Reaction of Fremy's Salt upon Benzaldehyde and Salicylaldehyde

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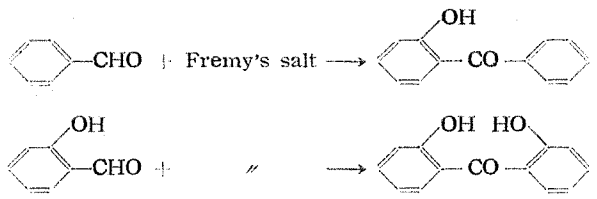
The reactions of Fremy's salt upon benzaldehyde and salicylaldehyde were investigated and as the reaction products o-oxybenzophenone and o,o'-dioxybenzophenone were identified, and the radical reaction scheme was suggested.

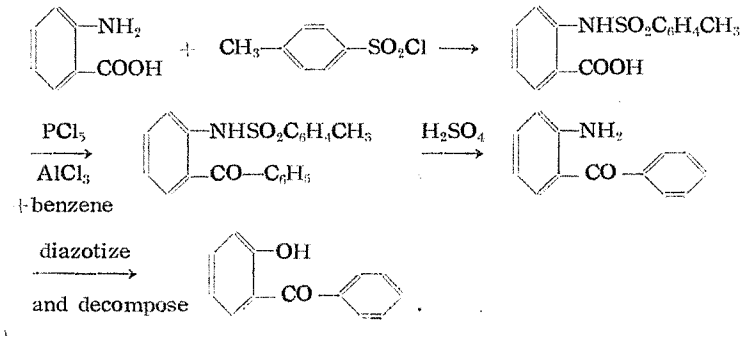
Recently H. J. Teuber[1] has published an interesting report about the preparation method of quinones by the oxidation of phenols with Fremy's salt, K-nitrosodisulfonate, and he assumed that this oxidation reaction is of radical nature. The authors have very much interested in this reaction and applied this reaction upon benzaldehyde and salicylaldehyde.

Unexpectedly the o-oxybenzophenone was obtained from benzaldehyde and 2,2'-dioxybenzophenone from salicylaldehyde:



In the case of salicylaldehyde a small amount of p-benzoquinone-carboxylic acid was also obtained.

The o-oxybenzophenone was authentically synthesized from anthranilic acid after the following course:



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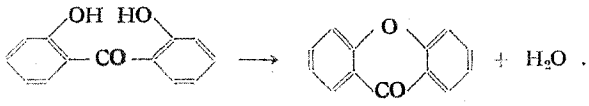
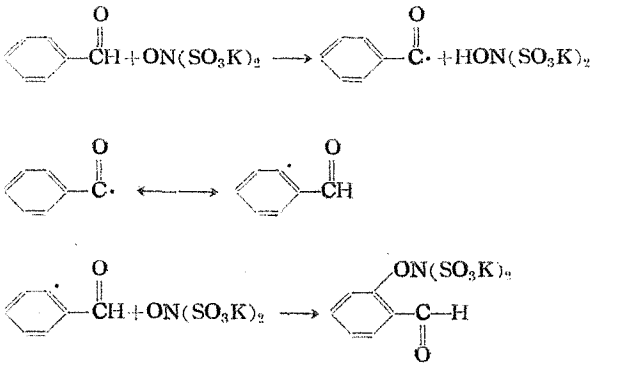
This authentic product showed no melting point depression with the above product. The 2,2′-dioxybenzophenone was converted into xanthone by dehydration.



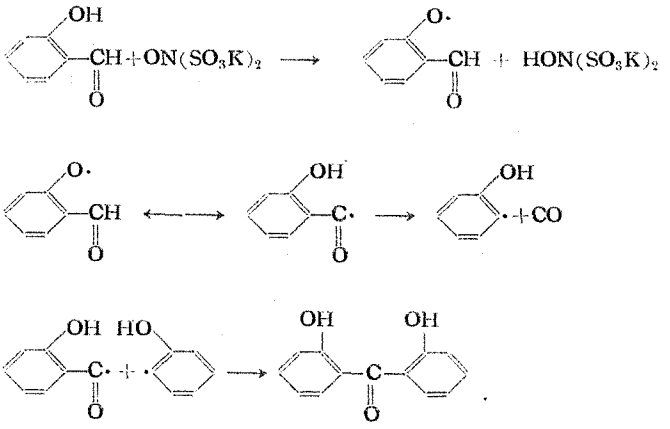
Xanthone was also synthesized by the known method from phenylsalicylate and this authentic sample showed also no meting point depression with the above product.

For the production of o-oxybenzophenone and o,o-′dioxybenzophenone the authors have suggested the following radical rerction scheme, although they are more or less ambiguous :

1.



2.



EXPERIMENTAL PART

1. Reaction of Fremy's salt upon benzaldehyde.

10.6 g. (0.1 mole) benzaldehyde was dissolved in 50 cc. methanol and to this solution 26.8 g. (0.1 mole) Fremy's salt, dissolved in about 1350 cc. water, was added slowly under stirring. After the addition of Fremy's salt the reaction solution was warmed gently to 40°, then the violet color of the Fremy's solution disappeared gradually. After stirring for 2~3 hrs, the cooled solution was extracted with ether. The ether extract was treated with 5~6 % Na_2CO_3 solution. Upon acidifying this alkaline solution an oily product separated. This oily product was again extracted with ether, the ether solution was distilled and a colorless fraction, boiling at 130~135°/10 mm, was collected. This product was oily at first, but it solidified on standing.

The yield of this product was 2.8 g. (28.3 % based on denzaldehyde). It melted at 36~37°. From the alkali-insoluble portion 6.5 g. (60 %) benzaldehyde was recovered by distillation. The above main product was insoluble in water, soluble in alcohol, ether, benzene and in caustic soda solution.

This product showed yellow-brownish color with $FeCl_3$, positive Liebermann's reaction and coupled with diazoniumsalt. Therefore it is clear that this compound contains phenolic hydroxyl-group. At the same time this compound gave the corresponding phenylhydrazone and semicarbazone. The melting point of the phenylhydrazone was 115° and that of semicarbazone was 215~217°. These data coinside very well with those of o-oxybenzophenone, given in the literature. Therefore the authors have synthesized the o-oxybenzophenone as shown above and confirmed no melting point depression with these two samples.

3. Reaction of Fremy's salt with salicylaldehyde.

12.2 g. (0.1 mole) Salicylaldehyde was dissolved in 80 cc. methanol and to this solution 26.8 g. (0.1 mole) Fremy's salt, dissolved in 1350 cc. water, was added maintaining the temperature at 15°. After stirring for 2~3 hrs., the reaction solution was extracted with ether. The ether extract was treated with 5~6 % NaOH solution. This alkaline solution was made acidic and extracted again with ether. After elimination of ether the residue was distilled under vacuum and the following fractions were obtained.

1. 95~98°/30 mm, 5.5 g.
2. 155~160°/30 mm, 2.2 g. m.p. 57~58°.

The melting points of semicarbazone and phenylhydrazone were 223~224° and 150~151° respectively. These values coinside with those of 2,2'-dioxybenzophenone, given in the literature. The existence of hydroxylgroup was also clear from the color reaction with $FeCl_3$. This product was therefore converted into xanthone by

warming it in conc. H_2SO_4, the procuct was colorless needles (m.p. 170~171°), showed greenish fluorescence and no melting point depression with an authentic sample of xanthone.

REFERENCE

(1) H.J. Teuber, *Chem. Ber.* **86**, 1036 (1953).