample of tri-*n*-butylamine picrate. No primary amine nitrogen was found; such would be expected since the conditions of hydrogenolysis favor alkylation, as has been shown by Adkins.[3] During hydrogenolysis the amide and peptide linkages of the compounds appear to be attacked to the same extent with conversion of their nitrogen to the fully alkylated base.

During butanolysis, primary amino nitrogen was liberated and ammonia appeared in all products except from nylon and butyl hippurate. No alkylated nitrogen product was detected. Peptide nitrogen is markedly more resistant to butanolysis than hydrogenolysis; this is particularly evident with butyl hippurate and nylon. Furthermore, the peptide linkages are more resistant to hydrogenolysis than the primary amide bonds of acetamide and polyacrylamide.

Hydrogenolysis produced marked changes in the forms of nitrogen as revealed by the Van Slyke nitrogen analyses summarized in Table II. Most striking is the enormous increase in the "ammonia" fraction which was all identified as tri-*n*-butylamine. After butanolysis the "phosphotungstic acid bases" and the "non-amino" nitrogen in the filtrate are increased at the expense of the "soluble amino" nitrogen. Similar but less drastic changes are produced upon zein II by hydrogenolysis with Raney nickel at 185°; as may also be seen with acetyl zein.

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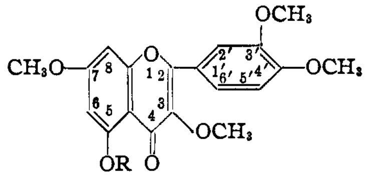
A Novel Acetylation of Quercetin 3,3',4',7-Tetramethyl Ether (5-Hydroxy-3,3',4',7-tetramethoxyflavone)

By J. H. LOOKER AND F. C. ERNEST

RECEIVED AUGUST 3, 1953

In an investigation of the methanesulfonation of quercetin and its derivatives,[1] we have observed that quercetin 3,3',4',7-tetramethyl ether (I) cannot be methanesulfonated by the action of methanesulfonyl chloride in pyridine. Several modifications of the usual procedure were then employed, one of which involved the action on I of a mixture of methanesulfonyl chloride and acetic acid in pyridine at room temperature. Instead of the methanesulfonate there was obtained a colorless, sulfur-free product, identified as 5-acetoxy-3,3',4',7-tetramethoxyflavone (II).



I, R = H
II, R = $COCH_3$

The difficulty encountered in attempting to methanesulfonate I is not surprising, since the 5-hydroxyl of I is known to be also difficult to methylate,[2,3] and acetylation has been reported only when the vigorous conditions of boiling acetic anhydride and anhydrous sodium acetate were used.[4] Our acetylation procedure accordingly seems remarkable, employing as it does very mild conditions.

Experimental

Quercetin 3,3',4',7-Tetramethyl Ether (I).—Quercetin was methylated by the method of Waliaschko,[5] with retention of the product, m.p. 155–157°, considered by Waliaschko to be a trimethyl ether, but subsequently shown[3] to be I, thus confirming Herzig's contention.[2]

5-Acetoxy-3,3',4',7-tetramethoxyflavone.—To 0.1 g. of quercetin 3,3',4',7-tetramethyl ether, dissolved in 11 ml. of reagent pyridine, was added first 0.7 ml. of glacial acetic acid, then 0.6 g. of methanesulfonyl chloride. Heat was evolved, and crystalline material (water-soluble) separated in approx. 30 seconds. The pyridine solution was decanted from solid material after 40 minutes, and the pyridine decantate permitted to stand at room temperature an additional 42 hours. The crude acetate was isolated by pouring the reaction mixture into 90 ml. of water, and permitting the aqueous suspension to stand for three hours. The crude, crystalline solid deposited was collected by filtration, washed with water and air-dried for several days; m.p. 165–170°. After sodium fusion, the crude product gave negative tests for sulfur both with lead acetate and sodium nitroprusside. The crude acetate was recrystallized twice from absolute ethanol to give colorless, silken needles, m.p. 169–171° (lit. m.p. 167–169°,[4] 171–172°[6]), no depression upon admixture with authentic 5-acetoxy-3,3',4',7-tetramethoxyflavone (m.p. 169–170.5°), prepared by the method of Herzig.[4]

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[1] J. H. Looker and A. L. Krieger, unpublished observations.

[2] J. Herzig, *Sitzungsber.*, **121**, 333 (1912).

[3] Methylation of the 5-hydroxyl of I has been achieved, however, by employment of dimethyl sulfate and solid potassium hydroxide [A. S. Gomm and M. Nierenstein, THIS JOURNAL, **53**, 4408 (1931)].

[4] J. Herzig, *Monatsh.*, **5**, 86 (1884).

[5] N. Waliaschko, *Ber.*, **42**, 727 (1909).

[6] N. Krassowski, *Chem. Centr.*, **80**, [I] 772 (1909).

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Chlorotetranitronaphthalenes

By WALTER E. MATHEWSON

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Although two isomeric bromotetranitronaphthalenes were described seventy years ago, no mention has been found in the literature of chlorotetranitronaphthalenes.

The two chlorotetranitronaphthalenes described here were prepared mainly for trial as colorimetric reagents. From their similarity to the bromotetranitronaphthalenes studied by Merz and Weith[1] one is tentatively designated as 4-chloro-1,3,6,8-tetranitronaphthalene, the other as 4-chloro-1,3,5,8-tetranitronaphthalene; the first corresponding to Merz and Weith's 4-bromo-1,3,6,8-tetranitronaphthalene of melting point 189°, the second to their 4-bromo-1,3,5,8-tetranitronaphthalene of melting point 245°. The 4-chloro-1,3,6,8-tetranitronaphthalene in benzene suspension with ammonia gave Merz and Weith's 1-amino-2,4,5,7-tetranitronaphthalene (4-amino-1,3,6,8-tetranitronaphthalene) of melting point 194°.

Merz and Weith prepared the bromotetranitronaphthalenes by a two-stage nitration involving intermediate precipitation of the partially nitrated material. They mention but do not describe in detail, a one-stage method which apparently, gave very low yields. The following process is much shorter than the two-stage method and gave yields fully equal to those obtained with it. However, the recovery of purified product was still low, amounting to some 25–27 parts of crystalline benzene-soluble chlorotetranitro compound, and 8–12 parts crude benzene-insoluble isomer, per 100 parts chloronaphthalene. For the acid nitration mixture, a smaller amount of oleum of higher sulfur trioxide content probably would be better than the 20% fuming sulfuric acid specified; however, it was not available for trial at the time the work was done.

Procedure.—One hundred grams (84 ml.) of 1-chloronaphthalene was dropped very slowly into 400 g. (270 ml.) of fuming nitric acid of specific gravity 1.50, the latter being swirled and kept cold in a bath of ice and water. The liquid was then added slowly to a cooled mixture of 400 g. (270 ml.) of the fuming nitric acid with 800 g. (435 ml.) oleum or fuming sulfuric acid of 20% sulfur trioxide content contained in a two-liter erlenmeyer flask, and kept at a temperature below 45°. The flask finally was heated in a boiling water-bath for one hour after the temperature of the mixture had reached 92°. After cooling, the nitration mixture was poured on crushed ice, the diluted acid syphoned off and the solid washed first by decantation, then in a buchner funnel (without pressing) until the acidity of the wash water was below *N*/100; the drained solid was then dried on filter paper supported on a pad of news-print. The granulated material held water very tenaciously, and although all surface moisture soon passed off, it was necessary to air-dry for several weeks.

The dry product was extracted with benzene in a large soxhlet tube, the soluble fraction crystallizing from the extract, and being further purified by recrystallization from benzene. Several methods were tried for the purification of the benzene-insoluble isomer, crystallization from glacial acetic acid probably giving the best results though the compound is not very soluble in this solvent, even at the boiling temperature. The crude 4-chloro-1,3,5,8-tetranitronaphthalene was more soluble in boiling *p*-dioxane but did not crystallize rapidly from the solution. The impurities in the crude extracted material increased the solubility of the 4-chloro-1,3,5,8-tetranitronaphthalene in dioxane and much lessened the tendency toward crystallization. Hot chlorobenzene, and hot 2,2′-dichlorodiethyl ether as solvents gave crystals of lower purity.

4-Chloro-1,3,6,8-tetranitronaphthalene.—This isomer was soluble in 4 to 4.5 parts of boiling benzene, approximately four-fifths separating on cooling in pale yellow needles containing an equimolecular amount of solvent. The crystallized compound when heated in a capillary tube fused and lost benzene at about 110°; however, 0.5 g. when exposed in an open dish at summer temperature effloresced rather rapidly, about four-fifths of the benzene passing off in 24 hours. The benzene compound was soluble in somewhat less than 110 parts of boiling 95% alcohol; in two parts of boiling glacial acetic acid; and in less than 14 parts of glacial acetic acid at 25°. It was very soluble in *p*-dioxane, dissolving in about its own weight of this liquid at 25°. Melting point of crystallized substance after heating for 30 minutes at 110°, 176°.

Anal. Calcd. for $C_{10}H_3(NO_2)_4Cl \cdot C_6H_6$: C_6H_6, 18.57. Found: (loss on heating for 30 minutes at 110°), C_6H_6, 18.48. Calcd. for benzene-free substance, $C_{10}H_3(NO_2)_4Cl$: Cl, 10.35. Found: Cl, 10.41.

4-Chloro-1,3,5,8-tetranitronaphthalene.—This compound was nearly insoluble in benzene and in alcohol. It dissolved in about 40 parts of boiling glacial acetic acid, approximately one-half separating in small yellowish white needles on cooling. It was soluble in 11 parts of boiling *p*-dioxane from which it crystallized in almost white, very fine needles; m.p. 259°.

Anal. Calcd.: Cl_2, 10.35. Found: Cl_2, 10.20.

The chlorotetranitronaphthalenes when dissolved at room temperature in very dilute alcoholic potassium hydroxide gave intensely red solutions that if tested immediately with silver salts showed only traces of chlorides. After warming or standing, the solutions gave heavy precipitates of silver chloride. Both isomers react with simple primary amines, even at high dilutions, to give deeply colored brown or yellow secondary amines.

It is apparent that the chlorotetranitronaphthalenes are acids, though not proton donors. However, because of the high lability given to the halogen by the ortho and para nitro groups the compounds behave as acid chlorides in most of their common reactions.

Grateful acknowledgment is made to Dr. J. O. Maloney for use of the facilities of the Kansas University Research Foundation in connection with this work.

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[1] V. Merz and W. Weith, *Ber.*, **15**, 2708 (1882).

Stability of Chromium Oxides

By M. A. Mosesman

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The recently described work of Schwartz, Fankuchen and Ward[1] on the thermal decomposition of chromium trioxide suggests that the results of some experiments we conducted along similar lines during the first half of 1951 might prove of interest. The objective of these experiments was to establish the stability of a promoted, alumina-supported chromic oxide catalyst under the reducing and oxidizing conditions to which the catalyst is subjected during the process of paraffin aromatization. In view of the desirability of studying such a reaction system *in situ* by X-ray diffraction, the previously described apparatus[2] utilizing a beryllium microreactor was employed.

The first phase of this work was devoted to a study of the thermal stability of bulk chromium trioxide in order to provide a reference case for subsequent investigation of the above-mentioned catalyst. Interest in the thermal characteristics of CrO_3 was predicated on the fact that the general preparative procedure for such catalysts involves the use of this water-soluble oxide for impregnating the support, followed by drying and calcination of the resulting mixture at temperatures sufficient to convert CrO_3 to Cr_2O_3. After drying for several weeks at 100°, C.P. CrO_3 was charged to the microreactor and the apparatus assembled and evacu-

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[1] R. S. Schwartz, I. Fankuchen and R. Ward, THIS JOURNAL, **74**, 1676 (1952).

[2] M. A. Mosesman, *ibid.*, **73**, 5635 (1951).