

Oxidation Reactions using Sodium Metaperiodate Supported on Silica Gel

By Dharmendra N. Gupta, Philip Hodge,* and (in part) J. Eric Davies, Chemistry Department, University of Lancaster, Bailrigg, Lancaster LA1 4YA

No reaction occurred when solutions of 2,5-di-*t*-butylhydroquinone, dibenzyl sulphide, *trans*-cyclohexane-1,2-diol or hydrazobenzene in methylene chloride were stirred with powdered sodium metaperiodate at 20 °C for several hours. However, these and several closely related substrates were oxidized in good yield, generally within a few hours, when solutions in methylene chloride, and in some cases benzene or ether, were stirred with sodium metaperiodate supported on silica gel. The supported reagent was prepared by evaporating to dryness an aqueous solution of sodium metaperiodate in the presence of silica gel, followed by heating at 120 °C *in vacuo*. The reagent appears to consist mainly of a monomolecular layer of sodium metaperiodate bound to the silica gel by the surface hydroxy-groups, together with a minor amount of crystalline anhydrous sodium metaperiodate.

THERE has recently been considerable interest in supported reagents, particularly those supported on cross-linked polystyrenes¹ and those supported on inorganic materials such as silica gel and alumina.^{2,3} The use of sodium metaperiodate as an oxidant in organic chemistry has been limited by its insolubility in non-polar solvents.^{4,5} We report that sodium metaperiodate supported on silica gel can be used to oxidize various organic compounds in methylene chloride, benzene, or ether. This reagent is an alternative to quaternary ammonium periodates⁶ and like most supported reagents^{1,2,3} it has the attractive feature that the reactions using it can be largely worked up by filtration. Our work suggests that the reagent consists mainly of a monomolecular layer of sodium metaperiodate bound to the silica gel by the surface hydroxy-groups, together with a minor amount of crystalline anhydrous sodium metaperiodate.

Preparation of the Reagent and its Scope as an Oxidant.

—Except where indicated otherwise the supported reagent was prepared by evaporating to dryness a solution

of sodium metaperiodate (1 part by weight) in water in the presence of chromatographic grade silica gel (10 parts). After being heated at 120 °C *in vacuo* the reagent was a free-flowing solid containing 0.36 mmol of sodium periodate per g. Oxidations carried out using this reagent at 20 °C are summarised in Table 1.

The oxidation of 2,5-di-*t*-butylhydroquinone (DBHQ), a typical hydroquinone, was investigated first. This substrate failed to react with suspensions of powdered sodium metaperiodate in methylene chloride, benzene, or ether during 6 h, but it reacted smoothly with a 10% molar excess of the supported reagent in methylene chloride or benzene to give 2,5-di-*t*-butyl-1,4-benzoquinone in 98 and 55% yields, respectively, in 3 h. No reaction occurred when ether was the solvent. Since 2.0 mmol of DBHQ in benzene reacted with 1.0 mmol of the supported reagent to give 1.7 mmol of the quinone, the sodium iodate formed by reaction of the sodium metaperiodate with DBHQ could itself oxidize DBHQ. It was not, therefore, surprising to find that the oxidation

TABLE I
Oxidations using sodium metaperiodate supported on silica gel

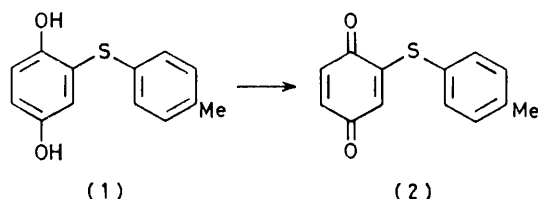
Substrate	Reaction conditions ^a Solvent, Reaction time (h)	Product	Yield ^b %
2,5-Di- <i>t</i> -butylhydroquinone	CH ₂ Cl ₂ , ^c 3	<i>p</i> -Quinone	99
	C ₆ H ₆ , ^d 3	<i>p</i> -Quinone	55 ^e
	C ₆ H ₆ , ^d 24	<i>p</i> -Quinone	86
Hydroquinone	CH ₂ Cl ₂ , 3	<i>p</i> -Quinone	98
1,2,3,4-Tetrahydronaphthalene-5,8-diol	CH ₂ Cl ₂ , 3	<i>p</i> -Quinone	86
2-Chlorohydroquinone	CH ₂ Cl ₂ , 2.5	<i>p</i> -Quinone ^f	97
2-Methoxyhydroquinone	CH ₂ Cl ₂ , 2.5	<i>p</i> -Quinone ^f	59 ^g
2-Methylnaphthalene-1,4-diol	CH ₂ Cl ₂ , 1	<i>p</i> -Quinone	91
	ether, 3	<i>p</i> -Quinone	91
	CH ₂ Cl ₂ , 2.5	<i>p</i> -Quinone (2)	100 ^g
4- <i>t</i> -Butylpyrocatechol	CH ₂ Cl ₂ , 2.5	<i>o</i> -Quinone	45 ^g
3,5-Di- <i>t</i> -butylpyrocatechol	CH ₂ Cl ₂ , 3	<i>o</i> -Quinone	75
Dibenzyl sulphide	CH ₂ Cl ₂ , ^g 96	Dibenzyl sulphoxide	66 ^g
<i>trans</i> -Cyclohexane-1,2-diol	CH ₂ Cl ₂ , 3	Hexane-1,6-dial	81 ^{e,g,h}
	ether, 3	Hexane-1,6-dial	23 ^e
	CH ₂ Cl ₂ , 3	Hexane-1,6-dial	95 ^{e,i}
<i>cis</i> -Cyclohexane-1,2-diol	CH ₂ Cl ₂ , 3	Hexane-1,6-dial	95 ^{e,i}
Hydrazobenzene	CH ₂ Cl ₂ , 1	Azobenzene	100
	ether, 6	Azobenzene	100

^a Reactions carried out at 20 °C. Unless indicated otherwise, 1.1 molar equivalents of supported reagent were used. ^b Unless indicated otherwise the yield given is that of crystalline material with satisfactory m.p. and/or spectral data. ^c When ether, acetone, or methyl acetate was the reaction solvent, no detectable (u.v.) reaction had occurred after 6 h. ^d Benzene is carcinogenic and can have deleterious long term effects. Similar experimental results would probably be obtained using toluene as a solvent. ^e Determined by ¹H n.m.r. spectroscopy. ^f Iodine also produced. ^g See Experimental section for details. ^h Hexane-1,6-dial dioxime prepared in 50% overall yield from diol. ⁱ Hexane-1,6-dial dioxime prepared in 53% overall yield from diol.

of some other hydroquinones (see Table 1) afforded iodine.

Several other hydroquinones and two pyrocatechols were then treated with the supported reagent in methylene chloride. Good yields of the corresponding quinones were usually obtained within a few hours (see Table 1). 2-Methylnaphthalene-1,4-diol also reacted satisfactorily when ether was the reaction solvent. In some cases filtering off the reagent and removing the solvent under reduced pressure left an essentially quantitative yield of the crystalline quinone and for such oxidations the present reagent is comparable in terms of efficiency and convenience with silver carbonate on Celite.⁷

The fact that the hydroquinone (1) reacted with a 10% molar excess of the reagent to give the quinone (2) suggested that hydroquinones are more readily oxidized than sulphides. Consistent with this it was found that to oxidize dibenzyl sulphide to the corresponding sulphoxide in good yield at 20 °C it was necessary to use a substantial excess of the reagent and a reaction time of 4 days. No reaction took place when the sulphide was treated with powdered sodium metaperiodate under otherwise similar conditions.



trans-Cyclohexane-1,2-diol (CHD) and hydrazobenzene reacted smoothly with the supported reagent in methylene chloride or ether to give hexane-1,6-dial and azobenzene respectively, but no reaction occurred if the supported reagent was replaced by powdered sodium metaperiodate. *cis*-Cyclohexane-1,2-diol also reacted smoothly with the supported reagent in methylene chloride.

Experiments to Clarify the Role of the Silica Gel.—Since silica gel has been successfully used to support other inorganic species,^{2,8} we considered it of interest to carry out experiments to clarify the role of the silica gel in the present reagent. That the reagent was not simply a physical mixture of sodium metaperiodate and silica gel was clear by the fact that there was no detectable reaction when DBHQ and CHD in methylene chloride were separately treated for 6 h with a mixture of ground sodium metaperiodate and silica gel (equal parts by weight).

When examined under a polarising microscope the supported reagent (10% loaded) was seen to be heterogeneous, but comparison with a physical mixture of ground sodium metaperiodate and silica gel (1:10 parts by weight) showed that the reagent contained only *ca.* 10% as much crystalline material as the physical mixture. The crystals were identified by laser Raman spectroscopy (see Table 2) as anhydrous sodium metaperiodate.⁹

X-Ray powder photographs of the supported reagent and the physical mixture confirmed these results. The photographs of the physical mixture showed intense lines at the positions expected¹⁰ for sodium metaperiodate, but the photographs of the reagent showed only weak lines at these positions superimposed on very diffuse bands. The photographs suggest, therefore, that most of the sodium periodate in the reagent was only present in the form of extremely small crystals (less than 50 Å thick¹¹) if it was crystalline at all.

TABLE 2

Raman spectra of sodium metaperiodate and related species^a

Sample	Spectrum (values in cm ⁻¹) ^b			
	270s	305s	791vs	855s
Aq. NaIO ₄	270s	305s	791vs	855s
Crystalline NaIO ₄	292m,	356m,	784vs	832s,
	301m	375m		874m
10% NaIO ₄ supported on silica gel		356m,	784vs	832m,
		375m		874w
10% NaIO ₄ on silanized silica gel		359w,	785vs,	833m,
		376w	794s	840w,
Minor component from 5% NaIO ₄ on silanized silica gel	290w	335m,	718m,br,	840m,
		615w,br	794vs	850w

^a See Experimental section for details of instrumentation, etc. ^b The following abbreviations are used: w = weak, m = medium, s = strong, vs = very strong, br = broad.

One possibility is that most of the sodium metaperiodate was present as a layer, possibly monomolecular, on the surface of the silica gel. Consistent with this there was a limit to the amount of oxidant that could be activated by a given weight of silica gel. Thus, when reagents containing 5, 10, 25, and 50 parts by weight of sodium metaperiodate per 100 parts of silica gel were separately treated with equimolar amounts of CHD in methylene chloride for 6 h, the yields of hexane-1,6-dial were 100, 100, 55, and 16% respectively. This indicates that the silica gel used in the present work could only successfully support *ca.* 12% by weight of sodium metaperiodate. With a 12% loaded reagent the *minimum* surface area required for a monomolecular layer is *ca.* 75 m² per g. The actual area required could easily be several times this value. By nitrogen adsorption at 90 K,¹² the surface area of the silica gel was 230 to 270 m² per g. The similarity of the values suggests that most of the sodium metaperiodate was present as a monomolecular layer on the surface of the silica gel.

If the oxidant was to be successfully coated onto the silica gel, the surface hydroxy-groups were required. Thus, reagents prepared using *silanized* silica gel and containing 5, 10, or 20 parts by weight of sodium metaperiodate per 100 parts of silica gel were unable to oxidize CHD to any detectable extent under similar reaction conditions to those used previously. The 5% and 10% loaded reagents (but not the 20%) were able to oxidize DBHQ in methylene chloride but the reactions only proceeded slowly during 20 h and at the end of this period the yields were less than 35%. The laser Raman spectra (see Table 2) of these reagents indicated that they not

only contained anhydrous sodium metaperiodate but a second unidentified crystalline material, a small relatively pure sample of which could be isolated from the 5% reagent. This material may well have been responsible for oxidizing the DBHQ.

EXPERIMENTAL

^1H N.m.r. spectra were measured at 60 MHz for solutions in deuteriochloroform. The polarising microscope had $\times 60$ magnification. Raman spectra were excited using the 514.5 nm line of a CRL argon ion laser and recorded on a Cary 81 spectrometer modified to a 90 °C viewing arrangement by Anaspec Ltd.; the solid samples were contained in spinning glass cells. X-Ray powder photographs were taken with a Philips PW 1024 camera using Cu-K_α radiation.

Methylene chloride was distilled from phosphorus pentoxide and stored over molecular sieves. Benzene* and ether were dried over sodium wire. The silica gel was British Drug Houses chromatographic grade, 60–120 mesh.

Preparation of Sodium Metaperiodate Supported on Silica Gel.—A mixture of sodium metaperiodate (2.00 g), silica gel (20.0 g), and de-ionised water (50 ml) was stirred at 20 °C for 30 min. The water was then removed at 10 mmHg using a rotary evaporator. Benzene (50 ml) was added and was evaporated similarly. The reagent was finally dried for 16 h *in vacuo* (0.5 mmHg) oven at 120 °C. The reagent generally contained, by iodimetry, *ca.* 0.36 mmol of sodium metaperiodate per g.

Other reagents with different loadings of oxidant and/or using silanized silica gel were prepared similarly. The silanized silica gel was prepared by treating silica gel (100 g) with hexamethyldisilazane (40 ml) in sodium-dried toluene (200 ml) at reflux temperature for 4 days. At the end of this period the product was filtered off, washed successively with toluene and methylene chloride, and then dried to constant weight at 60 °C and 0.5 mmHg.

Oxidations using Supported Reagents.—The starting materials, obtained commercially or prepared by literature methods, and all the isolated products (see Table 1) had m.p.s in good agreement with literature values. The oxidation reactions were monitored by u.v. and/or n.m.r. spectroscopy. The following reaction procedures are typical.

(a) *Oxidation of 2-(p-tolylsulphenyl)hydroquinone* (1). The substrate (464 mg) and sodium metaperiodate supported on silica gel (6.1 g, 10% loaded) were stirred in methylene chloride (20 ml) at 20 °C for 2.5 h. The solids were then filtered off and washed with methylene chloride (2×10 ml). Evaporation of the solvent from the combined filtrate and washings gave 2-(p-tolylsulphenyl)-1,4-benzoquinone (2) (461 mg), m.p. 107–109 °C (lit.,¹³ 108–110 °C), δ 2.41 (s, 3 H, C-methyl), 5.90 (d, J 2 Hz, 3-H), 6.60 (dd, J 2 and 10 Hz, 5-H), 6.79 (d, J 10 Hz, 6-H), and 7.30 p.p.m. (4 H, br m, ArH).

(b) *Oxidation of dibenzyl sulphide.* The substrate (428 mg) and sodium metaperiodate supported on silica gel (9.4 g, 10% loaded) were stirred in methylene chloride (15 ml) at 20 °C for 48 h. The solids were then filtered off and a sample of the filtrate analysed by ^1H n.m.r. spectroscopy. This showed the product to be a mixture of the sulphide (a

singlet at δ 3.57) and the sulphoxide (a singlet at δ 3.85) in the mole ratio 44 : 56. Fresh reagent (9.4 g) was added to the filtrate and the mixture stirred for a further 48 h. The solids were then filtered off and washed with methylene chloride (2×10 ml). Evaporation of the solvent from the combined filtrate and washings gave the product (373 mg). By ^1H n.m.r. spectroscopy it contained only the sulphide (6%) and sulphoxide (94% corresponding to 77% yield). Recrystallisation of the product from aqueous ethanol gave dibenzyl sulphoxide (302 mg, 66%), m.p. 132–134 °C (lit.,¹⁴ 135–136 °C).

(c) *Cleavage of trans-cyclohexane-1,2-diol.* The substrate (232 mg) and sodium metaperiodate supported on silica gel (6.1 g, 10% loaded) were stirred in methylene chloride (15 ml) for 3 h at 20 °C. The reaction was worked up in the usual way. By ^1H n.m.r. spectroscopy the product, a clear oil (185 mg) with ν_{max} (liquid film) 1720 cm^{-1} , was pure hexane-1,6-dial (81% yield); no starting material was present. The dialdehyde gave the dioxime (145 mg, 62%), m.p. 184–185 °C (lit.,¹⁵ 185–186 °C).

Attempted Oxidations Using Sodium Metaperiodate.—In several cases (see discussion) the experiments using the supported reagent were repeated using powdered sodium metaperiodate in place of the supported reagent. In no case did any reaction take place (by u.v. and/or ^1H n.m.r. spectroscopy). The powdered sodium metaperiodate, prepared using a ball mill or a pestle and mortar, consisted mainly of particles with diameters in the range 0.01 to 0.1 mm.

Calculation of Surface Area Required for a Monomolecular Layer of Sodium Metaperiodate.—The minimum surface area required for a monomolecular layer of sodium metaperiodate was calculated assuming that the tetrahedral periodate anion (I–O bond length 1.79 Å¹⁶) had three oxygen atoms in contact with the surface and that there was hexagonal close packing.

We thank the S.R.C. for financial support and Dr. R. W. H. Small for helpful discussions and for the X-ray photographs.

[1/459 Received, 23rd March, 1981]

REFERENCES

- 1 'Polymer-supported Reactions in Organic Synthesis,' ed. P. Hodge and D. C. Sherrington, John Wiley and Sons, Chichester, 1980.
- 2 A. McKillop and D. W. Young, *Synthesis*, 1979, 401 and 481.
- 3 G. H. Posner, *Angew. Chem. Intl. Edn.*, 1978, 17, 437; K-T. Lieu and Y-C. Tong, *J. Org. Chem.*, 1978, 43, 2717.
- 4 H. O. House, 'Modern Synthetic Reactions,' W. A. Benjamin Inc., Menlo Park, California, 1972, p. 353.
- 5 B. Sklarz, *Quart. Rev.*, 1967, 21, 3.
- 6 A. K. Qureshi and B. Sklarz, *J. Chem. Soc. C*, 1966, 412; G. E. Keck and S. A. Fleming, *Tetrahedron Lett.*, 1978, 4763 and 4767; E. Santaniello, F. Ponti, and A. Manzocchi, *Tetrahedron Lett.*, 1980, 2655.
- 7 V. Balogh, M. Fetizon, and M. Golfier, *J. Org. Chem.*, 1971, 36, 1339.
- 8 T. C. Jempty, L. L. Miller, and Y. Mazur, *J. Org. Chem.*, 1980, 45, 749; M. P. Brimeyer, A. Mehrota, S. Quici, A. Nigam, and S. L. Regen, *J. Org. Chem.*, 1980, 45, 4254.
- 9 H. Poulet and J. P. Mathieu, *J. Raman Spect.*, 1974, 2, 81.
- 10 'Powder Diffraction File,' JCPDS International Centre for Diffraction Data, Swarthmore, Pennsylvania, 1978.
- 11 J. M. Bijvoet, N. H. Kolkmeier, and C. H. Macgillavry, 'X-Ray Analysis of Crystals,' Butterworths, London, 1951, p. 51–54.
- 12 Lancaster University Undergraduate experiment based on the method of S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.*, 1938, 60, 309.

* Benzene is carcinogenic and can have deleterious long term effects. Similar experimental results would probably be obtained using toluene as a solvent.

¹³ H. S. Wilgus, E. Frauenglass, P. P. Chiesa, G. H. Nawn, F. J. Evans, and J. W. Gates, *Can. J. Chem.*, 1966, **44**, 603.

¹⁴ N. J. Leonard, and C. R. Johnson, *J. Org. Chem.*, 1962, **27**, 282.

¹⁵ A. L. Henne, and W. L. Perilstein, *J. Am. Chem. Soc.*, 1943, **65**, 2183.

¹⁶ F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, 1972, p. 480.