

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BANTING INSTITUTE, UNIVERSITY OF TORONTO]

## Oxidation of 1,2-Glycols or 1,2,3-Polyalcohols by Means of Lead Tetraacetate in Aqueous Solution

BY ERICH BAER, J. M. GROSHEINTZ AND HERMANN O. L. FISCHER

Criegee<sup>1</sup> found that lead tetraacetate oxidizes 1,2-glycols by breaking the bond between the hydroxyl-carrying carbon atoms, thereby forming aldehydes and ketones. This cleavage reaction takes place quantitatively at room temperature; its velocity depends greatly on the structure of the glycol and the *solvent* in which the reaction takes place. The method has found extensive application both in analytical and preparative procedures. The discoverer contended that non-aqueous solvents only can be used, *e. g.*, benzene, nitrobenzene, chloroform, di- and tetrachlorethane or glacial acetic acid. Considerable emphasis was placed on the drying of such solvents.

The same oxidative cleavage of glycols can be carried out in aqueous solution with periodic acid according to Malaprade.<sup>2</sup> This method is very suitable for the titration of glycols, and frequently has been used whenever it is desirable to work in water.

One of us (E. B.) observed that, contrary to prevailing views, the glycol cleavage with lead tetraacetate also may be carried out in moist organic solvents and even in aqueous solution, if the velocity of oxidation be higher than that of the hydrolysis of the oxidizing agent. Since the lead is easily removed quantitatively by dilute sulfuric acid, we believe that this modification will greatly extend the applicability of Criegee's method of oxidative glycol cleavage.

In preliminary qualitative experiments lead tetraacetate was added to aqueous solutions of glycerol, *d*-mannitol, *d*-glucose and *d*-mannose, either as a concentrated solution in glacial acetic acid or in a finely powdered form. In both cases the aqueous solution generally remained clear. Although slight brown turbidities sometimes occurred due to local excess of the reagent, these disappeared very rapidly. The end of the reaction is indicated by the immediate formation of a permanent brown precipitate of lead oxides. These compounds contained up to six adjacent hydroxyl groups and therefore a mixture of oxida-

tion products, giving mixed precipitates with substituted hydrazines, resulted.

In order to make a quantitative study of the oxidation with lead tetraacetate in aqueous solution we investigated the cleavage of 1,2-5,6-diacetone-*d*-mannitol and of pinacol. We chose these compounds since they possess only a single pair of vicinal hydroxyl groups and further because the oxidation of these substances (in organic solvents) is unambiguous and was already familiar to us.<sup>3</sup> Further, the cleavage products are easily determined quantitatively. A concentrated solution of the equivalent amount of lead tetraacetate in acetic acid was added to an aqueous solution of 1,2-5,6-diacetone-*d*-mannitol. Oxidation took place immediately and the acetone-*d*-glyceraldehyde which was formed was hydrolyzed quickly to *d*-glyceraldehyde in the presence of the dilute acetic acid. The amount of aldehyde present was equal to 99% of the theoretical yield. By oxidation of *d*-glyceraldehyde with bromine, *d*-(-)-glyceric acid was obtained in a yield of 76%. This is a convenient way of preparing *d*-(-)-glyceric acid and its derivatives. The procedure for preparing *d*-(-)-glyceric acid has been included at the end of this paper. Its antipode may be prepared similarly from *l*-glyceraldehyde<sup>3c</sup> recently synthesized by us.

The pinacol was oxidized in the same manner as above described and the yield of acetone was 95% of the theoretical.

The results of our quantitative studies of the oxidation of  $\alpha$ -glycols with lead tetraacetate in aqueous solutions indicate that these reactions follow the same course and go as thoroughly to completion in water as in non-aqueous solvents—a finding quite unexpected in view of Criegee's insistence on the necessity of drying all solvents.

From glycols containing two hydroxyl groups we turned our attention to compounds with three adjacent hydroxyl groups. Previous experiments<sup>4</sup> had already shown that compounds such as

(1) Rudolf Criegee, *Ann.*, **481**, 275 (1930); *Ber.*, **64**, 260 (1931); *Angew. Chem.*, **50**, 153 (1937); this last article contains a review of the literature concerned.

(2) Malaprade, *Compt. rend.*, **186**, 382 (1929).

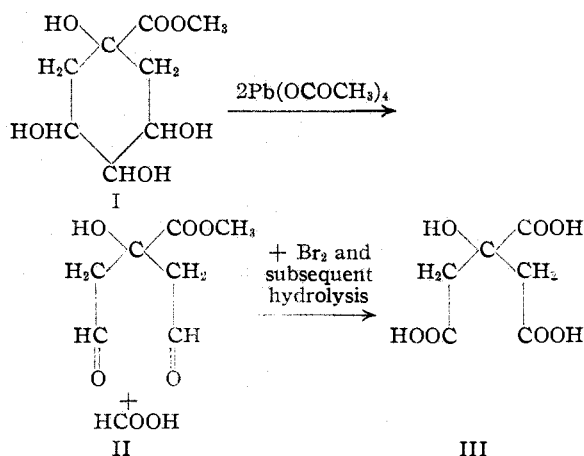
(3) (a) Criegee, *Ber.*, **64**, 264 (1931); (b) H. O. L. Fischer and E. Baer, *Helv. Chim. Acta*, **17**, 622 (1934); (c) E. Baer and H. O. L. Fischer, *THIS JOURNAL*, **61**, 761 (1939); and (d) *J. Biol. Chem.*, **128**, 463 (1939).

(4) H. O. L. Fischer and Dangschat, *Helv. Chim. Acta*, **17**, 1196 (1934); **17**, 1200 (1934); **18**, 1204 (1935).

quinic acid (1 mole) and shikimic acid (1 mole) could be oxidized with periodic acid (2 moles) in aqueous solution. Dialdehydes were formed and the central carbon atom was split out as formic acid.

In order to test the usefulness of lead tetraacetate for this reaction, we studied the oxidation of the methyl ester of quinic acid and found, in agreement with our expectations, that one mole of quinic acid methyl ester (I) in aqueous solution formed one mole of dialdehyde (II) and one mole of formic acid, using up two moles of lead tetraacetate.<sup>5</sup>

The reaction takes place according to the equation



Titration according to the method of Willstätter and Schudel showed an amount of dialdehyde present in the aqueous solution equal to the theoretical. The dialdehyde was then oxidized by bromine to the stable citric acid (III) which was isolated in a yield of 86% of the theoretical.

## Experimental

### A. Glycol Cleavage

**I. Lead Tetraacetate Oxidation of 1,2-5,6-Diacetone-*d*-mannitol.**—A colorless solution of 4.43 g. of lead tetraacetate (0.01 mole) in 25 cc. of warm glacial acetic acid<sup>6</sup> was added rapidly with constant agitation to a solution of 2.63 g. of diacetone-*d*-mannitol (m. p. 121–122°)<sup>3d</sup> (p. 466) (0.01 mole) in 60 cc. of water. The oxidation took place instantaneously and the mixture remained perfectly clear. After a few minutes 20 cc. of 1 *N* sulfuric acid was added, and the precipitate of lead sulfate was separated by centrifuging. During this procedure the cleavage product, acetone-*d*-glyceraldehyde, hydrolyzed

(5) Cases in which more lead tetraacetate is required will be described in a subsequent paper. (J. G.)

(6) The glacial acetic acid was warmed only for the purpose of dissolving the lead tetraacetate in a minimal quantity of solvent, thus keeping the ratio of water and acid as much as possible in favor of the water.

quickly to *d*-glyceraldehyde and acetone in the acid solution. Acetone was removed by evaporation *in vacuo* and the concentrate was made up to 50.00 cc. with distilled water (solution I). The product was not isolated at this stage. The precipitation of the 2,4-dinitrophenylhydrazone (m. p. 155–156°) and dimedone compound (m. p. 198°;  $[\alpha]_D +198^\circ$ ) from the above solution confirmed our expectation that the product of the reaction would be the same (*i. e.*, *d*-glyceraldehyde) in water as in non-aqueous solvents. The yield was determined by the method of Willstätter and Schudel.<sup>7</sup> In three such titrations, 5.00 cc. of solution I required 39.2, 39.4 and 39.6 cc. of 0.1 *N* iodine solution, equivalent to 176, 177 and 178 mg. of aldehyde, respectively. The yield was therefore 98.8% of the theoretical.

Solution I was dextro-rotatory,  $[\alpha]_{20}^D +9.0^\circ$ . We already have reported<sup>8</sup> the occurrence of solutions of glyceraldehyde with low specific rotation and have described a method for converting this material to a form with the characteristic maximal specific rotation of  $+14^\circ$ .

**II. Lead Tetraacetate Oxidation of Pinacol.**—A colorless solution of 4.43 g. of lead tetraacetate (0.01 mole) in 30 cc. of warm glacial acetic acid was added gradually with gentle agitation to 1.18 g. of pinacol (0.01 mole) dissolved in 50 cc. of distilled water. After a few minutes<sup>9</sup> 5 cc. of 5 *N* sulfuric acid was added, and the precipitated lead sulfate was separated by centrifuging. A perfectly clear solution was obtained, containing only the cleavage product, acetone (0.02 mole). The solution was then made up to 100.0 cc. with distilled water and the acetone determined quantitatively by the method of Messinger.<sup>10</sup> Two 5.0-cc. portions of the solution required 56.8 and 57.3 cc. of 0.1 *N* iodine solution, respectively, which correspond to 55.0 and 55.4 mg. of acetone, respectively; yield, 95% of the theoretical.

### B. Cleavage of 1,2,3-Polyalcohols

The oxidation of quinic acid methyl ester was carried out in two different ways with equally good results. (a) The lead tetraacetate dissolved in glacial acetic acid was added slowly to the aqueous solution of the substance to be oxidized, as described in the case of pinacol and diacetone-mannitol. (b) The aqueous solution of the substance to be oxidized was poured into a saturated solution of lead tetraacetate in glacial acetic acid. We shall describe the latter method only, since the inverted order of procedure is an interesting variation of the oxidation with lead tetraacetate in aqueous solution.

**Lead Tetraacetate Oxidation of Quinic Acid Methyl Ester.**—A solution of 6.18 g. of quinic acid methyl ester (0.03 mole) in 50 cc. of distilled water was poured into a mixture of 25 cc. of glacial acetic acid and 26.58 g. of lead tetraacetate (0.06 mole). The crystals of lead tetraacetate dissolved slowly as the oxidation proceeded. After ten minutes, 125 cc. of 1 *N* sulfuric acid was added, the solution was made up to 500.0 cc. and the precipitate

(7) Willstätter and Schudel, *Ber.*, **51**, 780 (1918).

(8) H. O. L. Fischer and E. Baer, *Helv. Chim. Acta*, **19**, 524 (1936); refs. 3b and 3c.

(9) The velocity of this reaction is much higher in aqueous solution than in organic solvents. Probably this will be the case for other compounds also.

(10) Messinger, *Ber.*, **21**, 3366 (1888).

of lead sulfate was removed by centrifuging. The dialdehyde formed was determined by titration according to Willstätter and Schudel; 25 cc. of the solution used up 61.0 cc. of 0.1 *N* iodine solution: dialdehyde calculated, 208.8 mg.; found, 211.0 mg.

For the oxidation of the dialdehyde the solution was freed from the excess of sulfuric acid by dropwise addition of barium acetate and diluted to 300 cc. with distilled water; 15 g. of bromine was added and the resulting mixture was placed in a tightly sealed bottle and allowed to stand for two days with occasional shaking. The excess bromine was removed by aeration, the hydrobromic acid formed was removed with silver acetate and the excess silver was precipitated with hydrogen sulfide. The mixture was then evaporated to dryness and the remaining citric acid monomethyl ester was saponified by boiling for half an hour with 60-cc. of 2 *N* sodium hydroxide. An amount of 1 *N* sulfuric acid (120 cc.) equivalent to the sodium hydroxide used was added and the solution evaporated to dryness under reduced pressure. The *citric acid* was separated from the sodium sulfate by extraction of the residue with ethyl acetate; 4.9 g. of crude citric acid was obtained (86% yield). Recrystallization from water yielded pure citric acid (m. p. 151°).

**Preparation of *d*-(—)-glyceric acid.**<sup>11</sup>—To an aqueous solution of *d*-glyceraldehyde prepared as described on page 2608, Col. 1, from 25 g. of diacetone-*d*-mannitol,<sup>3d</sup> 40 g. of bromine was added and the solution was shaken for two hours. After standing at room temperature for an additional fifteen hours, the excess bromine was removed by aeration and the bromide ions by shaking with silver carbonate or acetate. The silver ions were precipitated by hydrogen sulfide. The solution was then evaporated at 40° (10 mm.) to a dry sirup of constant weight; 15.4 g. (76% of the theoretical) of glyceric acid was obtained.

**Preparation of *d*-Glyceric Acid Methyl Ester (Dextrorotatory).**—Eleven grams of glyceric acid together with 250 cc. of dry methyl alcohol, containing 1.5% of hydrochloric

acid (gas), was refluxed for twenty-four hours. After shaking the liquid for twelve hours with finely powdered silver carbonate, the silver salts were removed by centrifuging. The methyl alcohol was evaporated at reduced pressure and the residue was distilled *in vacuo*: yield, 11.5 g. (92% of the theoretical) of glyceric acid methyl ester; b. p. (8 mm.) 114–116°. Calculated for C<sub>4</sub>H<sub>8</sub>O<sub>4</sub> (120): C, 40.00; H, 6.70. Found: C, 39.96; H, 6.70. *Optical rotation* in homogeneous substance: α<sup>20</sup><sub>D</sub> +5.92 (1-dm. tube, *d*<sup>20</sup>, 1.279, [α]<sup>20</sup><sub>D</sub> +4.7).<sup>12</sup>

**Preparation of the Calcium Salt of *d*-Glyceric Acid.**—Eight grams of *d*-glyceric acid methyl ester was added to a solution of 2.47 g. of calcium hydroxide in 40 cc. of distilled water. After warming on the water-bath for one hour, the solution was neutralized with a few drops of 5 *N* hydrochloric acid and filtered, while still hot. Warm ethanol was then added until the clear and hot solution became turbid and the mixture was allowed to cool in the refrigerator; 8.0 g. of calcium salt was precipitated after six hours (84% yield). Calcd. for (C<sub>3</sub>H<sub>5</sub>O<sub>4</sub>)<sub>2</sub>Ca·2H<sub>2</sub>O (286): Ca, 13.99. Found: Ca, 13.95. *Optical rotation* of the calcium salt containing 2 moles of crystal water, in aqueous solution: 1-dm. tube, *c* = 5.19, α<sup>20</sup><sub>D</sub> +0.67°, [α]<sup>20</sup><sub>D</sub> +12.9°.<sup>13</sup>

### Summary

It has been shown that oxidation with lead tetraacetate can be carried out quantitatively in aqueous solution and in water-containing solvents. This observation that the reaction does not always require dry organic solvents enlarges the field of its application. Lead tetraacetate yields the same oxidation products in water as in organic solvents, except in rare cases where secondary hydrolytic reactions may occur.

(12) Frankland and Turnbull, *J. Chem. Soc.*, 459 (1914).

(13) E. Fischer and Jacobs, *Ber.*, 40, 1069 (1907); Wohl and Schellenberg, *ibid.*, 55, 1404 (1922).

TORONTO, CANADA

RECEIVED JULY 5, 1939

(11) Wohl and Freudenberg, *Ber.*, 56, 309 (1923).

[CONTRIBUTION NO. 150 FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, THE UNIVERSITY OF TEXAS]

## The Nitrogen Compounds in Petroleum Distillates. XV. Counter-Current Acid Extraction of Kero Bases. Isolation of 2,4-Dimethyl-8-*n*-propylquinoline

BY W. NELSON AXE<sup>1</sup> AND J. R. BAILEY

### Introduction

It has been reported previously<sup>2</sup> that a satisfactory separation of 2,3-dimethyl-8-*n*-propyl- and 2,3,4,8-tetramethylquinoline from associated bases in the 300° boiling range of kero bases was accomplished by supplementing the conventional methods of processing petroleum bases with so-called fractional degassing of their acid sulfite solution under aeration.

(1) Research Department, Phillips Petroleum Company, Bartlesville, Oklahoma.

(2) W. N. Axe and J. R. Bailey, *THIS JOURNAL*, 60, 3028 (1938).

In Jantzen's monograph,<sup>3</sup> the author reports the isolation of the following products from coal tar bases (b. p. 238–266°), through employment of counter-current extraction: quinoline, each of the seven monomethylquinolines, 2,8-dimethylquinoline,<sup>4</sup> isoquinoline, 1- and 3-methylisoquinoline, 1,3-dimethylisoquinoline, two C<sub>10</sub>H<sub>9</sub>N bases (probably 6-methyl- and 5- or 7-methylisoquino-

(3) Ernst Jantzen, "Das fraktionierte Destillieren und das fraktionierte Verteilen," Verlag Chemie, Berlin, 1932, pp. 117–137.

(4) Isolated from California petroleum by Lake and Bailey, *THIS JOURNAL*, 55, 4143 (1933).