increased beyond those at 1000 and 912 cm^{-1} attributed to the transoid conformer. Evaporation and redeposition in an argon matrix of photolyzed **2** as in the case of **1** caused the spectrum to reverse to that of starting material.

All these changes are consistent with the production of the previously undetected s-cis conformer. The fact that no new peaks attributable to carbonyl stretching were observed is consistent with the interpretation that the stretching frequencies of the carbonyl band of the cisoid and transoid forms of **2** are coincident within the limits of resolution (0.1 cm^{-1}).

We are continuing matrix-isolation studies by various spectroscopic methods toward the determination of spectral parameters and barriers to rotation of conformers and the production of new chemical species.

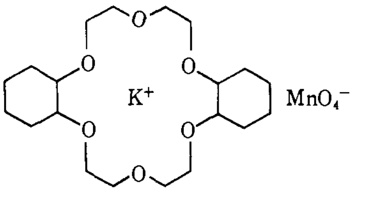
Acknowledgment. Acknowledgment is made to the Graduate School of the State University of New York at Stony Brook and the Research Foundation of the State University of New York and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

A. Krantz,* T. D. Goldfarb, C. Y. Lin
Department of Chemistry
State University of New York at Stony Brook
Stony Brook, New York 11790
Received February 15, 1972

Crown Polyether Chemistry. Potassium Permanganate Oxidations in Benzene[1]

Sir:

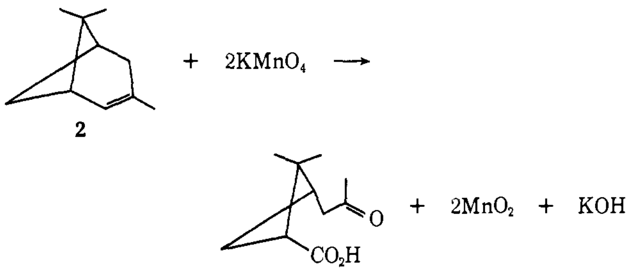
The crown polyethers and their ability to complex metal salts have aroused interest because of the possibility of increased salt solubility and increased anion reactivity in organic solvents.[2] Yet, few synthetic applications of these ethers have been reported. We have found that potassium permanganate can be solubilized in benzene by complexing with dicyclohexyl-18-crown-6 to provide a convenient and efficient oxidant, **1**,



1

for organic compounds under mild conditions. Thus far we have demonstrated oxidations of olefins, alcohols, aldehydes, and alkylbenzenes as shown in Table I. In the absence of the crown ether, potassium permanganate has no detectable solubility in benzene, and no reaction occurs with organic substrates.

The products of the oxidation reactions are ketones or potassium salts of carboxylic acids and are obtained in high yields without using excess oxidant. Intermediate products of consecutive oxidations were not obtained. For example, diols were not observed from olefins but aldehydes were detected and could be isolated from olefins and primary alcohols when the oxidations were carried to low conversion. The potassium salts of the acids are usually insoluble in benzene, and this is advantageous not only for product isolation but also because the salts are not subject to further oxidation. This is exemplified by the oxidation of α-pinene (**2**) to *cis*-pinonic acid (**3**) in 90% yield by this method.



2

3

In contrast, aqueous potassium permanganate oxidation of α-pinene gives pinonic acid in 40–60% yield.[3]

The reagent is prepared by stirring equimolar amounts of dicyclohexyl-18-crown-6 and potassium permanganate in benzene at 25° to give a clear, purple solution with concentrations of potassium permanganate as high as 0.06 *M*.[4] This is one of the few examples where an insoluble salt can be dissolved in a nonpolar solvent like benzene simply by adding crown ether. Normally, a more polar solvent (methanol) is needed to solubilize the salt followed by solvent exchange.[2a] Complex **1** can be isolated as a purple solid but is more stable in benzene (half-life (25°) ∼48 hr). Above 50°, **1** rapidly degrades to adipic acid and other products.[5] The absorption spectrum of **1** in benzene, 508 (2330), 525 (3170), 546 (3130), and 565 nm (1810), is very similar to that of aqueous permanganate ion.[6] The ^{55}Mn nmr spectrum of **1** in benzene is less structured and the half-line width much broader than the sharp, symmetrical resonance of aqueous permanganate ion. This is indicative of a less symmetric permanganate ion and suggests that potassium permanganate is ion paired in benzene.

The oxidations may be carried out homogeneously at 25° by mixing a solution of **1** in benzene with the compound to be oxidized. With olefins, *e.g.*, *trans*-stilbene, rapid decolorization of the reagent occurs

---

[1] Presented in part at the XXIIIrd IUPAC Meeting, Boston, Mass., July 1971.

[2] (a) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967); **92**, 391 (1970); *Fed. Proc., Fed. Amer. Soc. Exp. Biol.*, **27**, 1305 (1968); (b) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **84**, 16 (1972); (c) J. J. Christensen, J. O. Hill, and R. M. Izatt, *Science*, **174**, 459 (1971); (d) D. J. Sam and H. E. Simmons, *J. Org. Chem.*, in preparation; (e) our preliminary observations of the crown ether–potassium permanganate oxidations of organic substrates have been mentioned in the above references.

[3] V. L. Loeblich, F. C. Magne, and R. R. Mod, *Ind. Eng. Chem.*, 47, 1569 (1955); G. W. Hedrick and R. V. Lawrence, *ibid.*, **52**, 853 (1960); and A. Poplavskaya and M. I. Goryaev, *Zh. Obshch. Khim.*, **33**, 1492 (1963).

[4] Two isomers of dicyclohexyl-18-crown-6 were obtained from hydrogenation of dibenzo-18-crown-6. One isomer (mp 61–62°) gives 5.8×10^{-2} *M* potassium permanganate solubility in benzene while the other (mp 69–70°) gives 4.2×10^{-4} *M* solutions. The mixture of isomers was used in the oxidations and gave approximately 0.03 *M* permanganate solutions.

[5] Oxidations of compounds such as the sterically hindered 1,1-dineopentylethylene, which is completely resistant to alkaline permanganate, proceed slowly at 25° with our method. Such resistant oxidations cannot be accelerated by heating because of the concurrent reagent degradation.

[6] M. C. R. Symons and P. A. Traveleon, *J. Chem. Soc.*, 3503 (1962); M. Smith and M. C. R. Symons, *J. Chem. Phys.*, **25**, 1074 (1965).

Table I. Oxidations by Potassium Permanganate in Benzene (25°)

Starting material	Product[a]	Isolated yields, %	Stoichiometry Obsd	Stoichiometry Theory[c]
trans-Stilbene	Benzoic acid	100	2.68	2.67
Cyclohexene	Adipic acid	100	2.71	2.67
α-Pinene	Pinonic acid	90		
3-Methylenecyclobutanecarboxylic acid	3-Oxocyclobutanecarboxylic acid	[b]		
1-Heptanol	Heptanoic acid	70		
Benzyl alcohol	Benzoic acid	100	1.31	1.33
Benzhydrol	Benzophenone	100	0.71	0.67
Toluene (solvent)	Benzoic acid	78		
p-Xylene (solvent)	Toluic acid	100	2.00	2.00
Benzaldehyde	Benzoic acid			

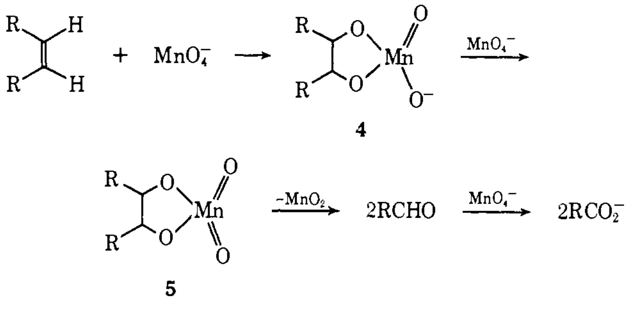
[a] The initially formed products were the potassium salts of the acids. [b] Clean but incomplete oxidation occurs. The starting material and product were precipitated by the KOH formed during the reaction. [c] Theory for corresponding aqueous oxidations.

within minutes, whereas alkylbenzenes such as toluene require up to 72 hr for complete reaction. For preparative reactions, it is more convenient to bypass prior complex formation. The crown ether is used in catalytic amounts, but efficient and abrasive stirring is needed to sustain solubilization of the oxidizing agent since the manganese dioxide formed coats the unreacted potassium permanganate. As an example, 12.2 g (68 mmol) of *trans*-stilbene, 28.6 g (181 mmol) of potassium permanganate, 2.4 g (6 mmol) of dicyclohexyl-18-crown-6, and 1.0 l. of benzene were rolled in a ball mill for 2 hr.[7] The product potassium benzoate was filtered along with manganese dioxide and then was dissolved in 5% sodium hydroxide solution. After filtration of manganese dioxide, the aqueous solution was extracted with ether to remove traces of crown ether. Acidification yielded 16.0 g (97%) of pure benzoic acid.

The mechanism of the oxidations in benzene is not known, but we speculate the reaction sequence for olefins (Scheme I) is similar to that generally accepted for aqueous systems.[8-10] In the first place the stoichiometries of the oxidations in benzene are the same as the corresponding aqueous oxidations (Table I). The reaction can be considered as initiated by [2 + 4] electrocyclic addition of permanganate ion to the olefinic π bond to form the usual manganate ester ion **4**. Attempts to observe **4** directly by ^{55}Mn and ^{1}H nmr experiments were unsuccessful, presumably because oxidation of **4** to **5** by electron transfer is rapid. The fourfold decrease in the relative rates of oxidation of cyclopentene (4.0), trimethylethylene (2.3), tetramethylethylene (2.0), and cyclohexene (1.0), which were determined by competition studies, is small but consistent with the olefin acting as an electron donor.[11]

Scheme I

$$3RCH{=}CHR + 8KMnO_4 \longrightarrow 6RCO_2K + 8MnO_2 + 2KOH + 2H_2O$$



4

5

In aqueous systems at high pH, diols are formed by hydrolysis of **4**, whereas at low pH ketols result from **5**. These products are not formed under our conditions even though low concentration of water may be produced. It is postulated that **5** fragments to manganese dioxide and two molecules of aldehyde. Such a [2 + 2 + 2] cheletropic change can be visualized as a thermally allowed ground-state process. The steps leading to aldehyde and carboxylate ion are rapid compared to the initial addition of permanganate ion. Aldehyde formation could not be suppressed even when the olefin was used in large excess; and the aldehyde, unaccompanied by further oxidation to acid, was detected only at very low olefin conversion.

We are developing the scope of these oxidations since this reagent should be especially adaptable where water solubility is a major limitation of where mild conditions are necessary. Since the oxidations proceed cleanly as exemplified by the stoichiometry values, the reagent has analytical utility. In particular, the degree of end-group unsaturation in water-insoluble polymers has been demonstrated. The oxidation of olefins to diketones using potassium permanganate in acetic anhydride[12] and the oxidation of olefins to acids by phase-transfer catalysis[13] provide other recent examples of permanganate oxidations in organic solvents.

---

(7) Although we have experienced no hazards from ball milling potassium permanganate, benzene, and organic substrates, caution should be exercised in such experiments.

(8) K. B. Wiberg and K. A. Saegebarth, *J. Amer. Chem. Soc.*, **79**, 2822 (1957).

(9) G. Wagner, *J. Russ. Chem. Soc.*, **27**, 219 (1895).

(10) J. Boeseken, *Recl. Trav. Chim. Pays-Bas*, **41**, 199 (1922); 47, 638 (1928).

(11) P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.*, **78**, 5430 (1956); E. P. Blanchard and H. E. Simmons, *ibid.*, **86**, 1337 (1964).

(12) K. B. Sharpless, R. F. Lauer, O. Repic, A. Y. Teranishi, and D. R. Williams, *ibid.*, **93**, 3303 (1971).

(13) C. M. Starks, *ibid.*, **93**, 195 (1971); N. A. Gibson and I. W. Hoskings, *Aust. J. Chem.*, **18**, 123 (1965).

Donnie J. Sam,* Howard F. Simmons
Contribution No. 1898, Central Research Department
E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

Received February 16, 1972

Monomeric Dialkylboranes

Sir:

We wish to report the first identification of monomeric dialkylboranes with characteristic infrared ab-