The Reactions of Aroyl Peroxides with Grignard Reagents. I. On the Formation of a Stable Complex Containing Peroxide

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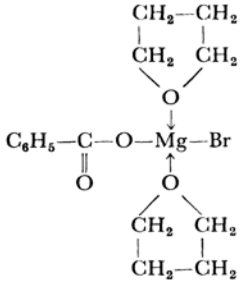
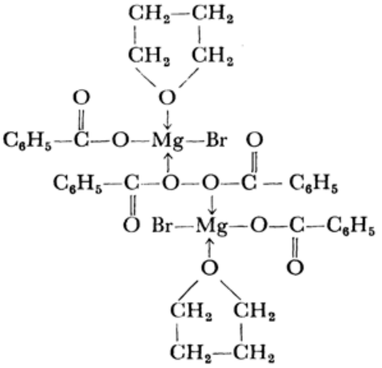
When a THF solution of BPO was mixed with the equimolar PhMgBr solution at 0°C under nitrogen stream and stirred for 2 hrs, 18—20% of BPO was found to remain in the solution. After the mixture was stood for 24 hr and/or even if it was heated at 50°C for 1 hr, the content of peroxide still remained unchanged. By adding ethyl ether to the concentrated reaction mixture, orange-yellow crystals were precipitated. The precipitate (ppt. 1) was filtered and dried in a vacuum-desiccator.[*1] The ppt. 1 is fairly stable in air, but dissolves in water releasing bromine, finally to leave $(PhCOO)_2Mg$ and THF. The yellow color of the THF solution of ppt. 1 disappeared suddenly by the addition of a suitable amount[*2] of PhMgBr solution, and the resulting mixture contained no peroxide.



[I]



[II]

On the other hand, when 50% molar excess of Grignard reagent to the peroxide was used and worked up similarly, no color change was observed during the course of the reaction, and white precipitate (ppt. 2), containing no peroxide was finally obtained. For the analysis of ppt. 2, the precipitate was dissolved in water, acidified and extracted with ether. Contents of Mg^{2+} and Br^- in the aqueous layer were analyzed by oxine-chelate method[1] and $AgNO_3$-titration method, respectively. Content of THF in the ether layer was determined by v.p.c. technique. Analytical results are as follows: Mg^{2+} 7.8 (6.6)%; Br^- 21.7 (21.6)%; $PhCOO^{\ominus}$ 31.9(32.8)%; and THF 37.5(39.1)%. The values given in parentheses are calculated by assuming the formula[I] to ppt. 2. The yield of ppt. 2 based on the BPO used was quantitative. If a suitable amount of BPO was added to a THF solution of ppt. 2, an orange-yellow color appeared after a few minutes. When this solution was concentrated, orange-yellow precipitate was obtained, having the same composition as the ppt. 1. The peroxide content of ppt. 1 was determined by iodometry. A portion of ppt. 1 was treated with $Fe(II)SO_4$ solution, and the amounts of Br^-, PhCOOH and THF were determined. From $[PhCOO]_{total}$ and $[PhCOO]_{BPO}$, one can estimate $[PhCOO^{\ominus}]$ in ppt. 1. Another portion of ppt. 1 was submitted to the analysis of Mg^{2+} content. Analytical results are as follows: Br^- 18.0(19.1)%; Mg^{2+} 5.5(5.8)%; $PhCOO^{\ominus}$ 35.0(29.0)%; BPO 18.4(29.0)%; and THF 15.7(17.2)%. The values given in parentheses are calculated by assuming the formula[II] to ppt. 1. Moreover, the same orange-yellow colored solution was obtained, if one added BPO to the completely carbonated PhMgBr solution. Taking account of the chemical behaviors of ppt. 1 and the said reaction, formula[II] seems to be reasonable. The fact that the ppt. 1 dissolves in water releasing bromine can be nicely explained by considering the electron-transfer from the Mg–Br linkage to the peroxidic linkage through the coordination bond. The lower content of BPO and the higher content of $PhCOO^{\ominus}$, compared with the calculated values, may be due to the gradual decomposition of the ppt. 1 by moisture.

[*1] From the filtrate, PhCOOPh was obtained.

[*2] When BPO was treated with 4/3 molar equivalent of PhMgBr, the peroxide was found to be consumed completely after 2 hrs at room temperature.

1) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Macmillan Co., N. Y. (1955), pp. 362, 607.