Tetrahedron Letters,Vol.28,No.34,pp 3899-3900,1987 0040-4039/87 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

UNUSUAL CATALYTIC ACTIVITY OF ANALOGUES OF 2-IODOXYBENZOIC ACID IN THE HYDROLYSIS OF ACTIVE PHOSPHATES

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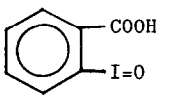
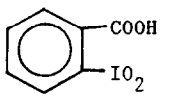
Abstract: 2-Iodoxybenzoic acids catalyze the hydrolysis of active phosphorus esters with ca. 60-110% of the efficiency of their 2-iodosobenzoic acid analogues. Iodoxy compounds with considerable potential for use as phosphorus decontamination agents have been synthesized.

The discovery by Moss and coworkers[1-4] of a variety of derivatives of 2-iodosobenzoic acid (IBA; **1**) that accelerate the hydrolysis of p-nitrophenyl diphenyl phosphate (PNPDPP) by up to 15,000 times in a CTAC micellar system represented a fundamental advance in the chemistry of phosphorus decontamination. The only disadvantage to the practical use of iodoso derivatives appears to be their instability;[5] one of the IBA derivatives prepared by Moss lost activity over a period of time, and it is likely that other iodosobenzoates present similar stability problems.[3] We now wish to report the surprising[6] catalytic efficiency of iodoxy analogues (**2**) of iodoso compounds previously found to be effective catalysts. In addition to its theoretical significance, this finding is of considerable practical importance because the stability of the iodoxy derivatives is far higher than their iodoso analogs. Moreover, iodoxy compounds are often simpler to prepare than the iodoso derivatives.



1 (IBA)



2 (IBX)

Iodoxybenzoic acids (IBX) are easily prepared from iodobenzoic acids by chlorination-hydrolysis, chlorination-oxidation, reaction with peroxymonosulfuric acid, or other methods.[5,7] Thus, 4-nitro- and 5-methyl-2-iodoxybenzoic acids were obtained via chlorination-hydrolysis of the corresponding 2-iodo acids,[8] 5-dodecyloxy-IBX was similarly prepared using Ac_2O/H_2O_2, followed by hydrolysis, and 5-butoxy- and 5-octyloxy-IBX were isolated from preparations of the corresponding iodoso derivatives. The corresponding IBA derivatives were synthesized by standard methods (see Table 1).[8]

p-Nitrophenyl diphenyl phosphate (PNPDPP) and p-nitrophenyl isopropylphenylphosphinate (NPIPP) were utilized for the kinetics measurements. Kinetics were carried out in 0.001M CTAC buffered to pH 8.5 (borate buffer) and were monitored spectrophotometrically for the appearance of p-nitrophenolate anion. Second-order rate constants were determined from rate measurements at several (usually seven) concentrations of catalyst (IBA or IBX). Details of the kinetics procedures have been reported elsewhere.[9,10]

The IBX derivatives tested possess from 56% (5-octyloxy-IBX) to 107% (5-butoxy-IBX) of the catalytic efficiency of the corresponding IBA compounds, as shown in Table 1. In absolute

terms, the most efficient catalyst vs. PNPDPP was 5-octyloxy-IBX, with k_2 = 4494, which was 99% of the iodoso activity. 5-Butoxy-IBX was nearly as efficient, with k_2 = 4450, and 97% of the iodoso activity. However, 4-nitro-IBX showed the greatest kinetic advantage compared to the iodoso, at 106%. Versus NPIPP, 5-butoxy-IBX was the most efficient, both in overall rate (k_2 = 433) and in advantage over the iodoso (107%). 5-Dodecyloxy- and 5-octyloxy-IBX possessed the next highest efficiencies, but with significantly lower advantages than the IBA derivatives (83 and 56%, resp.). 4-Nitro-IBX, although about four times less active than the 5-octyloxy, possessed 100% of the activity of the corresponding iodoso compound.

In conclusion, we have demonstrated that 2-iodoxybenzoic acids are highly active catalysts for the hydrolysis of phosphates and phosphinates. Their high activity and ease of synthesis[11] makes them attractive candidates for use as decontamination catalysts.

Acknowledgements. We thank the Army Research Office for financial support.

TABLE 1

Second-Order Rate Constants ($M^{-1}sec^{-1}$) for 2-Iodoxybenzoic Acid vs 2-Iodosobenzoic Acid Cleavages in 0.001M CTAC at pH 8.5

Catalyst[a]	vs. NPIPP			vs. PNPDPP		
	k_2(IBX)	k_2(IBA)	k_2[IBX]/k_2[IBA]	k_2(IBX)	k_2(IBA)	k_2[IBX]/k_2[IBA]
5-butoxy[c,b]	433	406	1.07	4450	4575	0.97
5-octyloxy[c,c]	256	461	0.56	4494	4526	0.99
5-dodecyloxy[b,c]	300	361	0.83	4012	4864	0.82
4-nitro[c,d]	66	66	1.00	1089	1032	1.06
5-methyl[c,b]	64	90	0.71	564	774	0.73

a. Footnotes denote the synthetic procedures used to prepare the IBX or IBA compounds, resp., from the corresponding 2-iodobenzoic acid. The quantity "k_2[IBX]/k_2[IBA]" represents the kinetic advantage of the IBX over the IBA derivative. High turnover numbers were indicated by experiments using large substrate:catalyst ratios.

b. (1) Ac_2O/H_2O_2, (2) H_2O.[12] c. Chlorination/hydrolysis.[13] d. Fuming nitric acid.[14]

References and Notes:

1. Moss, R. A.; Alwis, K. W.; Bizzigotti, G. O. J. Amer. Chem. Soc. 1983, 105, 681.
2. Moss, R. A.; Alwis, K. W.; Shin, J-S. Ibid. 1984, 106, 2651.
3. Moss, R. A.; Kim, K. Y.; Swarup, S. Ibid. 1986, 108, 788.
4. Moss, R. A.; Chatterjee, S; Wilk, B. J. Org. Chem. 1986, 51, 4303.
5. Examples are presented in Banks, D. F. Chem. Rev. 1966, 66, 243.
6. In ref. 2, Moss reported that IBX possessed only 28% of the activity of IBA.
7. Formo, M. W.; Johnson, J. R. In Organic Syntheses; Horning, E. C., Ed.; Wiley: New York, 1955; Coll. Vol. III, pp. 486-7.
8. For details, see Duell, B. L., Ph.D. Thesis, University of Florida, 1987.
9. Mackay, R. A.; Longo, F. R.; Knier, B. L.; Durst, H. D. J. Phys. Chem. 1987, 91, 861.
10. Katritzky, A. R.; Duell, B. L.; Durst, H. D. Langmuir, in press.
11. The 5-methyl- and 4-nitro-IBX precursors are both commercially available (Aldrich), thus large-scale synthesis should be quite feasible.
12. Pausacker, K. H. J. Chem. Soc. 1953, 107.
13. Lucas, H. J.; Kennedy, E. R; Formo, M. W. Ref. 7, pp. 482-6.
14. Morrison, G. F.; Hooz, J. J. Org. Chem. 1970, 35, 1196.

(Received in USA 7 May 1987)