On the Reproducibility of the Oxidative Bisdecarboxylation Reaction[1]

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In 1952 Doering, Farber, and Sayigh[3] reported a method for the replacement of a 1,2-dicarboxylic anhydride group by a double bond. This method involved an oxidation by lead dioxide in which two molecules of carbon dioxide were eliminated leaving an olefin. The reaction was applied to hexahydrophthalic anhydride, 4,5-dimethylhexahydrophthalic anhydride, bicyclo[2.2.2]octane-2,3-dicarboxylic anhydride, and 1-acetoxy- and 1-carbomethoxybicyclo[2.2.2]octane-2,3-dicarboxylic anhydride, giving the related olefins in yields of 20% to 35% of the theoretical.

Using this method, Beckmann and Schaber[4] reported the conversion of 2-methylbicyclo[2.2.1]heptane-2,3-dicarboxylic anhydride to aposantene in 15% of the theoretical yield. A related reaction has been reported by McElvain[5] in the conversion of nepetonic acid to 1-acetyl-3-methylcyclopentene.

During a study of the solvolysis of some bridgehead bromides the reaction between lead dioxide and 1-acetoxybicyclo[2.2.2]octane-2,3-dicarboxylic anhydride (I) was repeated. In contrast to the previous report[3] various samples of fresh commercial lead dioxide gave at the most only 4% of the theoretical yield in many attempts. An old sample of lead dioxide of unknown origin, while not duplicating the original yield, was considerably more active than the fresh material. The discoverers[3] recalled using only a single ancient sample of lead dioxide of unknown history.

In investigating this mystery, it was found from emission spectra[6] that the bisdecarboxylation was not effected by impurities in the lead dioxide. An X-ray crystal study[7] suggested that the important factor was particle size and not crystal structure. In fact, those samples of larger particle size (as determined roughly by sedimentation rate) were the more effective in the decarboxylation.

Samples of lead dioxide prepared by the aqueous decomposition of lead tetraacetate,[8] by the electrolysis of a lead nitrate solution,[9] and by the hypochlorite oxidation of lead acetate,[10] as well as Mallinckrodt *Analytical Reagent* grade all failed to decarboxylate I. These materials had slower rates of sedimentation than the one active sample and were therefore presumed to have smaller particle sizes.

A modification of the hypochlorite oxidation[10] described below finally led to the production of lead dioxide which was uniformly effective in the bisdecarboxylation reaction. The preparation was reproducible and gave lead dioxide which decarboxylated I consistently in 19% yield. The decarboxylation of 1-acetoxybicyclo[3.2.2]nonane-2,3-dicarboxylic anhydride has been performed consistently in 23% yield[11] using lead dioxide prepared in this manner.

EXPERIMENTAL

Active lead dioxide. A solution of 180 g. of sodium hydroxide in 500 ml. of water was added with stirring to a solution prepared by dissolving lead acetate trihydrate (300 g.) in 600 ml. of warm water. To the resultant suspension was added all at once a mixture of 220 g. of technical calcium hypochlorite (Fisher Scientific Co.). and 1500 ml. of water. The stirred mixture was heated rapidly to boiling and kept there for several minutes. After being cooled, the supernatant liquid was decanted and the yellow precipitate was washed in the following way: five hundred ml. of 1:1 nitric acid was cautiously added (in small portions at first) and the suspension was vigorously stirred. Fifteen hundred ml. of water was then added and after the precipitate settled, the liquid was decanted and the procedure was repeated at least four times. The now brown precipitate was washed once more with water and filtered with suction. It was dried overnight at 110° and ground with a mortar and pestle to yield 132 g. (70%) of dark brown powder.

The reaction of lead dioxide with nepatonic acid exploded at 250°[5]; accordingly the decarboxylation reactions should be conducted with the precautions indicated where explosions are expected.

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[3] W. von E. Doering, M. Farber, and A. Sayigh, *J. Am. Chem. Soc.*, **74**, 4370 (1952).

[4] S. Beckmann and R. Schaber, *Ann.*, **585**, 154 (1954).

[5] S. M. McElvain and E. J. Eisenbraun, *J. Am. Chem. Soc.*, **77**, 1599 (1955).

[6] Kindly determined by Mr. William Milligan, Metallurgy Dept., Yale University.

[7] Kindly performed by Mr. Kurt Servos, Geology Dept., Yale University.

[8] R. Kuhn and I. Hammer, *Chem. Ber.*, **83**, 413 (1950).

[9] W. C. Pierce and E. L. Haenisch, *Quantitative Analysis*, John Wiley and Sons, Inc., New York, 1948, p. 446.

[10] H. S. Booth *et al.*, *Inorganic Syntheses*, vol. 1, McGraw-Hill Book Co., New York, 1939, p. 45.

[11] James N. Tilley, Department of Chemistry, Yale University, unpublished results.

Chloroacetyl Chloride from Ketene and Chlorine

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This investigation was undertaken to determine the suitability of adding chlorine to ketene as a preparative method for chloroacetyl chloride. It