Ring Enlargement of Croconic Acid

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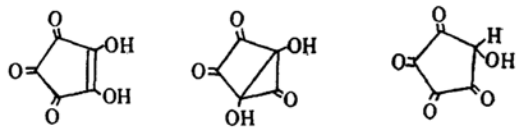
(Received March 3, 1958)

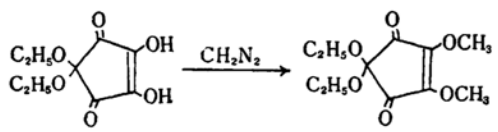
The structures I[1], II[2] and III[3] (III, as a tautomer of I in an aqueous solution) have been so far presented for croconic acid.



(I) (II) (III)

With the intention of clarifying the structure, various properties of the acid itself and its derivatives have been studied, and it has been concluded that the acid has the structure I and that a strong hydrogen bond is present[4].

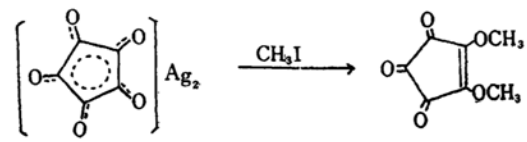
In 1938, R. Malachowski prepared various derivatives of croconic acid, and examination of its structure by chemical methods finally led to the formula I. In his research, treatment of the diethyl acetal of croconic acid with diazomethane yielded its dimethyl derivative (liquid).



On the other hand, during the course of our studies, it was noticed that the reaction between the acid and ethereal diazomethane yielded orange needles. On the basis of its properties and analyses, this reaction product appeared to be trimethoxy-*p*-benzoquinone resulting from ring enlargement of the acid and successive methylation. Accordingly, this quinone was synthesized from pyrogallol through a route which left no doubt as to the correctness of the structure of the synthetic product[5]. Comparison of infrared and ultraviolet spectra and a mixed melting point test showed the two specimens to be identical. Since croconic acid is insoluble in ether, the reaction is heterogeneous. The quinone is presumably formed by the following mechanism.

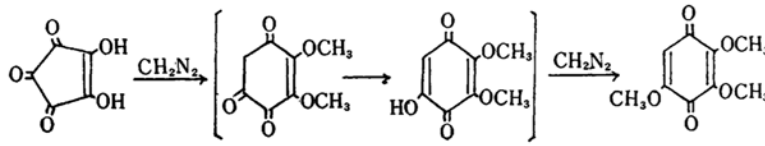
Though there are many cases in which the normal product is also produced in anomalous diazomethane reactions, careful scrutiny of the product showed that no dimethyl derivative of croconic acid had been formed. It is interesting that the abnormal reaction takes place in case of croconic acid itself, but does not in case of the acetal derivative.

For the purpose of comparison, the dimethyl ether of the acid was prepared by treating the silver salt with methyl iodide in absolute ether. The compound is, of course, different from the product obtained in the case of the reaction described above. It was, as expected from its structure, easily hydrolyzed to croconic acid even by the moisture in the air.



Experimental

Croconic acid.—Croconic acid is usually prepared by oxidation of an alkaline (potassium carbonate) solution of diaminotetrahydroxybenzene with manganese dioxide, or by treatment



1) R. Malachowski, *Ber.*, **71**, 2246 (1938).
2) R. Nietzki et al., ibid. **18**, 510, 1833 (1885), **19**, 294, 301, 772 (1886), **20**, 1617, 2118 (1887); G. E. Carpéni, *Compt. rend.*, **206**, 601 (1938).
3) Y. Hirata et al., *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **69**, 63 (1948).
4) K. Yamada et al., This Bulletin. **31**, 532 (1958).
5) H. O. Huisman, *Rec. trav. chim.*, **69**, 1145 (1950).

of sodium rhodizonate with an excess of alkali (R. Nietzki)[6]. With the former route the preparation of the diaminotetrahydroxybenzene is troublesome; with the latter route the yield is poor. In the present studies, sodium rhodizonate, easily obtainable from glyoxal[7], was oxidized with manganese dioxide to give potassium croconate in fairly good yield. Namely, to a solution of 7 g. of sodium rhodizonate in 350 ml. of water were added 30 g. of potassium carbonate and 20 g. of manganese dioxide which was freshly prepared from potassium permanganate. After the suspension was refluxed with shaking for one hour, it was filtered at once, and the potassium croconate appeared in the filtrate after cooling. The filtrate containing crystalline potassium croconate was acidified with hydrochloric acid, when the crystals disappeared. The addition of the barium chloride solution to this acidic solution gave 7.6 g. (ca. 85%) of golden barium croconate.

An excessive amount of barium croconate was added to a solution of sulfuric acid (3 N), and the mixture was warmed for about one hour. Excess barium croconate was filtered and the yellow filtrate was concentrated at 40° under reduced pressure, to give crude croconic acid.

The purification was carried out as follows. A saturated solution of crude croconic acid in warm water or alcohol (50°~60°) was cooled in an ice box, upon which there was obtained a small amount of crystals. The remaining solution was concentrated in a desiccator, when the second crop of crystals were obtained in the form of needles or plates. Croconic acid has no melting point, but becomes brown near 150°, and gradually decomposes.

Anal. Found: C, 42.16; H, 1.80. Calcd. for $C_5H_2O_5$: C, 42.25; H, 1.41%.

Reaction product of croconic acid with diazomethane.—A dry ethereal solution (15 ml.) of diazomethane prepared from nitrosomethylurea (containing CH_2N_2 0.007~0.009 M) was placed in a small flask with cooling, and to this 100 mg. (0.0007 M) of croconic acid was added. At first, the reaction occurred on the surface of the acid and the acid gradually dissolved. After thirty minutes, the reaction ceased. The solution became orange, and was left for a while. The orange crystals appearing on the surface of the flask were filtered. The filtrate was concentrated but this only gave an oily residue. The orange crystals were recrystallized from methanol, m. p. 157~158° (quinone prepared from pyrogallol, m.p. 158~160°), yield, 40 mg. Ultraviolet absorption maximum $\lambda_{max.}$ 288 mμ (log ε 4.08 in ethanol).

Anal. Found: C, 54.59; H, 5.49. O-CH_3 (Zeisel): 45.9% (1.96 groups). Calcd. for $C_9H_{10}O_5$: C, 54.55; H, 5.09%.

Purification of the oily material was undertaken, in order to examine the existence of another product, but nothing could be detected except that a further small amount of the above quinone was obtained. When a methanolic solution of croconic acid was added to the ethereal diazomethane, the yield was poor and the amount of the oily product increased.

Dimethyl croconate[1].—It was necessary that all the solvent and the reagents should be quite free from water and that the flask provided with a calcium chloride tube should be used. Since the reaction was heterogeneous, it was necessary to stir occasionally. The reaction was complete after one day at room temperature (10~15°). The product was recrystallized from benzene. Orange prism, m. p. 113~114°.

Anal. Found: C, 48.96; H, 3.65. Calcd. for $C_7H_6O_5$: C, 49.42; H, 3.56%.

The analytical data do not quite agree with the calculated values, probably owing to the hydrolysis of the sample in the air. When placed in dilute hydrochloric acid, the dimethyl croconate was at first insoluble, but after several seconds it started to dissolve fairly rapidly. The aqueous solution was warmed for thirty minutes, and upon evaporation of the solvent there was obtained free croconic acid. The free croconic acid itself is very soluble in water.

Summary

The reaction of croconic acid with diazomethane gives instead of its simple methylated product, a compound with an enlarged ring. Trimethoxy-*p*-benzoquinone was synthesized from pyrogallol, and was identified with the compound obtained from croconic acid.

The authors wish to make grateful acknowledgements to Mr. S. Senoh, Osaka City University, for microanalyses. They also express their gratitude to the Ministry of Education for financial support of this research.

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6) R. Nietzki et al., *Ber.*, **18**, 1842 (1885), **19**, 293 (1886).
7) B. Homolka, *Ber.*, **54**, 1393 (1921).