[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF ROCHESTER]

Reactions of Peracids. III. Nuclear Oxidation of Aromatic Compounds with Perbenzoic Acid[1]

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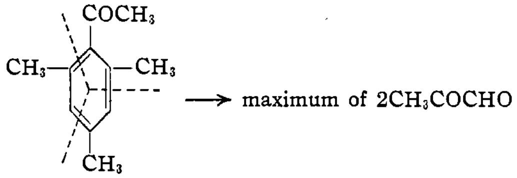
In a previous investigation[2] of the reaction of ketones with peracid it was noted that acetomesitylene (I) consumes somewhat more than one molar equivalent of perbenzoic acid (II), when allowed to react at room temperature with a slight excess of the reagent in moist chloroform solution. However, attempted saponification of the crude reaction product gave no trace of mesitol, which would be expected from the mesityl acetate arising as a product of the normal transformation $RCOCH_3 \rightarrow ROCOCH_3$. Accordingly, it was of some interest to treat I with a large, measured excess of perbenzoic acid, and determine both the maximum consumption of the peracid by the ketone and the nature of the products arising from the oxidation process.

In a preliminary experiment it was observed that when 0.10 mole of I was allowed to react at room temperature with 0.11 mole of II in dried chloroform solution, and the course of the reaction followed iodimetrically by titration of aliquots in the usual manner,[2] exactly 0.105 mole of the peracid reagent was consumed at the end of seven days. Working up the product, with or without a saponification step, gave a 65% recovery of unchanged I and tarry decomposition products in the distilling flask. It therefore seemed likely that each mole of I was consuming at least several molar equivalents of the peracid II, leaving the residual ketone untouched.

To investigate this point, a run was made in which the initial molar ratio of peracid:ketone was set at 5.93:1. The results of measurements of the progress of the reaction as a function of time elapsed are shown in Fig. 1. It is observed that after an initially rapid uptake of peracid, the consumption levels off at an approximate value of 2.2 to 2.5 moles of peracid per mole of ketone.

Since this high consumption of peracid far exceeds the one mole required for the acetyl → acetate transformation, it would appear probable that rather extensive oxidation of the aromatic nucleus is occurring. That this is the case was shown by a preparative scale run in which, after the action of excess II on acetomesitylene, a fair yield of pyruvaldehyde (isolated and purified as the disemicarbazone) was obtained, corresponding to nuclear oxidation through the mode of cleavage indicated in I below.

Now, since the sensitive nucleus of I possesses three electron-supplying methyl groups and a single electron-withdrawing acetyl group, it



I

would appear to offer an excellent target for attack by an electrophilic entity like $\overset{\cdot}{\underset{\cdot}{O}}{:}H^+$ from the peracid. Further, it seemed that this sensitivity should be greatly enhanced by elimination of the acetyl group, leaving the nucleus of mesitylene (III).

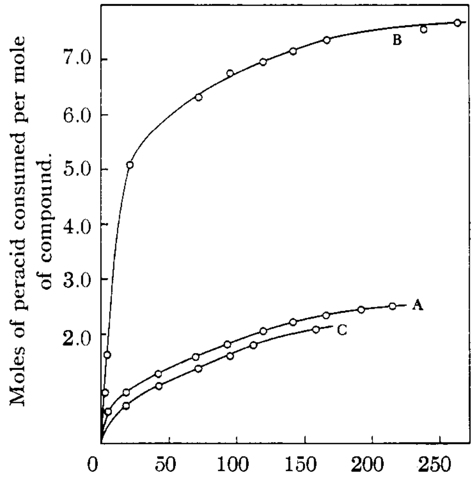


Fig. 1.—A, Acetomesitylene, initial moles peracid/mole compound = 5.93; B, mesitylene, initial molar ratio = 8.00; C, trimethylgallic acid, initial molar ratio = 6.10.

Accordingly, the reaction of mesitylene at room temperature with a large excess of II in dried chloroform solution was followed as a function of time, and the results plotted on Fig. 1. Roughly the same type of behavior as that shown by I was observed, but with mesitylene the far more rapid consumption of peracid ultimately reached a leveling-off point at about 7.8 moles of peracid per mole of mesitylene initially present, reflecting the greater sensitivity of III to nuclear electrophilic attack.

For further contrast, and to study the effect of other groups on sensitivity toward nuclear attack, trimethylgallic acid (IV) was allowed to react with excess perbenzoic acid, giving the rate curve again plotted in Fig. 1. Here too, the combination of three electron-supplying methoxyl

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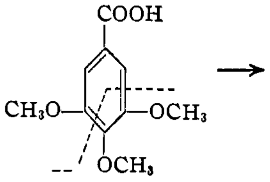
[1] A portion of this material was presented before the Organic Division at the 116th National Meeting in Atlantic City, N. J., September, 1949.

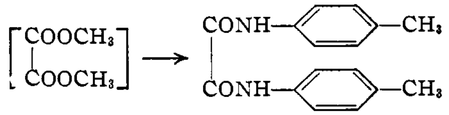
[2] Friess, THIS JOURNAL, **71**, 14 (1949).

groups and a single deactivating carboxyl group leads to behavior strikingly similar to that of I, and an effective consumption of peracid leveling off in the 2.0–2.5 molar equivalent range.

A preparative scale run on the peracid oxidation of IV gave an appreciable amount of dimethyl oxalate, which was isolated and purified as the crystalline di-*p*-toluidide, in accordance with the pattern of cleavage indicated in IV.



IV



This work on the cleavage of polymethoxylated aromatic nuclei is interestingly supplemented by the data of Fernholz,[3] who found that under far more vigorous conditions, *i. e.*, using a large excess of perbenzoic acid in boiling benzene solution, both N-acetylcolchinol and *v*-trimethoxybenzene gave dimethyl oxalate as a nuclear oxidation product.

Experimental[4]

Rate Runs.—In a representative rate run, a weighed amount of the aromatic compound was placed in the reaction flask and an aliquot of a stock perbenzoic acid solution pipetted in at zero time. The contents of the stoppered flask were swirled thoroughly to effect solution, and set aside in the dark at room temperature (25–30°). From time to time the flask was again swirled. One ml. aliquots were withdrawn at measured time intervals, pipetted into acidified sodium iodide solution, and the liberated iodine titrated with standard sodium thiosulfate solution to give the concentration of the residual perbenzoic acid present. Blank runs to correct for any spontaneous decrease in peracid strength were found to be unreliable, but from the uniformity and reproducibility of results on actual runs it appeared, as in the previous work with methyl ketones, that the presence of an added organic compound stabilizes the peracid against excessive self-decomposition.

Reaction of Acetomesitylene (I).—To 7.2 g. (0.045 mole) of acetomesitylene, $n^{22}\text{D}$ 1.5148, b. p. 120–121° (17 mm.), was added 228 ml. of a chloroform solution containing 0.099 mole of perbenzoic acid. The flask was stoppered, swirled thoroughly, and placed in the dark at room temperature. The initially cloudy solution became clear and golden-yellow in color within an hour. Twice, within the next seven days, the reaction mixture was extracted with 100-ml. portions of water. These water extracts were separately treated in the customary manner with semicarbazide hydrochloride and sodium acetate, followed by heating in a water-bath, to yield small, shiny crystals of the disemicarbazone of pyruvaldehyde; m. p. 253–254° after recrystallization from water (lit. values,[5] 250–254°, 254°); weight of product, 1.01 g.

At the end of seven days, titration of an aliquot of the reacting solution indicated the consumption of 1.74 molar equivalents of peracid. The acids were then extracted with two 100-ml. portions of 1 M sodium bicarbonate solution, followed by a 50-ml. water wash, drying over anhydrous sodium sulfate, and distillation of the chloroform solvent at the water pump. The residual yellow oil was dissolved in diluted ethanol, and treated with semicarbazide hydrochloride and sodium acetate to give an additional yield of 0.93 g. of pyruvaldehyde disemicarbazone, m. p. 253–254°; total weight of product obtained, 1.94 g.

Reaction of Trimethylgallic Acid (IV).—To 10.2 g. (0.048 mole) of trimethylgallic acid, m. p. 166–167°, was added 0.120 mole of perbenzoic acid in 297 ml. of dried chloroform solution. After thorough swirling to effect complete solution, the flask was set aside in the dark. At the end of fourteen days, no trace of residual peracid remained. The reaction mixture was extracted with sodium bicarbonate solution to remove acids, washed with water, dried over anhydrous sodium sulfate, and the chloroform removed under reduced pressure. The brown oil remaining gave no detectable carbonyl tests. It was mixed with 5.4 g. of *p*-toluidine, and heated on the steam-bath for four hours. After extraction with dilute hydrochloric acid to remove excess amine, a semi-solid residue was filtered and recrystallized from glacial acetic acid to give small white needles, m. p. and mixed m. p. with an authentic sample of oxal-di-*p*-toluidide, 268–269°; weight of product, 0.72 g. The bicarbonate extract furnished 1.5 g. of recovered IV upon fractional acidification and purification of the precipitated acids.

Summary

The nuclear oxidation reactions of acetomesitylene, mesitylene, and trimethylgallic acid with perbenzoic acid in chloroform solution were investigated. Multiple substitution by electron-supplying groups created great sensitivity of the aromatic nucleus toward peracid oxidation.

The oxidation of acetomesitylene furnished pyruvaldehyde as an isolable product; the peracid degradation of trimethylgallic acid yielded dimethyl oxalate.

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[3] Fernholz, *Angew. Chem.*, **60A**, 62 (1948).

[4] Melting points are corrected.

[5] (a) Mariella and Leech, THIS JOURNAL, **71**, 3559 (1949); (b) Wohl and Lange, *Ber.*, **41**, 3615 (1908).