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NUCLEOPHILIC 1,2-ADDITION TO THE CARBONYL GROUP OF p-QUINONES AND A NEW MOLECULAR REARRANGEMENT OF A PENTAOXYPHOSPHORANE

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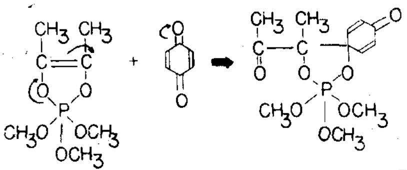
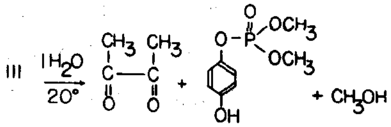
Bishop, Porter and Tong[2] have provided evidence for the *reversible* nucleophilic 1,2-addition of bisulfite and of hydroxide ions to the carbonyl group of p-quinones. The adducts could not be isolated and, therefore, their structures were not rigorously established. We report here the isolation of a crystalline adduct, III, resulting from the *irreversible* 1,2-addition of a carbon-nucleophile, I, to the carbonyl group of p-benzoquinone, II. The reaction was carried out in CH_2Cl_2 at 20°.



I; +48.5 PPM[3] II III; + 50.3 PPM[3]

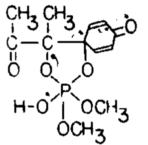
Evidently, the p-quinone tends to undergo 1,2-addition in preference to 1,4-addition, and the initial adduct is trapped by cyclization to the saturated oxyphosphorane III. The nucleophile[4], I, is the unsaturated oxyphosphorane[5,6,7] formed from trimethyl phosphite and biacetyl. In the formation of I, the phosphorus of trimethyl phosphite added to the carbonyl-<u>oxygen</u> of the α-diketone, just as it added also to the carbonyl-oxygen of <u>p</u>-quinones[8] and of <u>o</u>-quinones[5].

The oxyphosphorane III[9] was recrystallized from hexane and was dried at 20° under nitrogen; III melted with decomposition at 65° and was very sensitive to moisture. The structure of III follows from: (1) the presence of infrared bands (in CH_2Cl_2) at 5.84μ (acetyl C = O), 5.98μ (cyclohexadienone C = O), 6.13μ (C = C) and 9.35μ ($POCH_3$); (2) the presence of H^1 n.m.r. signals (in CCl_4) at 3.3 and 3.8 p.p.m. in the τ-scale ($4H^1$ multiplet due to vinyl-H^1), 6.40τ ($9H^1$ doublet, J_{HP} 12.5 c.p.s. due to CH_3O), 7.83τ ($3H^1$ singlet due to acetyl) and 8.65τ ($3H^1$ singlet due to CH_3C); (3) the relatively large <u>positive</u> P^{31} chemical shift (in CH_2Cl_2), +50.3 p.p.m. <u>vs</u> 85% H_3PO_4 (a decet due to splitting by the nine methoxy-protons)[4,5,6]; (4) the ultraviolet absorption (in CH_2Cl_2) with λ_{max} 230 mμ, ε = 9,600; (5) the formation of biacetyl (IV), dimethyl (4-hydroxyphenyl)phosphate[9] (V) and methanol (VI) when a benzene-solution of III was treated with <u>one mole equivalent</u> of water. V[9] was identical with an authentic sample, m.p. 71-72°, made from dimethyl phosphite, $(CH_3O)_2P(O)H$, and <u>p</u>-benzoquinone by the method of Ramirez and Dershowitz[10].

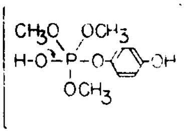


IV V; + 4.1 PPM[3] VI

The initial attack by water on III probably leads to displacement of a methoxy group[11] and formation of an intermediate, VII, which collapses to the observed products, IV and V. If the initial attack by the water on the oxyphosphorane III had resulted in an opening of the ring, the products should have been biacetyl and the intermediate VIII, which would collapse to hydroquinone and trimethyl phosphate[8]. The latter two were not observed in the hydrolysis of III when one mole of water was employed.

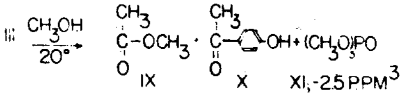


VII

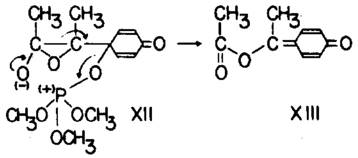


VIII

A second purpose of this Communication is to disclose a novel molecular rearrangement of an oxyphosphorane, III. An exothermic reaction occurred when the oxyphosphorane III was treated with methanol at 20°; the products were methyl acetate (IX), p-hydroxyacetophenone (X) and trimethyl phosphate (XI), in over 90% of the theory.



The rearrangement was faster and cleaner in methanol than in ethanol. Structure XII could be an intermediate; ejection of phosphate from XII would provide the driving force for the formation of XIII, which is the acetate of the cyclohexadienone-enol tautomer of p-hydroxyacetophenone. The acetate XIII should undergo methanolysis to the observed products, IX and X.



XII XIII

Other mechanisms are conceivable, but the one suggested here explains the formation of an enol-lactone (analogous to XIII) when the 2:1 acenaphthenequinone-trimethyl phosphite adduct was treated with methanol[12]. Structures resembling XII have been suggested by Kwart[13] to explain the formation of anhydride from the reaction of peroxy anions with α-diketones. Presumably, a polar solvent like methanol, with a relatively high dielectric constant but incapable of effecting hydrolysis of the oxyphosphorane III, would facilitate this rearrangement.

Not many additions to the carbonyl group of p-quinones, nucleophilic or otherwise[14,15] have been reported. We are pursuing our studies on additions of phosphorus compounds to quinones[5,8,10,16].

References

1. Investigation supported by Public Health Service Grant No. CA-04769-05 from the National Cancer Institute.

2. (a) C. A. Bishop, R. F. Porter and L. K. J. Tong, J. Am. Chem. Soc., 85, 3991 (1963); (b) C. A. Bishop and L. K. J. Tong, Tetrahedron Letters, No. 41, 3043 (1964).

3. δ P^{31} in p.p.m. vs 85% H_3PO_4, taken at 40.5 Mc/sec.

4. F. Ramirez, N. Ramanathan and N. B. Desai, J. Am. Chem. Soc., 85, 3465 (1963).

5. (a) F. Ramirez and N. B. Desai, *J. Am. Chem. Soc.*, **82**, 2652, (1960); (b) *ibid.*, **85**, 3252 (1963).

6. G. H. Birum and J. L. Dever, Abstracts, 135th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1958, p. 101P.

7. (a) V. A. Kukhtin, *Dokl. Akad. Nayk. S.S.S.R.*, **121**, 466 (1958); (b) V. A. Kukhtin and K. M. Orekhova, *J. Gen. Chem., U.S.S.R.*, **30**, 1229 (1960).

8. (a) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 956 (1957); (b) *ibid.*, **23**, 778 (1958); (c) *J. Am. Chem. Soc.*, **81**, 587 (1959); (d) F. Ramirez, B. H. Chen and S. Dershowitz, *J. Am. Chem. Soc.*, **81**, 4338 (1959).

9. The elemental analysis was in agreement with the formula.

10. F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 1282 (1957).

11. F. Ramirez, O. P. Madan, N. B. Desai, S. Meyerson and E. M. Banas, *J. Am. Chem. Soc.*, **85**, 2681 (1963).

12. (a) F. Ramirez and N. Ramanathan, *J. Org. Chem.*, **26**, 3041 (1961); (b) F. Ramirez, N. Ramanathan and N. B. Desai, *J. Am. Chem. Soc.*, **84**, 1317 (1962).

13. H. Kwart and N. J. Wegemer, *J. Am. Chem. Soc.*, **83**, 2746 (1961).

14. B. Eistert, H. Fink and A. Muller, *Chem. Ber.*, **95**, 2403 (1962).

15. D. Bryce-Smith and A. Gilbert, *Proc. Chem. Soc.*, 87 (1964).

16. (a) F. Ramirez and S. Dershowitz, *Chemistry and Industry*, 665 (1956); (b) *J. Am. Chem. Soc.*, **78**, 5614 (1956).