sample of "x-nitro-*o*-terphenyl" obtained from Dr. C. F. H. Allen.

*Anal.* Calc'd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76. Found: C, 78.75; H, 4.74.

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## Osmium Tetroxide-Catalyzed Periodate Oxidation of Olefinic Bonds

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The success of the permanganate-catalyzed oxidation of olefinic bonds with periodate[3] prompted the investigation of other catalysts, in particular reagents known to hydroxylate olefins. In the present note the preliminary results of the use of osmium tetroxide as the catalyst are disclosed.[4]

The new method has proved to be successful with some simple mono- and di-substituted olefins. With the permanganate-catalyzed reaction such olefins generally give an aldehyde and a carboxylic acid.[3] The osmium tetroxide technique has the advantage of not proceeding beyond the aldehydic oxidation state, thus affording the same products produced by ozonization followed by reductive cleavage. Catalytic amounts of osmium tetroxide are sufficient because periodate oxidizes osmium in its lower valence forms to the tetroxide, thus regenerating the hydroxylating agent. Hence this combination of two well-known reactions, namely osmium tetroxide hydroxylation of an olefin and periodate cleavage of a 1,2-glycol, permits the use of relatively small amounts of the very expensive and poisonous hydroxylating agent.

Two general procedures were developed. One involved the use of aqueous dioxane (75%), 1 mole-% of osmium tetroxide, and 210 mole-% of solid sodium metaperiodate at 25°. Dodecene-1 and *trans*-stilbene thus were readily oxidized to undecanal and benzaldehyde respectively in 68 and 85% yields (isolated as the 2,4-dinitrophenylhydrazones).

The second procedure involved the use of two immiscible liquid phases, *i.e.* ether and water. In this case a somewhat higher (up to 5 mole-%) proportion of osmium tetroxide was required to give a reasonably rapid reaction. The ether-water system was preferred for the oxidation of olefins giving aldehydes sensitive to self-condensation. Cyclohexene and cyclopentene thus afforded respectively 77 and 76% yields of the 2,4-dinitrophenylhydrazones of adipaldehyde and glutaraldehyde. By the dioxane method cyclohexene gave poor yields, perhaps due to cyclization of the dialdehyde. Dodecene-1, in contrast, gave poorer yields by the ether method.

1-Methylcyclohexene underwent oxidation very slowly and, under the optimum conditions for cyclohexene, gave only about 5% of uncharacterized carbonyl product. A potential use of the new method for selective oxidations is thus indicated.

Cyclohexene can be oxidized satisfactorily by the new method in aqueous medium alone. Acetonitrile also promises to be a useful solvent for these oxidations.

Preliminary experiments indicate that olefins are also oxidized by lead tetraacetate in the presence of catalytic amounts of osmium tetroxide. No noticeable reaction occurred at room temperature in benzene or in acetic acid solution until some water was added whereupon there was rapid consumption of the reagent. Water is evidently required in all of these reactions to effect hydrolysis of the intermediary osmate ester.

### EXPERIMENTAL

*Oxidation of dodecene-1 and of trans-stilbene. The aqueous dioxane procedure.* A mixture of 5 ml. of water, 15 ml. of purified[5] dioxane, freshly distilled from lithium aluminum hydride, 0.77 g. of dodecene-1, and 11.3 mg. of osmium tetroxide was stirred for 5 minutes during which time the mixture became dark brown (due to osmate ester formation). While the temperature of the stirred mixture was maintained at 24–26°, a total of 2.06 g. of finely powdered sodium metaperiodate was added in portions over a period of 30 minutes. The tan-colored slurry then was stirred for an additional 1.5 hours. The mixture (now pale yellow) was extracted thoroughly with ether and the combined organic layers (about 200 ml.) were filtered through anhydrous sodium sulfate. The ether solution then was treated with a solution of 1 g. of 2,4-dinitrophenylhydrazine in 5 ml. of concentrated sulfuric acid, 7.5 ml. of water, and 35 ml. of 95% ethanol. The two phase mixture was stirred for 70 minutes, then was evaporated to a volume of about 50 ml. The yellow 2,4-dinitrophenylhydrazone that separated amounted to 0.95 g., m.p. 98.5–101.5° (reported, m.p. 102°[6] and 106.5°[7]). A second crop obtained by concentration of the

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[3] R. U. Lemieux and E. von Rudloff, *Can. J. Chem.*, **33**, 1701, 1710 (1955); E. von Rudloff, *Can. J. Chem.*, **33**, 1714 (1955).

[4] The results of the search by M. Mugdan and D. P. Young, *J. Chem. Soc.*, 2988 (1949), for compounds to catalyze the hydroxylation of olefins by hydrogen peroxide have suggested several other possible catalysts for the periodate oxidation of olefins. Preliminary experiments have shown pertungstate, pervanadate, and pervanadic acid to be effective and this matter is receiving further attention. Ruthenium oxide also shows promise as a catalyst; *Cf.* Djerassi and R. R. Engle, *J. Am. Chem. Soc.* **75,** 3838 (1955).

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[6] E. T. Borrows, (Mrs.) B. M. C. Hargreaves, J. E. Page, J. C. L. Resuggan, and F. A. Robinson, *J. Chem. Soc.*, 197 (1947).

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mother liquor amounted to 0.14 g., m.p. 95.5–99°, making the total yield 1.09 g. (68%). Recrystallization of a sample of the first crop material from methanol raised the m.p. to 106.5–107.5° corr.

A 0.50-g. sample of *trans*-stilbene was similarly oxidized with 15.4 mg. of osmium tetroxide and 1.25 g. of sodium metaperiodate (addition time 70 minutes). A subsequent stirring period of only 25 minutes was required to effect decolorization of the dark mixture. The first crop of 2,4-dinitrophenylhydrazone, obtained as described above, amounted to 1.35 g. (85% yield) of bright orange needles, m.p. 240–241.5° corr. undepressed on admixture with authentic benzaldehyde 2,4-dinitrophenylhydrazone, m.p. 241.5–242.5° corr.

*Oxidation of cyclohexene and of cyclopentene.* Ether-water method. A mixture of 15 ml. of ether, 15 ml. of water, 0.405 g. of cyclohexene, and 65.4 mg. of osmium tetroxide was stirred while a total of 2.32 g. of finely powdered sodium metaperiodate was added over a 40-minute period. The temperature was maintained at 24–26° during the addition and for an 80-minute period thereafter during which period the initially dark reaction mixture changed to pale yellow and considerable sodium iodate separated. The mixture was extracted thoroughly with ethyl acetate, and the combined organic layers were filtered through a little sodium sulfate. The solution then was treated with 2.5 g. of 2,4-dinitrophenylhydrazine and 5 drops of concentrated hydrochloric acid which produced an immediate precipitation. After standing for 1 hour the yellow product was separated and washed with ethyl acetate and ether; yield 1.81 g. (77%), m.p. 234–235° corr. (dec.). Repeated recrystallization of a sample from nitromethane gave *adipaldehyde bis-2,4-dinitrophenylhydrazone*, as yellow needles, m.p. 241.2–241.6° corr. (dec.).

*Anal.* Calc'd for: $C_{18}H_{18}N_8O_8$: C, 45.57; H, 3.82. Found: C, 45.33; H, 3.71.

A 0.387-g. specimen of cyclopentene was similarly oxidized with 74.2 mg. of osmium tetroxide and 2.83 g. of sodium metaperiodate (addition time 40 minutes). The subsequent stirring period to dispel the dark color was 25 minutes. The first crop of 2,4-dinitrophenylhydrazone isolated as described above amounted to 1.85 g., m.p. 187.5–189° corr. (reported 186–187°[8] 192.5–193.3°[9]). A second crop amounting to 0.14 g., m.p. 181.5–183°, was isolated. A specimen of the first crop material, recrystallized from nitromethane, melted at 192–193°.

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## Reductive Cleavage of Tosylates

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In connection with some other work, it became necessary to convert several *p*-toluenesulfonic acid esters to the original alcohols. Normal hydrolytic procedures were not acceptable, as a further requirement was that the alkyl-oxygen bond of the alcohol remain intact during the cleavage. Several reductive methods for performing such an operation are available, and they have been used with varying degrees of success. Recently, Kenner and Murray[1] have utilized Raney nickel for such cleavages; however, large excesses of nickel are required and in our hands the reactions were very slow. It has now been found that sodium in liquid ammonia smoothly reduces *p*-toluenesulfonates to the parent alcohol and toluene. The fate of the sulfur has not been determined. The general procedure is to add the tosylate in ether to a stirred solution of sodium in ammonia. After the reaction is complete, as is evidenced by the discharge of the blue color, water is added and the product is extracted with ether and then is distilled. The yields of alcohol were about 55%. No attempt was made to determine conditions for maximum yields. It was found by experiment that *ca.* six atoms of sodium were required per mole of tosylate reduced. This method is clearly advantageous for work in which the alkyl-oxygen bond must not be broken, and it may also be of value for tosylates which eliminate easily under hydrolytic conditions, since no olefin has been detected in any of these reductions.

### EXPERIMENTAL

*Reductive cleavage of cyclohexyl p-toluenesulfonate.* To a stirred solution of 13.8 g. (0.60 mole) of sodium in 300 ml. of liquid ammonia, there was added over a period of 40 minutes 26.4 g. (0.104 mole) of cyclohexyl *p*-toluenesulfonate in 100 ml. of anhydrous ether. Soon after the addition was completed, the solution turned orange, and solid ammonium chloride then was added until the orange color was discharged. Water, 50 ml., was added and the ammonia was allowed to evaporate. After evaporation, 60 ml. of water was added and the aqueous mixture was extracted with four 50-ml. portions of ether. The ether was dried over sodium sulfate. Distillation gave a small fraction, b.p. 26–28° (9 mm.) followed by a main fraction, b.p. 60–61° (9 mm.), $n_D^{23}$ 1.4675. The infrared spectra of the main fraction was identical in all respects with that of a known sample of cyclohexanol. The yield was 5.57 g. (54%).

*Reductive cleavage of n-octyl p-toluenesulfonate.* In a manner entirely analogous to that described above, 18.31 g. (0.0645 mole) of *n*-octyl *p*-toluenesulfonate was reduced with 6.9 g. (0.30 mole) of sodium. Distillation afforded a small amount of toluene followed by a main fraction b.p. 86–88° (8 mm.), $n_D^{20}$ 1.4230, identical in all respects with that of a known sample of *n*-octyl alcohol (infrared spectra). The yield was 4.82 g. (56%).

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