On the Mechanism of the Baeyer–Villiger Oxidation of Ketones by Bis(trimethylsilyl) Peroxomonosulfate. Intermediacy of Dioxiranes†

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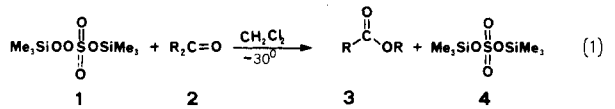
The Baeyer–Villiger oxidation of cyclohexanone (**2a**) and of acetophenone (**2b**) by bis(trimethylsilyl) peroxomonosulfate (**1**) has been reinvestigated using ^{18}O-labeling techniques. Starting with doubly labeled $Me_3Si^{18}O^{18}OSO_3SiMe_3$, mass spectrometric analyses allowed determination of the amount of label appearing in the carbonyl and the OR moiety of the ester (or of the lactone). It has been observed that **2a** also promotes the decomposition of **1** to yield oxygen gas, which was analyzed for its ^{18}O content. Furthermore, ketones **2a**, 4-heptanone, and acetone were found to enhance significantly the rate of oxidation of 1-methylcyclohexene (**10**) and of *trans*-β-methylstyrene (**13**) by **1**, yielding 2-methylcyclohexanone (**12**) and 1-phenylpropanone (**15**) derived from the isomerization of the initially formed epoxides. These observations, most notably the ^{18}O-tracer results, point to a mechanism involving the intermediacy of dioxiranes as the prevailing pathway.

The Baeyer–Villiger (BV) reaction allows the conversion of ketones into esters. It is a classic transformation in synthetic organic chemistry, with varied and extensive applications.[1] It is commonly performed by using organic peroxy acids[1] and occasionally with hydrogen peroxide[2] or its bis(trimethylsilyl) derivative.[3] The inexpensive, commercially available potassium peroxomonosulfate, $HOOSO_3^-K^+$ (potassium caroate),[4] has found so far only limited applications in preparative BV oxidations,[5] although originally Baeyer and Villiger employed peroxomonosulfuric acid, $HOOSO_3H$ (Caro's acid), to carry out the conversion of a variety of ketones into esters.[5c] Organic peroxo acids are nowadays preferred because, as an inorganic peroxo acid, the shortcomings of Caro's acid are linked to the necessity of using aqueous media and to the presence of strong acids (H_2SO_4, HSO_4^-). These conditions might bring about undesirable side reactions, e.g., hydrolysis of the esters or lactones.[5]

It is interesting to recall that as far back as 1899 Baeyer and Villiger suggested that a dioxirane was involved in the conversion of menthone into the corresponding lactone by Caro's acid.[5c] However, ^{18}O-labeling experiments reported later by von Doering and Dorfman showed that a dioxirane intermediate could not be involved in the BV oxidation of benzophenone to phenyl benzoate by peroxybenzoic acid.[6]

In 1979, an interesting variation of the BV reaction was introduced, showing that the bis(trimethylsilyl) derivative of Caro's acid, namely, bis(trimethylsilyl) peroxomonosulfate (**1**), exhibits a remarkable reactivity (eq 1).[7] The



1 2 3 4 (1)

solubility of **1** and its reduction product **4** in aprotic media (e.g., CH_2Cl_2) render this reagent particularly attractive and of broad scope. In fact, aromatic, cyclic, and even simple aliphatic alicyclic ketones are readily oxidized into their corresponding esters in high yields under mild conditions.[7]

Our interest in the mechanism of this reaction (eq 1) was drawn by the frequently neglected observation that many simple dialkyl ketones (most notably acetone) are reluctant to react with common organic peroxy acids.[8] Most often they do not yield, under normal reactions conditions, the esters as typical BV products, but instead "ketone diperoxides" (1,2,4,5-tetraoxanes) are formed.[8,9]

On the other hand, it is now established that dioxiranes **5** are generated in the reaction of ketones with potassium caroate at pH values close to neutrality.[10,11] Actually, more recently it has become possible to isolate a few dioxiranes as dilute solutions in the parent ketone by low-temperature distillation from buffered caroate–ketone mixtures.[10,12–14]

† Dedicated to Professor Giorgio Modena (University of Padova, Italy) on the occasion of his 65th birthday.

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(1) (a) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin: Menlo Park, CA, 1972; pp 321–329. (b) Krow, G. R. *Tetrahedron* **1981**, *37*, 2697, see also references therein.

(2) (a) Corey, E. J.; Arnold, Z.; Hutton, J. *Tetrahedron Lett.* **1970**, 307. (b) Corey, E. J.; Noyori, R. *Ibid.* **1970**, 311. (c) Grieco, P. A. *J. Org. Chem.* **1972**, *37*, 2363.

(3) Suzuki, M.; Takada, H.; Noyori, R. *J. Org. Chem.* **1982**, *47*, 902 and references.

(4) Available in the USA as Oxone (Du Pont Chemical Co.) and in Europe as Curox (Interox Peroxid-Chemie GmbH); the solid material is a ca. 2:1:1 molar mixture of $KHSO_5$, $KHSO_4$, and K_2SO_4 (triple salt).

(5) (a) Kennedy, R. J.; Stock, A. M. *J. Org. Chem.* **1960**, *25*, 1901. (b) Robinson, R.; Hart Smith, L. *J. Chem. Soc.* **1937**, 371. (c) Baeyer, A.; Villiger, V. *Chem. Ber.* **1899**, *32*, 3625; **1900**, *33*, 2479.

(6) von Doering, W. E.; Dorfman, E. *J. Am. Chem. Soc.* **1953**, *75*, 5595.

(7) Adam, W.; Rodriguez, A. *J. Org. Chem.* **1979**, *44*, 4969 and references.

(8) See, e.g.: (a) Hassel, C. H. *Org. React.* **1957**, *9*, 74. (b) Smith, P. A. S. In *Molecular Rearrangements*, de Maio, P., Ed.; Interscience: New York, 1963; Vol. 1, pp 577–589.

(9) Schulz, M.; Kirschke, K. In *Organic Peroxides*; Swern, D., Ed.; Wiley-Interscience: New York, 1972; Vol. 3, p 76.

(10) For recent reviews, see: (a) Curci, R. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI: Greenwich, CT; Vol. 2, Chapter 1, in press. (b) Adam, W.; Curci, R.; Edwards, J. O. *Acc. Chem. Res.* **1989**, *22*, 205. (c) Murray, R. W. *Chem. Rev.* **1989**, *89*, 1187.

(11) (a) Edwards, J. O.; Pater, R. H.; Curci, R.; Di Furia, F. *Photochem. Photobiol.* **1979**, *30*, 63. (b) Curci, R.; Fiorentino, M.; Troisi, L.; Edwards, J. O.; Pater, R. H. *J. Org. Chem.* **1980**, *45*, 4758. (c) Cicala, G.; Curci, R.; Fiorentino, M.; Laricchiuta, O. *Ibid.* **1982**, *47*, 2670. (d) Curci, R.; Fiorentino, M.; Serio, M. R. *J. Chem. Soc., Chem. Commun.* **1984**, 155.

(12) Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847.

(13) (a) Cassidei, L.; Fiorentino, M.; Mello, R.; Sciacovelli, O.; Curci, R. *J. Org. Chem.* **1987**, *52*, 699. (b) Mello, R.; Fiorentino, M.; Sciacovelli, O.; Curci, R. *Ibid.* **1988**, *53*, 3890.

(14) Adam, W.; Chan, Y.-Y.; Cremer, D.; Gauss, J.; Scheutzow, D.; Schindler, M. *J. Org. Chem.* **1987**, *52*, 2800 and references therein.

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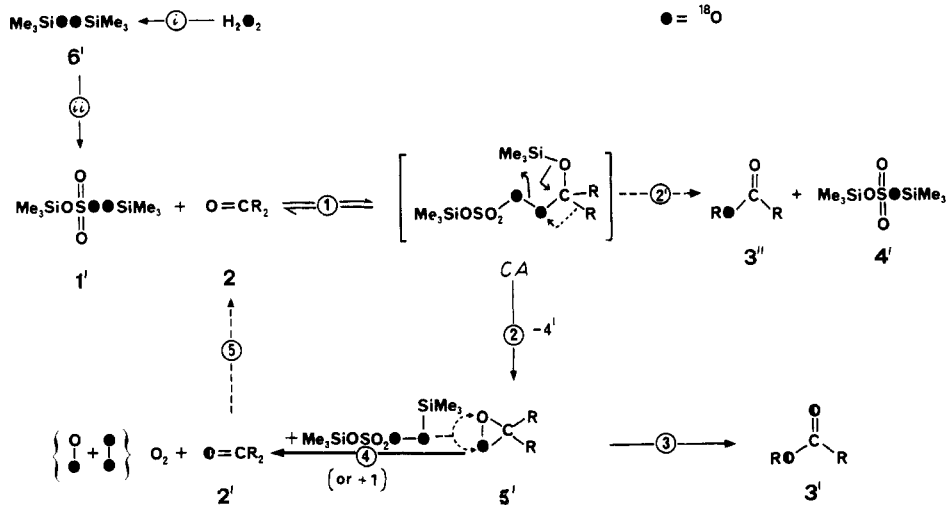
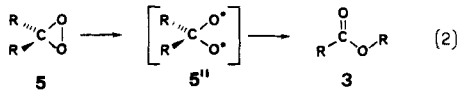
Scheme I



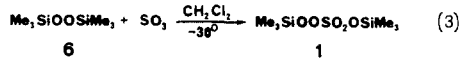
Since isolated dioxiranes rearrange into esters, either directly via dioxamethylene biradicals **5″** (eq 2),[10,15,16] or catalyzed by Lewis acids,[12] we deemed it desirable to have



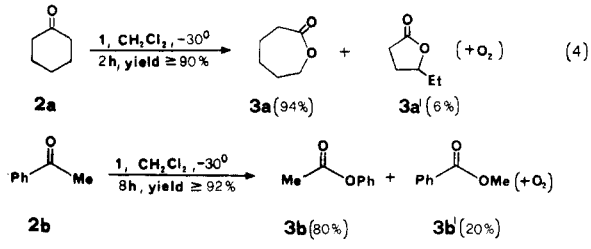
a closer look at the mechanism of the reaction in eq 1, in order to ascertain whether dioxirane intermediates could be involved in the transformation of ketones into esters by the trimethylsilyl reagent **1**. Our present results support this conclusion.

Results and Discussion

Conversion of Ketones into Esters. We have studied the reaction between two representative ketones, namely, cyclohexanone (**2a**) or acetophenone (**2b**), and bis(trimethylsilyl) peroxomonosulfate (**1**). The latter reagent was generated in CH_2Cl_2 upon reaction of bis(trimethylsilyl) peroxide (**6**) and sulfur trioxide according to a reported procedure (eq 3);[7] the formation of **1** can be monitored by running ^1H NMR spectra (see Experimental Section).[7]

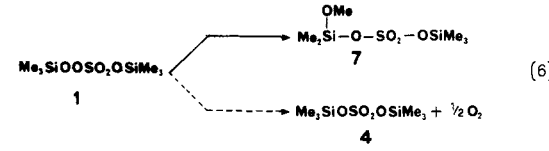


The reactions between each of the ketones and **1** were run under the conditions given in eq 4 and 5. They were followed by GC and GC/MS, determining yields and



product distributions at regular time intervals. The BV oxidation of cyclohexanone is quite clean, affording ϵ-caprolactone (**3a**) in high yield, accompanied only by some γ-caprolactone (**3a′**).[17] Noteworthy is that in the oxidation of acetophenone, besides the expected phenyl acetate (**3b**), sizeable amounts (~20%) of methyl benzoate (**3b′**) are also formed, in spite of the poor migratory aptitude of the methyl vs phenyl group in normal BV oxidations.[1,8]

Consistent with previous observations, we find that substantial excess (from 3- to 5-fold) of the oxidant is necessary to push the conversion of ketones **2a** or **2b** toward near completion under the given conditions. Also, evolution of oxygen gas was noted (see below) during the reaction of the ketones with the oxidant **1** (eq 4 and 5); however, oxygen gas is not the main product of bis(trimethylsilyl) peroxomonosulfate decomposition in the absence of ketone. In fact, as previously reported,[18] we could verify (^1H NMR monitoring) that trimethylsilyl methoxydimethylsilyl sulfate (**7**) is the almost exclusive product of normal (uncatalyzed) decomposition of **1** (eq 6). Under



the conditions employed, i.e., in CH_2Cl_2 at −30 °C, the rearrangement of **1** into **7** is much slower than either reaction in eq 4 or 5, requiring about 36 h for complete loss of peroxide titre (by iodometry).

^{18}O-Tracer Studies. Ester Formation. The sequence outlined in Scheme I allows one to recognize how ^{18}O labeling would permit establishment of whether dioxiranes are involved in ester formation.[10a] Analogous to the trimethylsilyl triflate catalyzed reaction of **6** with ketones,[3] we propose formation of Criegee's adduct, CA in Scheme I. Using bis(trimethylsilyl) peroxomonosulfate that is doubly labeled with ^{18}O (as in **1′**), provided that the ester product arises uniquely from Criegee's adduct (CA), no scrambling would occur and therefore no label should

(15) Adam, W.; Curci, R. *Chim. Ind. (Milan)* **1981**, *63*, 20 and references therein.

(16) (a) Sander, W. W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 254. (b) Sander, W. W. *J. Org. Chem.* **1988**, *53*, 121. (c) Ganzer, G. A.; Sheridan, R. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1986**, *108*, 1517. (d) Dunkin, I. R.; Shields, C. J. *J. Chem. Soc., Chem. Commun.* **1986**, 154.

(17) Difficulties previously reported (ref 7) in obtaining the lactone **3a** from cyclohexanone by this reaction should be ascribed to the aqueous workup then routinely adopted for its isolation.

(18) (a) Bressel, B.; Blaschette, A. *Z. Anorg. Allg. Chem.* **1970**, *377*, 182. (b) Blaschette, A.; Bressel, B.; Wannagat, U. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 450.

Table I. Oxygen-18 Tracer Studies of the Baeyer-Villiger Oxidation of Ketones by Bis(trimethylsilyl) Peroxomonosulfate

reactn in eq[a]	label in reagent	label in products	obsd ^{18}O % excess[b]	predicted ^{18}O % excess[c] dioxirane	CA
4	$Me_3Si^{18}O^{18}OSO_3SiMe_3$ (1′)		9.80[c]		
		ϵ-caprolactone (**3a**)[e]			
		total	4.80		
		C=O moiety	2.30	2.40	0.00
4	cyclohexanone-^{18}O (**2a′**)		12.10		
		ϵ-caprolactone (**3a**)[f]			
		total	5.00		
		C=O moiety	2.60	2.50[g]	5.00[g]
5	$Me_3Si^{18}O^{18}OSO_3SiMe_3$ (1′)[d]		26.60[d]		
		phenyl acetate (**3b**)[h]			
		total	12.70		
		C=O moiety	5.49	6.35	0.00
		OPh moiety	7.30	6.35	12.70

[a] See text for equation numbering and reaction conditions. [b] From mass spectral data (cf. Experimental Section and Table IV). Estimated standard error is ±3%. [c] Cf. Scheme I. [d] Amount of label is the same as that of its $Me_3SiOOSiMe_3$ precursor reported in Table IV (cf. Scheme I). [e] Isolated after 35% conversion of the ketone. [f] Isolated after over 95% conversion of the ketone. [g] Prediction based on total label actually retained in the lactone. [h] Analyzed by 15–20% conversion of the ketone.

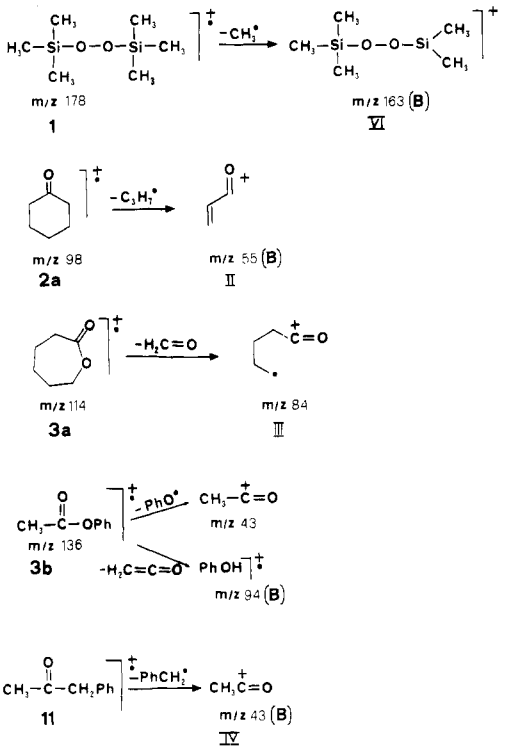
appear in the ester carbonyl (i.e., **3″**). By contrast, should the ester be formed via dioxirane **5′**, complete scrambling of the label between the carbonyl and the OR moiety is expected (as in **3′**).

Labeled hydrogen peroxide $H_2{}^{18,18}O_2$ was prepared by electric discharge[19] starting with $H_2{}^{18}O$. This material was employed in the synthesis of labeled bis(trimethylsilyl) peroxide (**6′**) by following the procedure reported for the unlabeled peroxide.[7] Doubly labeled bis(trimethylsilyl) peroxomonosulfate (**1′**) was generated in dry CH_2Cl_2 by reaction of **6′** with SO_3. Control experiments (see below, eq 7) revealed that **1′**, in the absence of ketone, practically retains all of the label originally present in **6′** (and in $H_2{}^{18,18}O_2$). In CH_2Cl_2 at −30 °C, the loss of label for **1′** alone was small (≤5%) during the reaction time (10–30 min) that was necessary to transform the ketones into esters.

The reactions of **1′** with unlabeled cyclohexanone (**2a**) or acetophenone (**2b**) were followed (GC or GC/MS) over the first 15–40% conversion of the ketone; lactone **3a** or the ester **3b** products were analyzed either directly using aliquots of the reaction mixture (GC/MS) or by MS after isolation (column chromatography). In the mass spectra, the relative intensity of peak M + 2 with respect to the parent ion (M) allowed us to determine the amount of total ^{18}O label. The relative intensity of peaks I + 2 and I given by appropriate fragments (Chart I) permitted estimation of the distribution of the label between the carbonyl and the OR moiety. The results in Table I (first and third entry) are unequivocal in showing that—as required by a dioxirane mechanism—extensive scrambling of the ^{18}O label occurs during the oxidation of both cyclohexanone and acetophenone. For the latter the scrambling was not complete, as more label is retained in the OR moiety. This indicates that the dioxirane mechanism prevails but it is not exclusive, since some 15–20% of unscrambled ester presumably arises directly from the breakdown of the CA intermediate (Scheme I). However, for cyclohexanone oxidation the label in the ϵ-caprolactone carbonyl is nearly half of the total, suggesting that the dioxirane mechanism occurs almost exclusively (≥96%).

In another series of experiments unlabeled peroxide **1** and ^{18}O-labeled (~12%) cyclohexanone (**2a′**) were used (second entry, Table I). It was found that the ϵ-caprolactone product contained less than half of the total label originally present in **2a′**. This indicates that, at variance with the silyl peroxide, the exchange of ^{18}O label of the ketone with $(Me_3Si)_2SO_4$ (**4**), adventitous water, $(Me_3Si)_2O$, or through recycling of the ketone via steps **1** + **2** + **4** + **5** (Scheme I) might be significant over longer reaction times. Nonetheless, the total label retained in the ϵ-caprolactone isolated was again almost completely scrambled (Table I), which is consistent with the dioxirane mechanism.

Chart I



Evolved Oxygen Gas. An important clue concerning the reaction mechanism came in the observation that ketones are capable of enhancing dramatically the decomposition of **1** and of diverting the reaction toward the production of dioxygen (eq 6). When ^{18}O-labeled bis(trimethylsilyl) peroxomonosulfate (**1′**) was used, ^{18}O label appeared in the dioxygen evolved.

Several careful studies have demonstrated the convenience and the usefulness of the double ^{18}O-labeling method and mass spectral analysis of the dioxygen produced in determining the peroxide decomposition mechanisms.[20,21]

(19) Ball, R. E.; Edwards, J. O.; Jones, P. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2458.

Table II. Mass Spectral Analysis of Oxygen Gas from the Decomposition of Doubly ^{18}O-Labeled Bis(trimethylsilyl) Peroxomonosulfate and of a Sample of Its Hydrogen Peroxide Precursor[a]

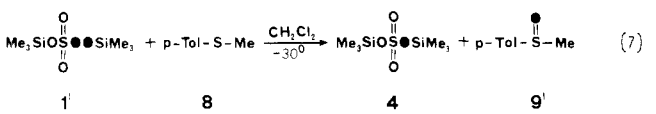
entry	time,[b] h	% mole fractions[c] $^{32}O_2$	$^{34}O_2$	$^{36}O_2$
a oxidn of $H_2{}^{18,18}O_2$[d]	1	88.40	1.00	10.60
b uncat. decn of $Me_3Si^{18}O^{18}OSO_3SiMe_3$[e,f]	30[i]	88.55	0.45	11.00
c decn of $Me_3Si^{18}O^{18}OSO_3SiMe_3$,[g] cat. by cyclohexanone[h]	10	92.70	6.40	0.90

based on $^{36}O_2$, entries b and c. $100 \times (11.00 - 0.90/11.00) = 92\%$ scrambling of peroxide oxygen

[a] Refer to Scheme I. [b] Time interval allowed for oxygen evolution. [c] Corrected for natural abundance. Estimated standard error is ±3%. [d] Upon oxidation with $Ce(SO_4)_2$ in 20% aqueous H_2SO_4 (ref 22). [e] Obtained from same labeled hydrogen peroxide preparation in entry (a) (cf. sequence in Scheme I). [f] 0.42 M in CH_2Cl_2 at −10 °C. [g] Same preparation in entry b. [h] Initial concentrations were 0.42 M silyl peroxide and 0.04 M cyclohexanone in CH_2Cl_2 at −10 °C. [i] With respect to the stoichiometry, only small amounts of O_2 gas were evolved; after this time, ^1H NMR analysis of solutions revealed that over 90% of the silyl peroxide had decomposed into **7** (eq 6).

In Table II we have collected the results of analyses of gas evolved during the uncatalyzed and the cyclohexanone-catalyzed decomposition of doubly ^{18}O-labeled bis(trimethylsilyl) peroxomonosulfate (**1′**); these are to be compared to the data for oxidation of the $H_2{}^{18,18}O_2$, sample precursor of **1′** (cf. Scheme I), by ceric ammonium sulfate in aqueous acidic solution.[22] Concerning the latter reaction, our results confirm that no scrambling occurs during the oxidation of H_2O_2 by Ce(IV).[20,21] Also, there is practically no scrambling of label (~13%, ^{18}O) in the small amount of dioxygen produced during the uncatalyzed decomposition of **1′** (second entry, Table II).[23] However, when **2a** is present in the ketone-catalyzed process, the composition of evolved oxygen gas indicates ~39% loss of the ^{18}O label and most of the labeled oxygen now appears scrambled as $^{34}O_2$ (last entry, Table II). Inspection of Scheme I reveals that this result can be nicely accommodated within the dioxirane mechanism. In fact, unlabeled bis(trimethylsilyl) peroxomonosulfate (**1**) is the dominant (~87%) species and most of the labeled dioxygen would result from the attack of unlabeled **1** on the labeled (~6.5%) dioxirane **6′**.[11a]

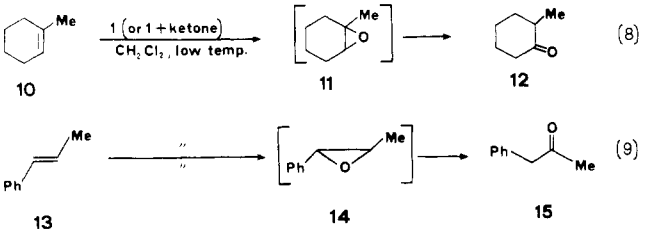
Oxygen Transfer to Organic Substrates. Bis(trimethylsilyl) peroxomonosulfate (**1**) is an excellent agent for oxygen transfer to nucleophilic substrates.[18] As an example, the reaction of this peroxide with *p*-tolyl methyl sulfide (**8**) is nearly instantaneous even at −30 °C, yielding



(7)

the parent sulfoxide **9**. Actually this reaction (eq 7) offers a means to check indirectly the ^{18}O content of labeled peroxide **1′** under the conditions adopted in other labeling experiments (see Experimental Section, Table IV). In fact, in separate runs in which the peroxide **1′** was left standing alone in CH_2Cl_2 at −30 °C, quenching of aliquots with **8** and rapid GC/MS analyses of the sulfoxide product for ^{18}O content permitted us to establish that the loss of label of **1′** was normally negligible during the period of time necessary to bring its reaction with ketones nearly to completion.

We also observed that **1** oxidizes alkenes such as 1-methylcyclohexene (**10**) and *trans*-β-methylstyrene (**13**), although at a rate much slower than sulfide oxidation, producing 2-methylcyclohexanone (**12**) and benzyl methyl ketone (**15**), respectively, in high yield, most likely via the parent epoxides **11** or **14** (eq 8 and 9). Indeed, we could



(8)
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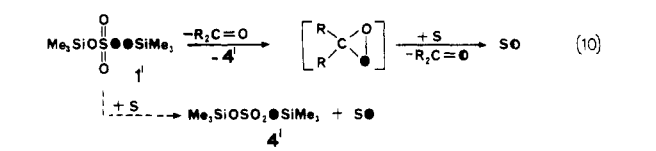
verify that a sample of independently synthesized epoxide **11** quickly isomerizes into **12** in the presence of $(Me_3Si)_2SO_4$ in CH_2Cl_2.[24] Noteworthily, ketones markedly enhance the rate of alkene oxidation by the silyl peroxide **1**; pertinent examples are collected in Table III. Inspection of data therein reveals that acetone—a ketone that does not undergo appreciable BV oxidation[1,8]—renders feasible the oxidation of alkene **13** by **1**, even at a temperature as low as −75 °C. At −32 °C during 3 h, the ketones employed all increase the rate of alkene conversion, with the catalytic activity in the order cyclohexanone > acetone ≅ 4-heptanone (cf. Table III). These findings parallel the observations concerning catalysis by ketones in the decomposition and/or oxygen transfer to substrates by peroxomonosulfate, $HOOSO_2O^-$, a system well investigated and known to generate dioxirane intermediates.[10,11]

Again, ^{18}O-tracer studies were helpful in supporting the hypothesis that, in the reaction of bis(trimethylsilyl) peroxide with ketones, dioxiranes might be produced that are responsible for peroxide oxygen transfer to substrates. Using doubly ^{18}O-labeled peroxide **1′**, in fact, it can be predicted that 25% of the label initially present in the peroxide should appear in the oxidized substrate (eq 10).



(10)

The amount of total label retained in the substrate would, of course, be 50% if substrate oxidation were not mediated by dioxirane. By using 12.8% ^{18}O doubly labeled silyl peroxide **1′** and unlabeled acetone catalyst in CH_2Cl_2 at

(20) (a) Koubek, E.; Haggett, M. L.; Battaglia, C. J.; Ibne-Rasa, K. M.; Pyun, H. Y.; Edwards, J. O. *J. Am. Chem. Soc.* **1963**, *85*, 2263. (b) Koubek, E.; Levey, G.; Edwards, J. O. *Inorg. Chem.* **1964**, *3*, 1331. (c) Ball, R. E.; Edwards, J. O.; Haggett, M. L.; Jones, P. *J. Am. Chem. Soc.* **1967**, *89*, 2331. (d) Koubek, E.; Welsch, J. E. *J. Org. Chem.* **1968**, *33*, 445. (e) Mc Isaac, J. E.; Ball, R. E.; Behrman, E. J. *J. Org. Chem.* **1971**, *36*, 3048.

(21) For a review, see: Edwards, J. O.; Fleischauer, P. D. *Inorg. Chem. Acta, Rev.* **1964**, *2*, 53.

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(23) This result is in itself interesting. It should be noted, in fact, that in the decomposition of peroxomonosulfate in water at pH 7.4 and 9.4, the double ^{18}O labeling of the peroxide yields mainly $^{34}O_2$. This indicates almost complete scrambling and a mechanism of nucleophilic attack by $^-O_3SOO^-$ at the O–O bond of $HOOSO_3^-$ (ref 20a). On the contrary, mostly $^{36}O_2$ is produced from the uncatalyzed decomposition of **1** (no scrambling). Thus, the decomposition of the bis(trimethylsilyl) derivative of Caro's acid would seem to occur unimolecularly or —more likely— through an activated complex involving nucleophilic attack of **1** at the electrophilic sulfur center of another molecule of the same species (cf. ref 21 and 20a).

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Table III. Catalysis by Ketones in the Oxidation of Alkenes by Bis(trimethylsilyl) Peroxomonosulfate[a]

alkene	ketone catalyst	temp, °C	reactn time, h	% conv[b]	product	% yield[c]
1-methylcyclohexene (10)	none	−32	3	46	1-methylcyclohexanone (12)	90
10	cyclohexanone (2a)	−32	3	94	12	97
10	acetone	−32	3	75	12	96
10	4-heptanone	−32	3	80	12	95
10	none	−75	16	≤5	12	≤2
10	acetone	−75	16	23	12	95
trans-β-methylstyrene (13)	none	−4	1.5	40	benzyl methyl ketone (15)	92
13	acetone	−4	1.0	98	15	95
13	none	−32	3.0	45	15	96
13	acetone	−32	3.0	68	15	95
13	cyclohexanone (2a)	−32	3.0	88	15	97

[a] All runs carried out in CH_2Cl_2 solvent with initial concentrations 0.08 M silyl peroxide, 0.02 M alkene, and ca. 0.001 M ketone. [b] Based on residual alkene (GC analyses). [c] Based on alkene consumed (GC and GC/MS analyses).

−30 °C, we tested the distribution of the oxygen label in the oxidation of *trans*-β-methylstyrene (eq 9). Monitoring the formation of benzyl methyl ketone (15) by GC/MS over the first 25–30% of reaction, we found that it contained ca. 22% of the ^{18}O label initially present in 1′ (last entry Table IV, Experimental Section). A parallel run, where the silyl peroxide 1′ was left standing alone in CH_2Cl_2 at −30 °C for an equal period of time (ca. 30 min), quenched with *p*-TolSMe, and analyzed by MS of the ^{18}O label in the sulfoxide product, permitted verification that the loss of peroxide ^{18}O label in 1′ was negligible (≤5%).

Conclusions

The above observations are rather stringent in suggesting the intermediacy of dioxiranes in the reaction of the bis(trimethylsilyl) derivative of Caro's acid with ketones. Closely related to the case at hand, Edwards and Pater have studied the oxidation of cyclohexanone to ε-caprolactone by peroxomonosulfate at pH 8.5, adopting ^{18}O-labeling techniques akin to those described above.[25] They were able to demonstrate that the dioxirane mechanism, while accounting for ketone catalysis of peroxide decomposition, was not operative for the conversion of the ketone into the ester by peroxomonosulfate.[25] The same conclusion was reached when the latter reaction was investigated at lower pH values (6.2–7.5).[25] Thus, replacing peroxomonosulfate by its bis(trimethyl)silyl derivative 1 as oxygen transfer agent, and water by CH_2Cl_2 as solvent, dioxiranes appear to operate as intermediates for both the ketone-catalyzed peroxide decomposition yielding O_2 gas *and* for ketone oxidation into lactone or ester. Although it is clear that these changes are sufficient to promote dioxirane formation from the CA intermediate, rather than the latter's proceeding directly to the ester (cf. Scheme I), the mechanistic details require further investigation.

Be this as it may, it is of interest to note that in the oxidation of acetophenone (2b), the preferential migration of Ph over Me is much less pronounced than commonly observed in the heterolytic rearrangement of several peroxides.[1,8] However, en route from the dioxirane to the ester, formation of dioxamethylene biradicals 5″ (eq 2) should be unimportant; in fact, if the ester arises from biradical 5″, the migratory aptitude Me ≫ Ph should prevail, as found for the β-scission of alkoxy radicals derived from peroxides.[27] Consequently, it is likely that in the present case the polar rearrangement of the dioxirane is catalyzed by Lewis acids[12] such as $(Me_3Si)_2SO_4$ or $(Me_3Si)_2SO_5$.

Experimental Section

Melting points and boiling points were not corrected; NMR and IR spectra were run on a Varian Model XL200 and on a Perkin-Elmer Model 1710 (FT) instrument, respectively. GLC analyses were performed on a DANI 3800 chromatograph, equipped with SE30 or OV101, 30 m × 0.25 μm i.d. capillary columns. Mass spectra of organic substates were obtained on a GC/MS Hewlett-Packard Model 5970 or on a Varian-Mat CH5 instrument (70 eV); for oxygen gas, a Balzer (Model QMG 511) quadrupole spectrometer (40-eV ionization energy) was employed.

Materials. Cyclohexanone (2a), acetophenone (2b), acetone, 4-heptanone, ε-caprolactone (3a), γ-caprolactone (3a′), phenyl acetate (3b), methyl benzoate (3b′), *p*-tolyl methyl sulfide (8), *p*-tolyl methyl sulfoxide (9), 1-methylcyclohexene (10), *trans*-β-methylstyrene (13), 2-methylcyclohexanone (12), and 1-phenyl-2-propanone (15) were commercial products; they were purified by standard methods. Commercial sulfur trioxide (Aldrich) was employed as received. 1,2-Epoxy-1-methylcyclohexanone (11) was prepared by epoxidation of 10 with 3-chloroperoxybenzoic acid (Aldrich):[28] bp 45–47 °C (21 mmHg) [lit.[28a] bp 85–88 °C (30 mmHg)]. Bis(trimethylsilyl) sulfate (4) was prepared from trimethylsilyl chloride (Aldrich) and H_2SO_4:[29] bp 87–90 °C (4 mmHg); ^1H NMR ($CDCl_3$, 200 MHz) δ 0.51 (s).

Cyclohexanone-^{18}O (2a′) was obtained upon exchange of the unlabeled material 2a with $H_2{}^{18}O$ (MSD Isotopes) in the presence of H_2SO_4 catalyst.[30] **Hydrogen Peroxide-$^{18}O_2$** was prepared by passing $H_2{}^{18}O$ (94–98 atom % ^{18}O, MSD Isotopes) through an electric discharge tube, using described equipment.[19,31] The product $H_2{}^{18,18}O_2$ was rinsed from the cold traps with normal 80–82% H_2O_2 (Interox Peroxid-Chemie GmbH) so that the resulting hydrogen peroxide had the desired isotopic enrichment of atom % ^{18}O.

Bis(trimethylsilyl) peroxide (6) and bis(trimethylsilyl) peroxide-$^{18}O_2$ (6′) were prepared upon reaction of trimethylsilyl chloride (Aldrich) with the complex DABCO·$(H_2O_2)_2$[32] or DABCO·$(H_2{}^{18,18}O_2)_2$, respectively, according to a reported procedure:[33] bp 42 °C (30 mmHg); ^1H NMR ($CDCl_3$, 200 MHz) δ 0.16 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz) δ −1.69 (s); mass spectrum, *m/z* (rel intensity) 178 (2), 165 (8), 164 (15), 163 (100), 135 (6), 134 (11), 133 (77), 119 (6), 117 (6), 89 (5), 74 (11), 73 (15), 59 (18), 45 (7).

Bis(trimethylsilyl) peroxomonosulfate (1) and bis(trimethylsilyl) peroxo-$^{18}O_2$-monosulfate (1′) were generated in situ upon reaction of sulfur trioxide with 6 or 6′, respectively, in CH_2Cl_2 (or CD_2Cl_2), at −30 °C:[7,18] ^1H NMR (CD_2Cl_2, 200 MHz,

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Table IV. Example of Mass Spectral Data for Calculation of ^{18}O Excess in Labeled Reagents, Product, and Their Fragments[a]

reactn in eq[b]	starting materials and products	I (m/z)	natural		labeled		^{18}O % excess[c]
			$I+2$	$I+4$	$I+2$	$I+4$	
4	(i) $Me_3SiOOSiMe_3$ (6)[d]	100 (178) (M)	8.00	[e]	9.05	9.10	10.15
	fragment VI	100 (163) (B)	7.80	0.20	8.20	9.65	9.85
	(ii) lactone (**3a**)	100 (114) (M)	0.80		5.60		4.80
	fragment III a	100 (84) (B)	1.80		4.10		2.30
4 bis	(i) cyclohexanone (**2a**)	100 (98) (M)	0.60		12.50		11.90
	fragment II a	100 (55)	1.20		13.30		12.10
	(ii) lactone (**3a**)	100 (114) (M)	0.80		5.80		5.00
	fragment III a	100 (84) (B)	1.80		4.40		2.60
5	(i) $Me_3SiOOSiMe_3$ (6)[d]						
	fragment VI	100 (163) (B)	8.00	0.20	11.20	23.60	26.60
	(ii) phenyl acetate (**3b**)	100 (136) (M)	0.95		13.65		12.70
	fragment MeCO (IV)	100 (43)	0.70		6.19		5.49
	fragment PhOH (V)	100 (94) (B)	0.45		7.75		7.30
7	(i) $Me_3SiOOSiMe_3$ (6)[d]						
	fragment VI	100 (163) (B)	7.80	0.20	8.40	9.65	10.05
	(ii) *p*-TolSOMe (8)	100 (154) (M)	4.70	[e]	9.25	0.30	4.85
9	(i) $Me_3SiOOSiMe_3$						
	fragment VI	100 (163)	8.00	0.20	9.20	11.80	12.80
	(ii) benzyl methyl ketone (**15**)	100 (134) (M)	0.70		3.55		2.85
	fragment MeCO (IV)	100 (43) (B)	1.50		4.30		2.80

[a] Relative intensities of peaks are averages of values from three to eight mass spectrometric runs for each sample, agreeing within ±5%. For fragments, cf. Chart I. [b] See text. [c] See Experimental Section for calculation of label excess. [d] Mass spectral analysis of $Me_3SiOOSiMe_3$ used actually as precursor for 1 (or labeled 1′) in the given reaction (cf. Scheme I. [e] Not detected.

−30 °C) δ 0.38 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 50 MHz, −30 °C) δ −0.53 (s).

Reaction of Bis(trimethylsilyl) Peroxomonosulfate with Ketones. A reported[7] general procedure was followed: the ketone (1–1.5 mmol) in dry CH_2Cl_2 (10 mL) was added under dry N_2 during 4–5 min to 1 or 1′ (5–8 mmol) in 20 mL of dry CH_2Cl_2, at −30 °C. The reaction was monitored by GC or GC/MS. After 70–90% conversion of the ketone (30–60 min), alternative to aqueous workup,[7] the products can be isolated directly by flash chromatography (silica gel, CH_2Cl_2) of the reaction mixture, yielding residual ketone (if any) and the ester or the lactone in ≥90% yield.

Oxidation of Alkenes. Under conditions similar to those above, the alkene or a mixture of alkene and ketone in CH_2Cl_2 was quickly added to a solution of the peroxide in dry CH_2Cl_2 at low temperature (cf. Table IV). Aliquots were withdrawn periodically and analyzed by GC or GC/MS; pure samples of the ketone products **12** or **15** could be obtained by column flash chromatography of the reaction mixtures.

Oxygen Gas Product. For mass spectrometric analyses, samples of the oxygen gas evolved were collected by employing the described procedure and apparatus:[20,31] the labeled silyl peroxide 1′ (~0.4 M) in 15 mL of dry CH_2Cl_2, at −30 °C, was transferred in a 100-mL reaction vessel; contained in a side arm of the same vessel was a solution of cyclohexanone in dry CH_2Cl_2. The reaction flask and its contents were attached to a vacuum line, cooled at −80 °C, and thoroughly flushed with a stream of helium for 30–60 min. Then, the helium flow was terminated and blank samples of residual gas taken to check on the efficiency of the purging process. The reaction vessel was allowed the warm up to ca. −10 °C and the side arm was turned into a position enabling the two solutions to be mixed. After a suitable time (cf. Table II), the reaction vessel was again cooled to ca. −80 °C and a sample of gas (now helium and oxygen) taken into a gas ampule for mass spectrometric analysis. The same apparatus was used to obtain gas samples from the decomposition of 1 in the absence of ketone and from the reaction of doubly labeled hydrogen peroxide with cerium ammonium sulfate (in water, at 20 °C).[20,31]

Mass Spectral Determinations. For doubly ^{18}O-labeled bis(trimethylsilyl) peroxide (**6′**) the percent of *excess* ^{18}O label was calculated from $100 \times \{[(I+4)+(I+2)/I]_{labeled} - [(I+4)+(I+2)/I]_{natural}\}$. Under the analysis conditions (70-eV ionization energy in most of the cases), the peroxide gave a low intensity peak for the parent ion (M); hence, excess label was more conveniently determined with reference to the base peak m/z 163 (M − CH_3) (cf. Table IV). Excess of percent ^{18}O-label of other compounds and their fragments were estimated according to $100 \times \{[(I+2/I)_{labeled} - (I+2/I)_{natural}]\}$.

Pertinent examples are collected in Table IV. For each sample mass spectra were run from three to eight times, averaging ($I+2/I$) values, which agreed within ±5%, in most of the cases. The procedures for the analysis of labeled oxygen gas have been described;[20,31] a standard error of ±3% was estimated for the mole fraction values reported in Table II.

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Registry No. 1, 23115-33-5; 1′, 123810-17-3; **2a**, 108-94-1; **2a′**, 73007-69-9; **2b**, 98-86-2; **3a**, 502-44-3; **3a′**, 695-06-7; **3b**, 122-79-2; **3b′**, 93-58-3; **6**, 5796-98-5; **6′**, 87413-34-1; **8**, 623-13-2; **9**, 934-72-5; **10**, 108-87-2; **12**, 583-60-8; **13**, 873-66-5; **15**, 103-79-7; DABCO·$(H_2O_2)_2$, 39810-25-8; DABCO·$(H_2{}^{18}O_2)_2$, 123776-40-9; sulfur trioxide, 7446-11-9.