normalized relative kinetic acidity at C2 of 4 is within the expected range, about one-half that at C1 of 3 and around 2000 times greater than that of C2 and C4 of 1, the standard for comparison. On the other hand, exchange at C4 of 4 can be seen to be more than 3 orders of magnitude faster than that of acyclic 1 and even about 2 powers of 10 greater than that of cyclic 2. The origin of this extraordinary enhancement cannot be assessed unequivocally. The relative exchange rates may or may not parallel equilibrium acidities in these compounds. If they do, then such factors as the gauche effect,[15] s character of the C–H bonds (hybridization),[16] angle strain (I strain), eclipsing (torsional) interactions between vicinal hydrogens, and inductive effects all should be considered.[17] However, these inherent properties often are outweighed by solvation effects[18] and complications may arise from internal return and ion pairing.[19] In view of these uncertainties, attention will be focused on just two features of these systems: torsion and a "1,4-effect".

Contributions of torsion, angle strain, and hybridization of the C–H bonds are difficult to separate in most carbocyclic compounds. Enol or enolate formation in 2 would relieve eclipsing between hydrogens at C2 and C3, but this would be counterbalanced by an increase in eclipsing strain between hydrogens at C3, C4, and C5 due to the attendant conformational restrictions accompanying the change in hybridization at C2. In contrast, 4 affords a system in which eclipsing interactions are present only at C4 and C5. They would promote exchange at C4 since carbanion or enol formation would relieve most of the eclipsing strain. A measure of the energy associated with such torsional interactions may be obtained by comparing the heats of formation of 2-thiolene (12.76 kcal/mol), which has four eclipsed protons, and 3-thiolene (11.31 kcal/mol),[20] which has no eclipsed protons. These data would lead to the prediction of an increased rate of exchange at C4 of 4 arising from four eclipsed protons not paralleled at C2, with no eclipsed protons, if the transition state for isotopic exchange resembles an enol or enolate. Torsional strain comparable to the 1.45 kcal/mol stability difference between the model compounds could account for about 1 order of magnitude of the enhanced kinetic acidity seen at C4 of 4.

An unusual feature brought out in Table I is the fact that exchange at C3 of 3 is 16–27 times faster than that of 1, indicating the existence of a 1,4-interaction between the sulfur atom and the C4 position of 4. A similar high kinetic acidity at C3 of 1-methoxy-2-propanone has been observed in the laboratories of both Hine[21] and Bothner-By.[22] The origin of this "1,4-effect" is unknown and preliminary results indicate that it is even larger in cyclic than in acyclic systems.[23]

In summary, the results reported here demonstrate that the kinetic acidity of C–H bonds at C4 of 4 is about 1000–5000 times higher than those at C2 and C4 of 1. Two factors which reasonably could contribute to this enhanced kinetic acidity are torsional strain between vicinal hydrogens and a 1,4-effect of the heteroatom of unknown origin, each of which might contribute an order of magnitude to the rate enhancement. However, lack of knowledge of the structure of the transition state in these exchanges makes these suggestions speculative. It is predicted that, in general, five-membered-ring heterocyclic enols or enolates having sp^2 hybridization at C3 and C4 and sp^3 hybridization at C2 and C5 will be formed ten to 100 times faster than the corresponding isomers having sp^2 hybridization at C2 and C3 and sp^3 hybridization at C4 and C5. Further studies to test this hypothesis are in progress.

Acknowledgment. Partial support of this work through a grant from the Brown-Hazen Fund of the Research Corporation is acknowledged with gratitude. Additional assistance was provided by a Faculty Summer Research Grant to F.W.C. and a Graduate Student Research Fund grant to J.J.G. from The American University.

Registry No. 1, 96-22-0; 2, 120-92-3; 3, 14109-72-9; 4, 1003-04-9; methanethiol, 74-93-1; bromoacetone, 598-31-2.

(15) Epiotis, N. D.; Yates, R. L.; Bernardi, F.; Wolfe, S. *J. Am. Chem. Soc.* **1976**, *98*, 5435 and references cited therein.
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(18) Pross, A.; DeFrees, D. J.; Levi, B. A.; Pollack, S. K.; Radom, L.; Hehre, W. J. *J. Org. Chem.* **1981**, *46*, 1693.
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(21) Hine, J.; Hampton, K. G.; Menon, B. C. *J. Am. Chem. Soc.* **1967**, *89*, 2664.
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(23) J. J. Guth, unpublished observations.

Thermal and Photochemical Rearrangement of (*o*-Tolylcarbonyl)trimethylsilane. A 1,5-Shift of a Trimethylsilyl Group from Oxygen to Carbon

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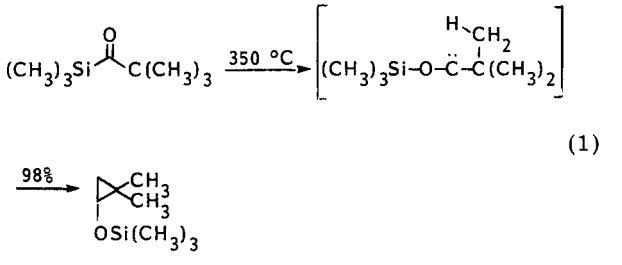
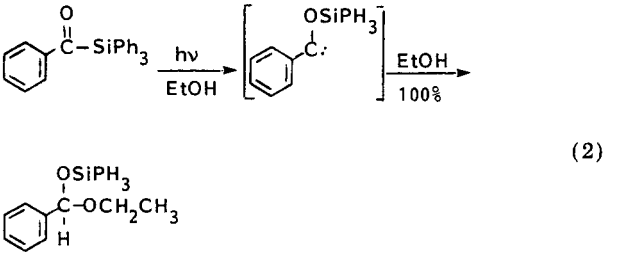
The pioneering studies of Brook and co-workers have established that siloxycarbenes are available in high yield from acylsilanes by either thermal[1] or photochemical activation[2,3] as illustrated below (eq 1 and 2). Of special



(1)



(2)

interest to us was the high-yield insertion of the thermally generated siloxycarbene into carbon–hydrogen bonds. If

(1) Bassindale, A. R.; Brook A. G.; Harris, J. *J. Organomet. Chem.* **1975**, *90*, C6–C8.
(2) Duff, J. M.; Brook, A. G. *Can. J. Chem.* **1973**, *51*, 2869–2883.
(3) For recent mechanistic studies, see: Bourgue, R. A.; Daus, P. D.; Dalton, C. J. *J. Am. Chem. Soc.* **1981**, *103*, 697–699, 699–700.

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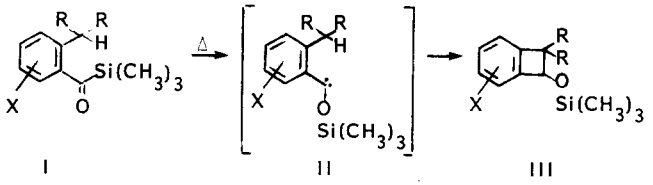
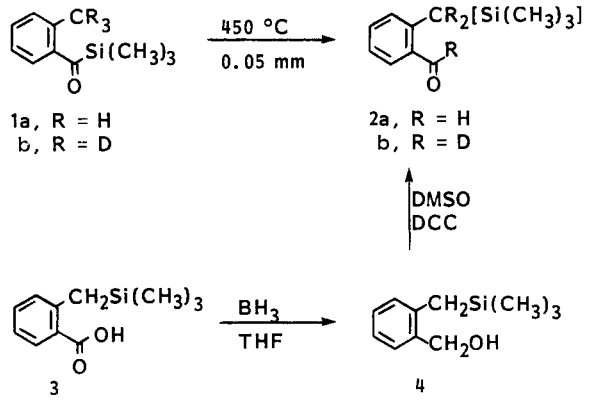
Scheme I. Proposed Strategy to Benzocyclobutenols



Scheme II. Thermolysis of (o-Tolylcarbonyl)trimethylsilane



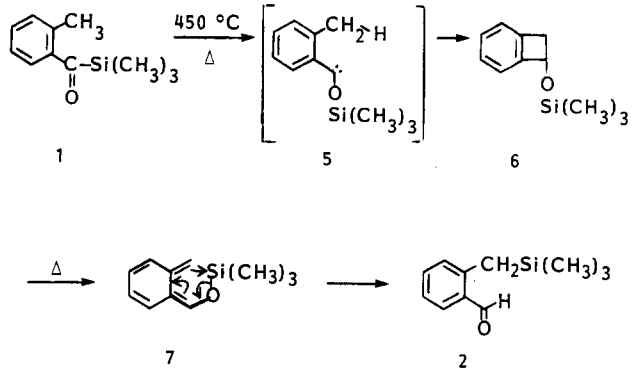
this could be applied to acylsilanes of type I (Scheme I), then a versatile route to benzocyclobutene systems required for our anthracyclinone studies would be available.[4] We report here the products from thermal and photochemical activation of acylsilane 1.

Vacuum pyrolysis of **1a** at 450 °C through a quartz tube filled with quartz chips cleanly afforded one isolable product in 70% yield.[5] Spectroscopic and analytical data suggest that this product was the aldehyde **2a** (Scheme II), and this was rigorously confirmed by the preparation of **2a** from the known **3**.[6] Rearrangement of the trideuterio analogue **1b**, available in connection with another study, afforded **2b** with complete retention of deuterium.

While our initial goal, a route from acylsilane to benzocyclobutenols (Scheme I), had been thwarted,[7] we sought to establish whether a benzocyclobutenol derivative was a plausible intermediate in the **1** → **2** conversion. Indeed, thermal rearrangement of **6** under the same conditions as for **1a** afforded **2a** in 71% yield after chromatography. Thus, the reaction of **1a** reasonably occurs via the sequence outlined in Scheme III; however, the direct conversion **5** → **7** cannot be ruled out. While 1,5-shifts of a trialkylsilyl group from oxygen to carbon were unreported at the time this work was done, Cameron[8] has since observed such a migration in a silyloxy diene system.

In an attempt to bypass the **6** → **7** → **2** steps, the photochemistry of **1a** was briefly examined. The acylsilane **1a** was photochemically quite stable in rigorously dried benzene.[9] However, irradiation of **1** in undried benzene gave o-methylbenzaldehyde (98%) on workup (Scheme IV), and in methanol the unstable acetal **8** was formed in 90% yield. If the carbene **5** is generated photochemically, it apparently has insufficient thermal energy to insert efficiently into the benzylic carbon–hydrogen bond.[10] The stability of **1a** in anhydrous benzene presumably derives from the proposed reversal of **5** to **1a**.[2]

Scheme III. Suggested Mechanistic Sequence for the 1 → 2 Conversion



In summary, these results suggest that thermal activation of acylsilane **1** affords benzocyclobutene **6** which undergoes further thermal rearrangement to **2** which is the thermodynamic product in this system. The clean nature of the reaction suggests (phenylcarbonyl)trimethylsilanes may serve as convenient sources of thermally generated carbenes for insertion and rearrangement reactions.

Experimental Section[11]

Vacuum Pyrolysis of 1a and 1b. The acylsilane **1a**[12] (1.20 g, 6.25 mmol) was slowly vaporized (1 h) through a quartz tube filled with quartz chips held at 450 °C under 0.05 mm pressure in the apparatus previously described.[4b] The resulting crude yellow oil was filtered through silica gel (1.5 × 20 cm column, 5% ether/petroleum ether as the eluant) to give 840 mg (70%) of **2a**: IR (CCl_4) 2960 (m), 2904 (w), 2730 (w), 1697 (s), 1602 (m), 1570 (m), 1482 (m), 1450 (m), 1417 (m), 1279 (m), 1250 (s), 1208 (m), 1188 (m), 1150 (s), 850 cm^{-1} (vs); NMR δ 10.03 (s, 1 H), 7.77–7.55 (m, 1 H), 7.40–6.87 (m, 3 H), 2.67 (s, 2 H), –0.05 (s, 9 H).

Anal. Calcd for $C_{11}H_{16}OSi$: C, 68.7; H, 8.4. Found: C, 68.6; H, 8.4.

Similarly, 1.09 g of **1b** was pyrolyzed to afford after chromatography 740 mg (74%) of **2b**. The ^1H NMR spectrum showed the complete absence of the aldehyde and methylene hydrogens: IR (CCl_4) 2960 (m), 2105 (w), 2045 (w), 1690 (s), 1602 (m), 1569 (m), 1480 (m), 1446 (m), 1417 (m), 1278 (m), 1250 (m), 1211 (m), 846 cm^{-1} (s); exact mass calcd for $C_{11}H_{13}D_3OSi$ 195.1159, obsd 195.1164.

Vacuum Pyrolysis of 6. A 1.0-g (5.21 mmol) sample of **6** was vaporized over a period of 45 min through the pyrolysis tube (450 °C) previously described.[4b] The TLC of the crude pyrolysate showed one major product and a trace of starting material. Chromatography of this reaction product on silica gel (2.5 × 25

(4) (a) Jackson, D. K.; Narasimhan, L.; Swenton, J. S. *J. Am. Chem. Soc.* **1979**, *101*, 3989–3990. (b) Swenton, J. S.; Anderson, D. K.; Jackson, D. K.; Narasimhan, L. *J. Org. Chem.* **1981**, *46*, 4825–4836.

(5) When the reaction was conducted at 350 °C, only partial conversion of **1a** to **2a** was observed whereas at >600 °C several uncharacterized products in addition to **2a** were formed.

(6) Eaborn, C.; Jackson, R. A.; Pierce, R. *J. Chem. Soc., Perkin Trans. 1* **1975**, 470–474. Coughlin, D. J.; Salomon, R. G. *J. Org. Chem.* **1979**, *44*, 3784–3790.

(7) For a superior route to benzocyclobutenones, see: Chenard, B. L.; Slapak, C.; Anderson, D. K.; Swenton, J. S. *J. Chem. Soc., Chem. Commun.* **1981**, 179–180.

(8) Anderson, G.; Cameron, D. W.; Feutrell, G. I.; Read, R. W. *Tetrahedron Lett.* **1981**, 4347–4348.

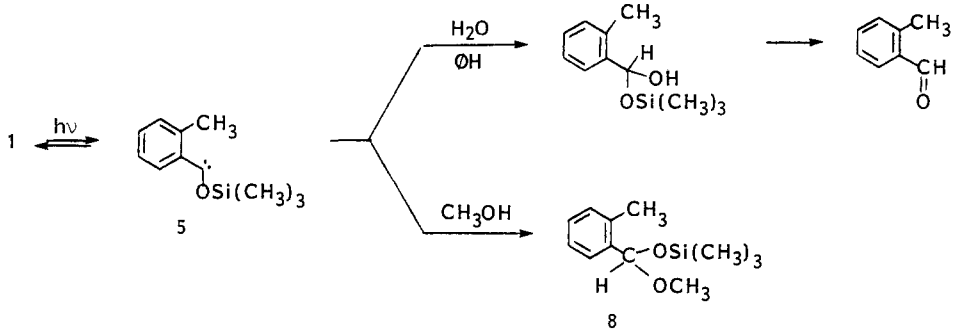
(9) The trimethylsilyl ether **6** was photochemically stable in methanol (distilled from sodium) in the time interval required for reaction of **1**.

(10) Compound **1a** was also photochemically stable in benzene at 80 °C.

(11) All melting points were taken with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Measurements of standard samples indicated that the observed melting points were probably 1–2 °C lower than the corrected value. Infrared spectra were recorded on a Perkin-Elmer Model 283B grating spectrometer. ^1H NMR spectra were taken at 60 MHz (CCl_4) with a Varian EM-360 instrument using either tetramethylsilane or methylene chloride as the standard. Mass spectra and exact mass measurements were obtained by Mr. C. R. Weisenberger on a Consolidated Electronic MS-9 double-focusing mass spectrometer. Silica gel was from E. Merck Co. Butyllithium in hexane (Ventrol) was titrated in tetrahydrofuran with 1,10-phenanthroline as the indicator. A workup as usual refers to extraction with ether, washing of the ether layers with saturated brine solution, drying over calcium sulfate, and concentration in vacuo.

(12) Picard, J.; Calas, R.; Dunogues, J.; Duffout, N.; Gerval, J.; Lapouyade, P. *J. Org. Chem.* **1979**, *44*, 420–424. The analogous procedure was used for the preparation of **1b**.

Scheme IV



cm column, 2% ether/petroleum ether as the eluant) gave 706 mg of **2a** which showed IR and NMR spectra identical with those reported above.

Irradiation of 1a. A solution of 60 mg of acylsilane **1a** in 5 mL of dry methanol (distilled twice from sodium) in a quartz tube was irradiated with a 450-W medium-pressure Hanovia lamp (Pyrex filter, $\lambda > 280$ nm). The reaction was completed in 15 min. The solvent was then removed in vacuo to give ca. 63 mg (90%) of clear liquid whose ^{1}H NMR spectrum showed that it was primarily the expected mixed acetal. This mixed acetal was further purified via preparative GLC (2 ft × $^1/_8$ in. column, 5% SE-30 on Chromasorb G, 120 °C): IR (neat) 2948 (s), 1252 (s), 1124 (s), 1078 (s), 1045 (s, br), 890 (s), 876 (s), 839 (s), 748 cm^{-1} (s); ^{1}H NMR δ 7.52–6.97 (m, 4 H), 5.74 (s, 1 H), 3.15 (s, 3 H), 2.33 (s, 3 H), 0.10 (s, 9 H); exact mass calcd for $C_{12}H_{20}O_2Si - CH_3$ 209.0998, obsd 209.1003.

Compound 6. To a solution of 2.0 g (16.67 mmol) of benzocyclobutenol[13] in 5 mL of dry pyridine was added 10.76 g (66.67 mmol) of hexamethyldisilazane. To this stirred solution was added dropwise 7.23 g (66.67 mmol) of chlorotrimethylsilane; a white precipitate formed immediately. This reaction mixture was stirred at room temperature under nitrogen for 2 h and then partitioned between 200 mL of methylene chloride and 50 mL of 5% sodium bicarbonate. The organic layer was separated and washed again with 30 mL of 5% sodium bicarbonate, 20 mL of water, and finally 20 mL of saturated sodium chloride. Workup gave ~3 g of pale yellow liquid which was then passed through a 3.5 × 15 cm silica gel column (4% ether/petroleum ether as the eluant) to give 2.2 g (69%) of silylated benzocyclobutenol as colorless liquid: IR (neat) 2955 (s), 1352 (s), 1251 (s), 1205 (s,br), 1155 (s), 1139 (s), 1118 (s), 1090 (s), 1067 (s), 905 (s), 881 (s), 838 cm^{-1} (s); NMR δ 7.20 (br s, 4 H), 5.30 (X of ABX, J_{AX} = 2 Hz, J_{BX} = 4 Hz, 1 H), 3.29 (center of AB of ABX, $\Delta\nu$ = 32 Hz, J_{AB} = 14 Hz, J_{AX} = 2 Hz, J_{BX} = 4 Hz, 2 H), 0.20 (s, 9 H).

Anal. Calcd for $C_{11}H_{16}OSi$: C, 68.7; H, 8.4. Found: C, 68.9; H, 8.4.

2-[2-(Trideuteriomethyl)phenyl]-5,5-dimethyl-2-oxazoline.[14] A solution of 8.76 g (34.5 mmol) of 2-(2-bromophenyl)-5,5-dimethyl-2-oxazoline in 90 mL of dry tetrahydrofuran was cooled to −78 °C, and 21.7 mL (1.59 M) of *n*-butyllithium was added. The resulting anion was quenched immediately with 5 g (34.5 mmol) of perdeuteriomethyl iodide (> 99% d_3), and the reaction mixture was warmed to room temperature gradually and then stirred for another 30 min. The workup gave 7.60 g of crude product, whose NMR showed that there was ~6% of aryl coupling product in the reaction mixture. However, the coupling product was easily separated from the desired product by column chromatography on silica gel (20% ether/petroleum ether as the eluant, 3 × 40 cm column): 0-200 mL, nil; 200–600 mL, 5.3 g (80%) of the methylated product; 600–650 mL, nil; 650–900 mL, 0.57 g (5%) of the coupling product. This material showed the following: IR (neat) 2964 (s), 1641 (s), 1035 (s), 706 cm^{-1} (s); NMR δ 7.90–7.60 (m, 1 H), 7.33–6.90 (m, 3 H), 3.90 (s, 2 H), 1.32 (s, 6 H); exact mass calcd for $C_{12}H_{12}D_3NO$ 192.1342, obsd 192.1347.

Compound 1b. The oxazoline from above was hydrolyzed[14] to the carboxylic acid (5.2 g in 100 mL of 3 N hydrochloric acid), and after the workup the crude acid was recrystallized from hexane (mp 93–95 °C). Esterification with diazomethane afforded the crude ester which was converted to the acylsilane **1b** by the procedure of Picard.[9] This compound was obtained as a bright yellow liquid and showed the following: IR (neat) 2958 (m), 1613 (s), 1567 (m), 1258 (s), 1204 (m), 843 (vs), 776 (m), 747 (m), 698 (m), 623 cm^{-1} (m); NMR δ 7.8–6.97 (m, 4 H), 0.27 (s, 9 H); exact mass calcd for $C_{11}H_{13}D_3OSi$ 195.1159, obsd 195.1164.

Authentic Synthesis of 2a. To a solution of 0.40 g (1.9 mmol) of **3**[6] in 10 mL of dry tetrahydrofuran at 0 °C was slowly added 2.0 mL of a 1.0 M solution of borane–tetrahydrofuran complex. Gas evolution was immediate, and then the reaction mixture was stirred for 24 h at room temperature. The reaction was quenched by addition of 5 mL of 3 N hydrochloric acid and extracted with chloroform. The workup followed by passing of the crude product through silica gel (1.5 × 20 cm column, 10% ether/petroleum ether as the eluant) gave 312 mg (84%) of the alcohol as a colorless liquid: IR (neat) 3320 (s, br), 2954 (s), 2895 (m), 1487 (m), 1452 (m), 1416 (m), 1249 (s), 1209 (m), 1188 (m), 1155 (m), 1038 (m), 1003 (m), 845 (vs), 764 (m), 742 (m), 690 cm^{-1} (m); NMR δ 7.37–6.77 (m, 4 H), 4.45 (s, 2 H), 2.40 (br s, 1 H), 2.13 (s, 2 H), 0.02 (s, 9 H).

Anal. Calcd for $C_{11}H_{18}OSi$: C, 68.0; H, 9.3. Found: C, 68.4; H, 9.4.

A 200-mg (1.03 mmol) sample of this alcohol in 5 mL of dimethyl sulfoxide and 5 mL of dry benzene was treated with 640 mg (3.09 mmol) of dicyclohexylcarbodiimide and 66 mg of dichloroacetic acid. After being stirred for 5 h at room temperature, the reaction mixture was added to a solution of 20 mL of ethyl acetate, 5 mL of methanol, and 315 mg of oxalic acid. Removal of the urea by filtration followed by a standard workup and filtration of the crude product through silica gel (1.5 × 20 cm column, 10% ether/petroleum ether as the eluant) gave 170 mg (86%) of **2a** identical in all respects with the pyrolysis product.

Acknowledgment. We thank the National Science Foundation for partial support of this work.

Registry No. **1a**, 65284-33-5; **1b**, 81522-27-2; **2a**, 81522-28-3; **2b**, 81522-29-4; **3**, 71435-93-3; **4**, 57754-01-5; **6**, 81522-30-7; **8**, 81522-31-8; benzocyclobutenol, 35447-99-5; 2-[2-(trideuteriomethyl)phenyl]-5,5-dimethyl-2-oxazoline, 81522-32-9; 2-(2-bromophenyl)-5,5-dimethyl-2-oxazoline, 81522-33-0; 2-(trideuteriomethyl)benzoic acid, 19137-02-1.

(13) Dhawan, K. L.; Gowland, B. D.; Durst, T. *J. Org. Chem.* **1980**, *45*, 922–924.

(14) This chemistry closely follows that of: Meyers, A. I.; Temple, D. L.; Haidukewych, D.; Mihelich, E. D. *J. Org. Chem.* **1974**, *39*, 2787–2793.

Stereo- and Regioselectivities in the Epoxidation of Some Allylic Alcohols by the Dioxirane Intermediate Generated in the Reaction of Potassium Caroate with Acetone

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We have recently reported a new process for olefin epoxidation involving peroxide reactive intermediates that arise from the reaction of potassium peroxomonosulfate ($KHSO_5$, hereafter called caroate) with ketones.[1] Kinetics

0022-3263/82/1947-2670$01.25/0