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A NEW CARBON OXIDE

SYNTHESIS OF HEXAHYDROXYBENZENE TRIS OXALATE

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Little work has been done on the synthesis of carbon oxides, that is, compounds containing carbon and oxygen, but not hydrogen. A simple statistical illustration may help to point out the vast potential of this neglected area: the number of organic compounds amounts to approximately one million, perhaps fifteen to twenty times the number of compounds which do not contain carbon.[1] Considering the binary compounds of oxygen with just one "inorganic" element, say nitrogen, we find eight oxides reported.[2] Yet only four carbon oxides have been adequately characterized: carbon monoxide, carbon dioxide, carbon suboxide, and mellitic trianhydride. In addition, the following hydrates of the polyketo alicyclic carbon oxides have been prepared: octahydroxycyclobutane,[3] leuconic acid[4] and triquinoyl.[4] Infrared studies on these compounds suggest that they are not carbon oxides at all, but rather polyhydroxycycloalkanes. We wish to report the synthesis of a new carbon oxide. Treatment of hexahydroxybenzene with oxalyl chloride in tetrahydrofuran produced this oxide, hexahydroxybenzene tris oxalate, as a tetrahydrofuran solvate. The oxide was thermally unstable and hygroscopic. A sodium fusion revealed that the compound contained no halogen. The oxide could be dried in a vacuum to yield a partially desolvated material which contained only 0·2% of tetrahydrofuran. Recrystallization of the dried material from tetrahydrofuran produced the original solvate. The infrared spectrum of the dried material in Kel-F showed no absorptions due to —OH and —CH groups. This evidence supports the theory that the solvate contained tetrahydrofuran. The IR spectrum of the oxide showed an absorption at 5·50 μ, with a shoulder at 5·63 μ, as compared to the infrared spectrum of catechol oxalate which showed absorptions at 5·53 and 5·63 μ. Hydrolysis of the oxide furnished close to the theoretical amounts of hexahydroxybenzene and oxalic acid.

EXPERIMENTAL

Infrared spectra were obtained on a Perkin-Elmer Infracord, Model 137. Since heat and humidity decompose the oxide, all filtrations were carried out in an atmosphere of dry nitrogen, and all transfers were made in a refrigerated dry box.

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[1] C. W. Keenan and J. H. Wood, *General College Chemistry*, p. 628, 2nd ed, Harper, New York (1961).

[2] T. Moeller, *Inorganic Chemistry*, pp. 591–613, Wiley, New York (1952).

[3] R. West, H. Y. Niu and M. Ito, *J. Amer. Chem. Soc.* **85**, 2584 (1963).

[4] A. J. Fatiadi, H. S. Isbell and W. F. Sager, *J. Res. Nat. Bureau Standards*, **67A**, 153 (1963).

Hexahydroxybenzene tris oxalate. Hexahydroxybenzene (713 mg) and 25 ml of a 10% solution of oxalyl chloride in tetrahydrofuran were refluxed for four hours. When the reaction mixture was cooled, white crystals separated. The crystals were washed with tetrahydrofuran, recrystallized from a 10% solution of oxalyl chloride in tetrahydrofuran, and dried in a stream of nitrogen. (*Anal.* Calcd. for $C_{12}O_{12}$·3·65 THF: C, 53·3; H, 4·9. Found: C, 53·0; H, 5·2%). A portion of the material was dried at a pressure of 10 μ for 5 min at 100° and then for 30 min at 70°. (*Anal.* Calcd. for $C_{12}H_{12}$·0·2 THF: C, 43·8; H, 0·5. Found: C, 43·7; H, 0·8%).

Hydrolysis of hexahydroxybenzene tris oxalate. Hexahydroxybenzene tris oxalate (150 mg) was heated on the steam bath with 1·5 cm^3 of concentrated hydrochloric acid for 5 min. The suspended crystals were collected from the cooled reaction mixture and were washed with 1 cm^3 of concentrated hydrochloric acid. The hexahydroxybenzene thus isolated proved identical to an authentic sample and weighed 76·9 mg. (theoretical yield from $C_{12}O_{12}$·0·2 THF, 74·7 mg). The filtrate was mixed with 150 ml of water, 12·5 ml of Zimmerman–Reinhardt solution, and 15 ml of 1:8 sulfuric acid, and titrated with permanganate. To reach the end-point, 9·9 ml of 0·250N permanganate was required, equivalent to 111 mg of oxalic acid (calcd. 116 mg).

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