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 (8) Using a mortar and pestle and working in a glove bag under an atmosphere of dry nitrogen, lumps of potassium superoxide, purchased from K & K Chemicals, were ground to a fine consistency before use.
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 (10) Relatively stable solutions containing substantial concentrations (~0.2 M) of potassium superoxide can be obtained in dry DMSO in the presence of a macrocyclic polyether.⁶
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 (15) Determined by the disappearance of 1-bromooctane.

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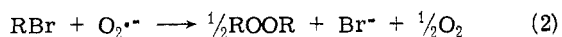
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Superoxide Chemistry. A Convenient Synthesis of Dialkyl Peroxides

Summary: A convenient synthesis of dialkyl peroxides from the reaction of alkyl bromides or alkyl sulfonate esters with potassium superoxide, the latter solubilized in benzene by crown ethers, is described.

Sir: The chemistry of the superoxide radical anion, $O_2^{\cdot-}$, in organic systems has been studied very little. On a synthetic scale, superoxide is available to the chemist from two sources, either as the alkali metal salts, potassium superoxide (KO_2) and sodium superoxide (NaO_2), or from the electrochemical reduction of oxygen to $O_2^{\cdot-}$ (eq 1).¹ The use of



the alkali metal salts in organic reactions has not been fruitful owing to the lack of solubility of these salts in many organic systems.² The electrochemical method is experimentally more complex, but it has been used on a limited scale for several organic reactions.^{1d,3} Two groups reported in 1970 that electrochemically generated superoxide will react with alkyl halides to form dialkyl peroxides according to eq 2.^{4,5}

In view of the recently reported solubilization of KO_2 in dimethyl sulfoxide with the aid of dicyclohexyl-18-crown-6,⁶ we wish to report our observations on the solubilization of KO_2 by crown ethers in various other aprotic solvents, including benzene, tetrahydrofuran, and dimethylformamide.⁷ Using this method we have developed a convenient synthesis of dialkyl peroxides from various alkyl bromides and alkyl sulfonate esters (i.e., mesylates and tosylates). The following simple procedure can be used for this synthesis.

Potassium superoxide⁸ (0.0050 mol) was weighed directly into a dry flask containing a magnetic stirring bar and was immediately covered with dry benzene (15 ml). The alkyl

Table I
 The Reactions of Alkyl Bromides and Sulfonate Esters with KO_2 in the Presence of Crown Ethers^a

Substrate (R-X)	Products, %		
	Peroxide (ROOR)	Alcohol (ROH)	Olefins ^b
<i>n</i> -C ₅ H ₁₁ -Br	53 ^c		
<i>n</i> -C ₆ H ₁₃ -Br	54 ^c		
<i>n</i> -C ₇ H ₁₅ -Br	56 ^c		
<i>n</i> -C ₁₆ H ₃₃ -Br	44 ^d	21	
<i>n</i> -C ₁₈ H ₃₇ -Br	77 ^e	21	
<i>n</i> -C ₁₈ H ₃₇ -Br ^f	61	18	
<i>c</i> -C ₆ H ₁₁ -Br			67
<i>c</i> -C ₆ H ₉ -Br	42 ^e		24
C ₆ H ₁₃ CH(CH ₃)-Br	55 ^e		37 ^g
<i>n</i> -C ₁₈ H ₃₇ -OTos ^h	50	42	
<i>n</i> -C ₁₈ H ₃₇ -OMs ^d	46	40	
C ₆ H ₁₃ CH(CH ₃)-OTos ⁱ	52	13	16 ^g
C ₆ H ₁₃ CH(CH ₃)-OMs ^j	44	19	14 ^g

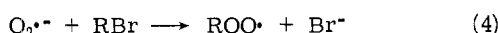
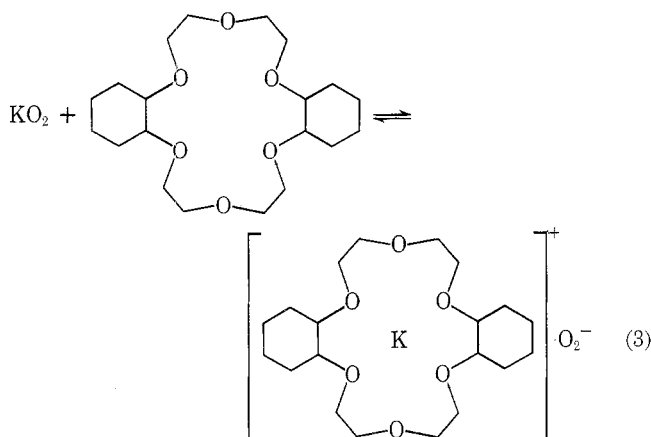
^a Dicyclohexyl-18-crown-6 used except where noted otherwise.
^b VPC analyses for olefins were carried out using an F & M Scientific Model 5750 research chromatograph equipped with a flame ionization detector. A 3-ft stainless steel column packed with 26.6% Carbowax 20M on Gas-Chrom Z was used with a helium flow rate of 35-40 cc/min. The column was programmed for 4 min at 90° and then to increase 8° per minute to 225°. ^c Reference 16.
^d S. Wawzonek, P. D. Klimstra, and R. E. Kallio, *J. Org. Chem.*, **25**, 621 (1960). ^e Satisfactory analytical data has been obtained for this compound. ^f 18-Crown-6 was used in this experiment. ^g A mixture of 1-octene, *cis*-2-octene, and *trans*-2-octene was found. ^h V. C. Sekera and C. S. Marvel, *J. Am. Chem. Soc.*, **55**, 345 (1933). ⁱ A. Streitwieser, Jr., T. D. Walsh, and J. R. Wolfe, *ibid.*, **87**, 3682 (1965). ^j H. A. Weiner and R. A. Sneen, *ibid.*, **87**, 287 (1965).

bromide or alkyl sulfonate ester (0.0050 mol) and dicyclohexyl-18-crown-6 (0.0050 mol) were then added to the flask. The pieces of KO_2 were carefully crushed with a heavy glass rod. The resulting mixture was protected from moisture with a $CaCl_2$ drying tube and was stirred vigorously. The reaction may be followed by VPC or TLC¹⁰ and occasionally requires additional KO_2 to reach completion. The reaction was usually complete within 3 to 6 hr at room temperature. The reaction may be worked up by pouring it into saturated aqueous sodium chloride solution (50 ml) and extracting with methylene chloride or benzene.¹² The product can be isolated by chromatography on silica gel using, for example, benzene as the eluent.

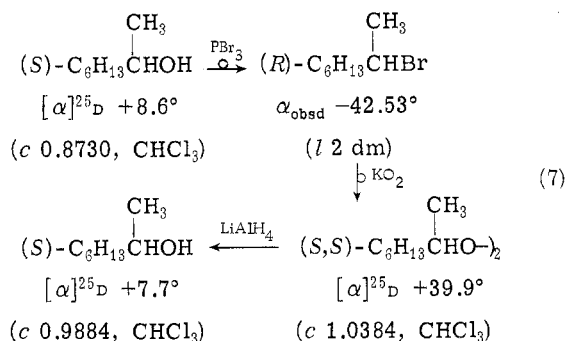
Using this procedure, we have obtained the results summarized in Table I. Yields of peroxides and alcohols were determined from isolation of the products, whereas the yields of olefinic products were determined by VPC. In addition to these results we offer the following observations and comments on these reactions.

By analogy to recent reports of the solubilization of various inorganic salts in organic media by the crown ethers,⁷ we assume that the equilibrium shown in eq 3 is responsible for the solubilization of KO_2 . The dicyclohexyl-18-crown-6 used in these experiments was a mixture of stereoisomers. A stoichiometric quantity of crown ether was used in all the reactions reported in Table I. In a similar experiment, using only 0.1 equiv of crown ether relative to KO_2 , 1-bromohexane was converted to di-*n*-hexyl peroxide in 50% yield. The reaction time was somewhat longer than when a full equivalent of crown ether was used. 18-Crown-6 and dibenzo-18-crown-6 also were effective in solubilizing KO_2 in benzene, although the latter was itself sparingly soluble in this solvent.

The formation of dialkyl peroxides by eq 2 was proposed by Dietz et al.⁵ to occur stepwise according to eq 4-6. Sum-



mation of these equations gives eq 2. Two displacements of bromide are seen in these equations and it was suggested⁵ that these occurred by SN2 mechanisms. We have examined the stereochemistry of the reaction as outlined below.



The entire three-step reaction sequence (7) proceeds with a net 94% retention of configuration. Since the first step is known to proceed with complete inversion at the asymmetric carbon¹³ and the last step¹⁴ proceeds with retention of configuration, we conclude that the conversion of 2-bromooctane to di-2-octyl peroxide must occur with inversion at the asymmetric carbon. This result is consistent with the SN2 mechanism postulated for the reaction steps depicted in eq 4 and 6.

The yields of primary dialkyl peroxides obtained by the present method are comparable with, and in some cases better than, those reported for the generally used methods of peroxide synthesis.¹⁵ Yields of secondary dialkyl peroxides, except for the cyclohexyl example, are better than those obtained by other methods. The procedure is considerably simpler than the generally used method of displacement of mesylates with alkaline hydrogen peroxide.¹⁶

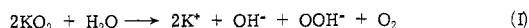
The formation of alcohols as significant by-products in these reactions is not completely understood as yet and remains under investigation.

References and Notes

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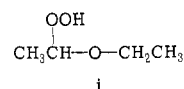
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- (8) Supplied by the Ventron Corporation, Beverly, Mass. 01915, as small chunks of a caked yellow powder. Potassium superoxide reacts rapidly with water, producing peroxide, hydroxide, and oxygen according to the eq 1.⁵ Care should be taken to avoid reaction of large quantities of KO₂



with water in the presence of organic materials. Precautions similar to those used with hydrogen peroxide are recommended.⁹ In the present experiments, excessive contact with atmospheric moisture was avoided by using larger pieces of the solid and quickly covering them with dry solvent. More rigorous anhydrous conditions could be attained in a dry-box.

- (9) "Kirk-Othmer Encyclopedia of Chemical Technology", Vol. 14, 2nd ed, Wiley, New York, N.Y., 1967, pp 748-749, 762-764.
- (10) Peroxides and hydroperoxides can be visualized on silica gel tic plates by spraying with a freshly prepared (remains effective for about 1 day) solution of ammonium thiocyanate (0.625 g), concentrated sulfuric acid (0.125 ml), and ferrous ammonium sulfate [FeSO₄(NH₄)₂SO₄, 0.875 g] in water (12.5 ml).¹¹ With this spray, peroxidic materials give a rust-red-colored spot.
- (11) R. D. Mair and R. T. Hall, in "Organic Peroxides", Vol. II, D. Swern, Ed., Wiley-Interscience, New York, N.Y., 1971, pp 553-560.
- (12) Extraction of several reactions with ether resulted in formation of a peroxidic product tentatively considered to have structure i. Since i is an



intermediate in the formation of the potentially explosive polymeric ether peroxides [A. Rieche, *Angew. Chem.*, **70**, 251 (1958)], use of ether should be avoided until the nature of i is clarified.

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Reaction of Nitrimes with Cyanide Ions

Summary: The nitrimes of fenchone, menthone, camphor, and benzophenone were treated with KCN in aqueous methanol to give unstable cyanonitrime intermediates which decompose with the loss of N₂O to afford α-fenchene-1-carboxamide, ρ-menth-3-ene-3-carboxamide, camphene-1-carboxamide, and α-methoxydiphenylacetamide, respectively.

Sir: The reaction of fenchone nitrime (1) with cyanide ion was reported by Passerini to afford a mixture of isomeric fenchone cyanohydrins.¹ We have reinvestigated this reaction duplicating the conditions of Passerini and have found that the products actually isolated are the rearranged amides 3 and 4 formed in 80% yield in a ratio of 85:15, respectively. The structure of the major product 3 was deduced from the spectral data [NMR (CDCl₃) δ 1.05 (s, 3 H), 1.10 (s, 3 H), 4.91 (m, 1 H), 5.07 (m, 1 H); ir (CHCl₃) 3520, 3400, 1665, 895 cm⁻¹] and by conversion to ketopinic amide (6) which was prepared independently from ketopinic acid (5)² as shown in Scheme I.