Aromatic Benzoyloxylation with Benzoyl Peroxide - Iodine

Shizunobu Hashimoto, Wataro Koike and Masafumi Yamamoto

Department of Applied Chemistry, Doshisha University, Karasuma-imadegawa, Kamikyo-ku, Kyoto

(Received May 28, 1969)

Recently it was reported that the reaction products of benzoyl peroxide (BPO) with aromatic substrates could be modified by the presence of cupric chloride[1,2] or oxygen.[3] In such cases, BPO acted as an oxygenating agent on an unactivated aromatic nucleus. In 1945, Perret and Perrot[4] reported their findings on the reaction products of BPO with unsaturated compounds in the presence of iodine. With aromatic compounds, benzoic acid, the aryl benzoates, and the iodinated products were identified, but the yields of the monobenzoyloxylated products were poor. Little has been reported, however, about either the qualitative or mechanistic aspects of this reaction.

We wish here to report that aromatic compounds are benzoyloxylated in high yields by BPO in the presence of small amounts of iodine. Pure monooxygenated materials are obtained by this method of aromatic substitution; this suggests possible synthetic usefulness and also provides the possibility of a new route for aromatic oxygenation.

A toluene solution of BPO was mixed with iodine and heated at 80°C. Figure 1 shows the variation in the yields of phenyltoluenes, tolyl benzoates, and benzoic acid as a function of the initial concentration of iodine. In a control experiment with the peroxide and toluene, less than 3 mol% of the nuclear oxygenation product was found. As the initial concentration of iodine was increased, however, the formation of tolyl benzoates and benzoic acid became the major pathway. When the molar ratios of iodine to BPO are below 0.25, the amount of the oxygenation product decreased substantially. On the other hand, above this ratio the yield of tolyl benzoates and benzoic acid increased to 72—79 mol% and 80—92 mol% respectively. Small amounts of phenyltoluenes, iodobenzene, and iodotoluenes were also obtained.

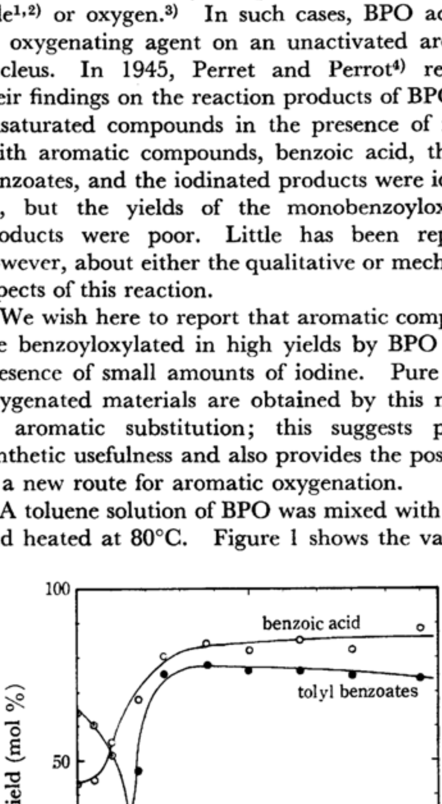


Fig. 1. Variation in iodine:BPO ratio.
BPO; 0.025 mol, Toluene; 100 m*l*, 80°C, 50 hr

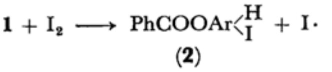
The relative rates for this benzoyloxylation of a number of monosubstituted benzenoid compounds relative to benzene (obtained by the competitive method, using gas-liquid chromatography for the analysis of the products of the competition) were: PhOMe : PhEt : PhMe : PhPr-*i* : PhH : PhCl=6.27: 3.10 : 2.85 : 2.18 : 1 : 0.20. The isomer distribution and the partial rate factors (f) for toluene were *o*-, 53% *m*-, 16% and *p*-, 31%, and f_o=4.53 f_m=1.37 and f_p=5.30.

The effects of substituents on the peroxide were also examined by carrying out the reaction of *p,p'*-disubstituted benzoyl peroxide with benzene in the presence of iodine at 80°C. The mol% yields of phenyl *p*-substituted benzoate was OCH_3 : CH_3 : H : Cl : Br=86.5 : 84.0 : 75.3 : 94.6 : 95.0.

On the basis of our experimental findings, it seems that the oxidizing agent is not a polar intermediate but a benzoyloxy radical which exhibits electrophilic properties.[2] The ester could arise from the capture of **1** by iodine, an efficient radical scavenger, followed by the loss of hydrogen iodide. In the absence of iodine, the initially-formed free radical **1** is not sufficiently stable to allow the formation of the ester; hence, the benzoyloxy radical is free to undergo decarboxylation, with the resultant formation of phenylated products.

$$\mathrm{PhCOO\cdot + ArH \rightleftarrows PhCOOArH\cdot}$$

(1)



$$\mathrm{1 + I_2 \longrightarrow PhCOOAr\langle{}^{H}_{I} + I\cdot}$$

(2)

$$\mathrm{2 \longrightarrow PhCOOAr + HI}$$

$$\mathrm{PhCOO\cdot + HI \longrightarrow PhCOOH + I\cdot}$$

---

[1] P. Kovacic and M. E. Kurz, *Tetrahedron Letters*, **1966**, 2689.

[2] S. Hashimoto, W. Koike and Y. Matsuda, Abstracts of Papers presented at the Symposium on Organic Reaction Mechanisms, Yamagata, October, 1968, p. 72.

[3] T. Nakata, K. Tokumaru and O. Simamura, *Tetrahedron Letters*, **1967**, 3303.

[4] A. Perret and R. Perrot, *Helv. Chim. Acta.*, **28**, 558 (1945).