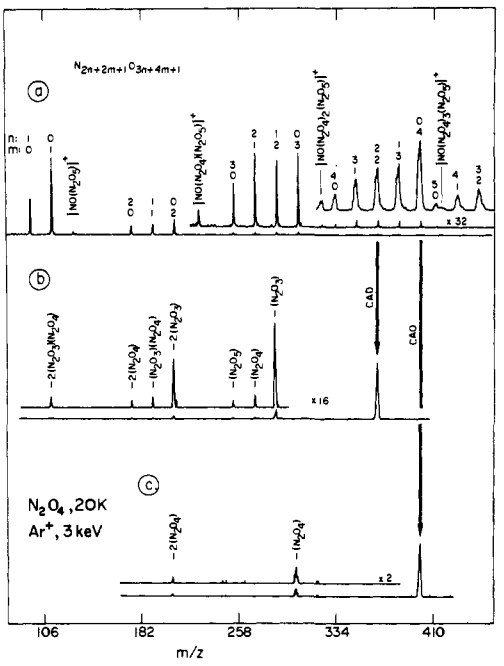

Figure 2. (a) Positive SIMS spectrum of solid N_2O_4 obtained with a 3-keV Ar^+ beam. (b,c) Daughter ion spectra obtained by dissociating $N_9O_{15}^+$ and $N_9O_{17}^+$ ions with Ar under single-collision conditions.

the rest, these specific losses are collision gas pressure independent and originate in long-lived metastable clusters.

The positive SIMS of NO obtained with Ar^+ is dominated by the cluster series $N_{2n+1}O_{3n+1}^+$ whose intensity decays approximately exponentially as n increases. The positive SIMS of N_2O and N_2O_4 is similarly dominated by the cluster series $N_{2n+2m+1}O_{3n+4m+1}^+$, which decreases in intensity as both n and m increase, more rapidly with n. The CAD study of the $N_{2n+1}O_{3n+1}^+$ series shows that these clusters only fragment by losing units of 76 amu. This suggests that the internal structure is $NO^+(N_2O_3)_n$. The CAD spectra of the $N_{2n+2m+1}O_{3n+4m+1}^+$ series obtained from solid N_2O_4 contain daughter ions corresponding to losses of N_2O_3, N_2O_4, and minor losses of N_2O_5 (Figure 2). No other losses were observed. This implies a structure $NO^+(N_2O_3)_n(N_2O_4)_m$ with the loss of N_2O_5 accounted for by small amounts of $NO^+(N_2O_3)_{n+1}(N_2O_4)_{m-2}(N_2O_5)$. The loss of N_2O_3 is between 4 and 10 times more likely than the loss of N_2O_4 when both are present in the cluster. CAD measurements on the same cluster series generated from Ar^+ bombardment of solid N_2O produced similar results, indicating that the composition and structure of the clusters are independent of whether the target was solid N_2O or N_2O_4.

The proposed mechanism for cluster formation from insulating low-temperature solids is outlined in detail elsewhere.[9] It consists of the following steps: (i) primary damage center formation in the solid, (ii) conversion of primary to secondary damage centers by chemical reactions, (iii) ejection of a large molecular aggregate containing a central charge, (iv) conversion of the aggregate into the final stable cluster by evaporative loss of the least firmly held constituent molecules accompanied by cooling. Although the mechanism is compatible with the available observations, until recently it was only supported indirectly. The observation of the secondary damage centers in solid nitrogen oxides by matrix-isolation spectroscopy[11] has now provided the first direct support for steps i and ii.

The present CAD results lend credence to the proposed steps i–iv in that they show the clusters to have the internal structure demanded by these steps: they consist of a central ion and one or more loosely attached solvating molecules. The central ion appears to be derived from that species within the impacted region of the solid which has the lowest ionization potential. The preferred solvating molecules appear to be selected from among all those present in the impact region as being the most polarizable and polar, i.e., most likely to become attached to the central ion before or during the ejection process and least likely to be shaken off during the ejection or thereafter.

The observed cluster metastability also supports the proposed step iv.[12] It is reasonable that vibrational excitation should be the longest lived and metastability the easiest to observe on the even N_n^+ clusters: V–R and V–T energy transfer from a vibrationally excited species will be particularly slow when no low-frequency vibrations are available in the central ion (N_2^+, as opposed to N_3^+) and the solvating molecules (N_2).[13] Once the transfer occurs, the energy provided is adequate for the ejection of a small number of relatively firmly held solvating molecules from a small cluster or a larger number of more loosely held ones from a large cluster. Additional complications would arise if some of the clusters were solid and some liquid.[14]

Acknowledgment. This work was supported by the National Science Foundation (CHE 81-21122).

Registry No. N_2, 7727-37-9; NO, 10102-43-9; N_2O, 10024-97-2; N_2O_4, 10544-72-6; Ar^+, 14791-69-6; N_2O_3, 10544-73-7; N_2O_5, 10102-03-1.

(11) Liang, J.; Michl, J. *J. Am. Chem. Soc.*, preceding paper in this issue.

(12) Metastable clusters from particle-induced desorption on room-temperature solids have been reported before: Blakley, C. R.; Carmody, J. J.; Vestal, M. *Anal. Chem.* **1980**, *52*, 1636. Campana, J. E.; Green, B. N. *J. Am. Chem. Soc.* **1984**, *106*, 531 and references therein.

(13) Oxtoby, D. W. *Annu. Rev. Phys. Chem.* **1981**, *32*, 77; *Adv. Chem. Phys.* **1981**, *47*, 487. Legay, F. In "Chemical and Biomedical Applications of Lasers"; Moore, C. B., Ed.; Academic Press: New York, 1978; Vol. 2.

(14) For a leading reference to the "melting" and "freezing" of clusters, see: Berry, R. S.; Jellinek, J.; Natanson, G. *Chem. Phys. Lett.* **1984**, *107*, 227.

Stereocontrolled 1,1,2-Trialkylation of Ketones

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Intermolecular addition of carbon electrophiles to olefins not bearing heteroatom substituents (e.g., enol ethers, enamines, etc.) has achieved little synthetic use due to the requirements of fairly potent electrophiles and the instability of the initial cations which lead to products derived from rearrangements or further condensations.[1] The ability of silicon to stabilize positive charge has led to its introduction as a regio- and chemoselectivity control element.[2] The potential importance of addition of carbon electrophiles to olefins has been shown by the rapid adoption of allyl- and vinylsilanes as important synthetic building blocks. The ability of a cyclopropyl ring to stabilize an adjacent positive charge and the utility of strained rings for further structural elaboration[3] led

(1) For some recent examples, see: Shono, T.; Nishiguchi, I.; Sasaki, M.; Ikeda, H.; Kurita, M. *J. Org. Chem.* **1983**, *48*, 2503 and references therein. Klein, H.; Erbe, A.; Mayr, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 82. Wada, Y. Yamazaki, T.; Nishiura, K.; Tanimoto, S.; Okano, M. *Bull, Chem. Jpn.* **1978**, *51*, 1821. Snider, B. B.; Cordova, R.; Price, R. T. *J. Org. Chem.* **1982**, *47*, 3643. Wookulich, P. M.; Uskokovic, M. R. *Ibid.* **1982**, *47*, 1600. Snider, B. B.; Rodini, D. J.; van Straten, J. *J. Am. Chem. Soc.* **1980**, *102*, 5872. Beak, P.; Berger, K. R. *Ibid.* **1980**, *102*, 3848. Hoffmann, H. M. R.; Tsushima, T. *Ibid.* **1977**, *99*, 6008. Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 173.

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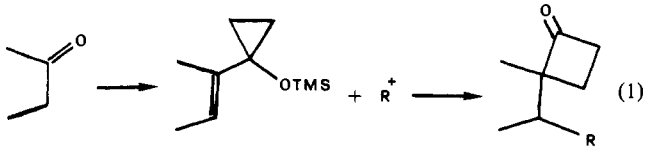
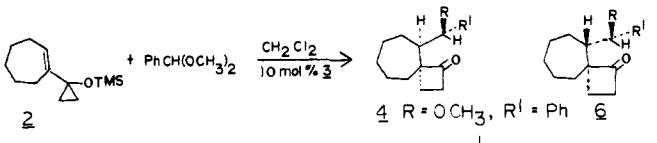
us to explore the addition of carbon electrophiles to vinylcyclopropanols as outlined in eq 1. The possibility that the (trimethylsiloxy)cyclopropyl group could be an effective neighboring group that might substantially enhance the reactivity of the olefins[4] (i.e., be the equivalent of a composite functional group and thereby permit use of electrophiles that normally do not react with olefins), the utility of the cyclobutanones for further structural elaboration,[5] and the ready accessibility of the starting materials from ketones[6] led us to explore this reaction.



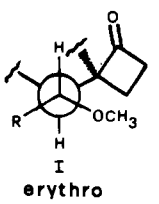
(1)

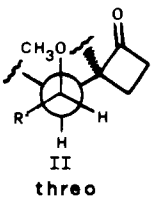
Initial attempts were quite disappointing. Treatment of **1** with acylating agents in the presence of a Lewis acid produced complicated reaction mixtures. In considering more selective carbon electrophiles, our attention was drawn to the directed aldol reaction between enol silyl ethers and acetals in the presence of trimethylsilyl triflate.[7] In the hope that the reactivity of **1** was substantially enhanced over that of an olefin and might begin to approach that of an enol silyl ether, we subjected **2** (1 equiv, concentration 0.5 M), simply available from cycloheptanone with diphenylsulfonium cyclopropylide in 82% yield,[6a,c] and the dimethyl acetal (1.2 equiv) of benzaldehyde in methylene chloride to 10 mol % of $TMSOSO_2CF_3$ (**3**) at −40 °C (1 h). Four diastereomeric products assigned structures **4**–**7**[8] formed in a ratio of 7.4:1.9:1:0.12 in 93% yield. Mechanistic considerations[4] led us to assign the



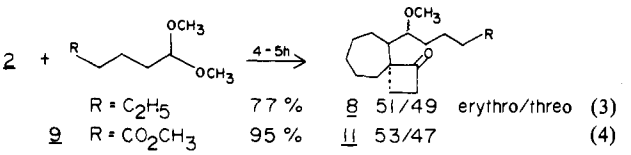
(2)

Z ring stereochemistry as depicted for **4** and **5** for the major products, which is further supported by the ^{13}C NMR shift of the β-carbon of the cyclobutanone (**4**, δ 19.93; **5**, δ 20.37).[9] The epimeric nature at the benzylic position was clearly revealed by the appearance of the methine proton at that position as a doublet, J = 10.5 Hz, at δ 3.79 for **1** and a doublet, J = 3 Hz, at δ 4.60 for **5**. Considering the conformations that minimize steric interactions (i.e., I and II), these coupling constants are in agreement with the major product as depicted in **4**. In all other cases there also existed a complementarity of the chemical shifts of the methine proton and the methoxyl protons—a feature also consistent with their relative orientations with respect to the anisotropic carbonyl group. In the case of **4** and **5**, the anisotropic phenyl group disrupts this correlation. The minor isomers **6** and **7**, which could not be separated from each other, showed a similar pattern for the methine and methoxy regions of the ^1H NMR spectra.

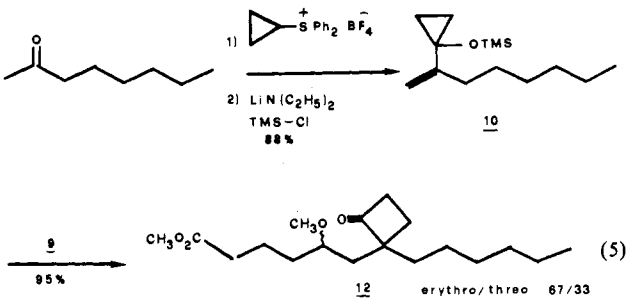




Use of an aliphatic aldehyde led exclusively to the *Z* alkylation products as an almost 1:1 erythro/threo mixture (**8**[8] in eq 3).



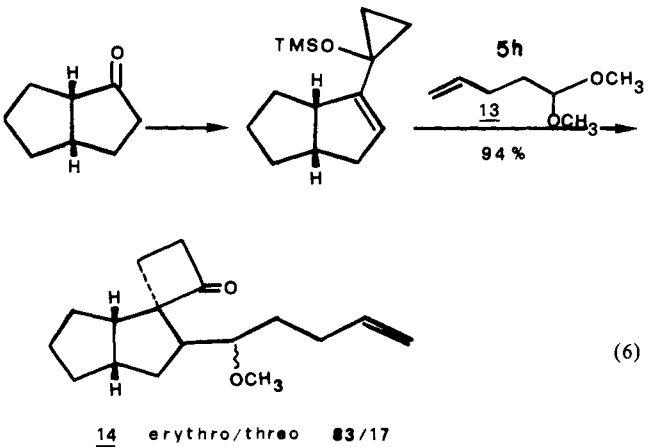
Indeed, in all cases except that of eq 2, only the *Z* alkylation products resulted. In order to test the chemo- and regio-selectivity of the process, acetal **9** bearing an ester group (eq 4) and vinylcyclopropanol **10**, which is available as a single regioisomer in the base opening of the oxaspiropentane (eq 5),[6b] gave the now



(5)

expected *Z* alkylation products **11**[8] and **12**.[8] In each case, the erythro/threo assignments were based upon the coupling constants and chemical shifts in the ^1H NMR spectra as outlined above.

The question of diastereoselectivity with a substituted ketone was explored starting from the vinylcyclopropanol derivative derived from bicyclo[3.3.0]octan-2-one.[10] Again, only one alkylation product (**14**[8]) is generated (as an 83:17 mixture epimeric at the methoxy group) as shown in eq 6. The stereochemistry



(6)

is assigned on the basis of attack by the methoxycarbonium ion on the convex face of the bicyclo[3.3.0]octene and the reaction proceeding by net trans addition. This example also demonstrates

(3) For a leading reference, see: Trost, B. M.; Jungheim, L. N. *J. Am. Chem. Soc.* **1980**, *102*, 7910. For a review, see: Salaun, J. *Chem. Rev.* **1983**, *83*, 619.

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(5) For reviews, see: Trost, B. M. *Acc. Chem. Res.* **1974**, *7*, 85; *Pure Appl. Chem.* **1975**, *43*, 563. Brady, W. T. *Tetrahedron* **1981**, *37*, 2949.

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(7) Murata, S.; Suzuki, M.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 3248.

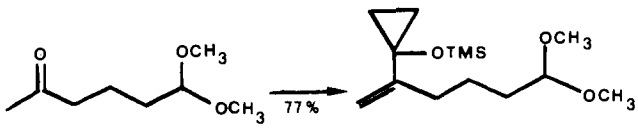
(8) All new compounds have been fully characterized by spectral means including combustion analysis and/or high-resolution mass spectroscopy.

(9) Trost, B. M.; Scudder, P. H. *J. Am. Chem. Soc.* **1977**, *99*, 7601.

(10) Mao, M. K.-T. Ph.D. Thesis, University of Wisconsin, Madison, 1980.

the compatibility of isolated double bonds as present in the acetal **13**.

The excellent efficiency of this new alkylation reaction (77–95% isolated yields) suggested the possibility of an intramolecular version. The keto acetal **15** was converted to the requisite vinylcyclopropanol silyl ether **16** in standard fashion in 77% yield. Exposure to a catalytic amount of **3** gave the cyclized product as a 67:33 mixture of **17**[8] and **18**[8]. The stereochemical assignment



15 16

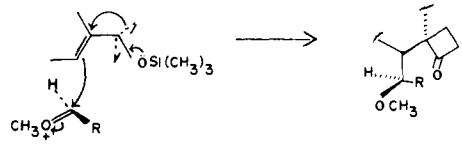
(7)

17 18

erythro/threo 67/33

rests upon the higher field shift for the methine proton in **18** due to the shielding by the carbonyl group (**17** 3.5, tt, J = 10.5, 4Hz; **18** 3.08, m) and the higher field for the ^{13}C shift of an axial compared to an equatorial carbonyl group (**17** 213.96; **18** 212.69).[9]

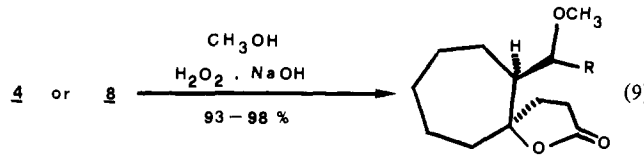
The juxtaposition of the trimethylsiloxy, cyclopropyl, and olefin groups into a composite functional group can be viewed as an extended enol silyl ether. In particular, the delocalization of additional electron density by the trimethylsiloxy group into the olefin is mediated by the cyclopropyl ring. Thus, by analogy to reaction of enol silyl ethers with acetals, an extended orientation as depicted in eq 8 would be expected. The stereochemistry



(8)

predicted by this model indeed corresponds to the major observed product in each case with selectivities as high as 8:1. The special reactivity associated with this type of composite functional group is illustrated by the failure of simple olefins to react under these conditions.

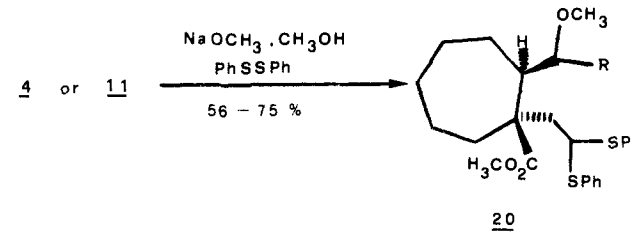
The further utility of this concept for stereocontrolled vicinal trialkylation of ketones derives from the reactivity of a cyclobutanone. For example, basic hydrogen peroxide transforms the cyclobutanones into γ-butyro lactones **19**[8] (eq 9).[11] A chemo-



(9)

19

selective seco-sulfenylation[12] to **20**[8] provides clean chemodifferentiation of all three alkyl groups (eq 10). In the case of **11**, the primary ester is selectively demethylated by the liberated thiophenoxide to give the acid **20b** as the product, which was esterified with trimethylchlorosilane in methanol[13] to **20c**. This simple



20

(10)

method for the stereocontrolled introduction of three different alkyl groups into ketones and aldehydes as summarized in eq 1 offers great flexibility for further elaboration.

Acknowledgment. We thank the National Sciene Foundation and the General Medical Sciences of the National Institutes of Health for their generous support of our programs. The Italian CNR provided partial support for A.B. (NATO fellowship).

Registry No. 1, 91239-03-1; **2**, 39834-33-8; **3**, 27607-77-8; **4**, 91239-04-2; **5**, 91279-99-1; **6**, 91280-00-1; **7**, 91280-01-2; *erythro*-**8**, 91239-05-3; *threo*-**8**, 91280-02-3; **9**, 23068-91-9; **10**, 39834-29-2; *erythro*-**11**, 91239-06-4; *threo*-**11**, 91280-03-4; *erythro*-**12**, 91239-07-5; *threo*-**12**, 91239-08-6; **13**, 14152-71-7; *erythro*-**14**, 91239-09-7; *threo*-**14**, 91280-04-5; **15**, 36727-63-6; **16**, 91239-10-0; **17**, 91239-11-1; **18**, 91239-12-2; **19a**, 91239-13-3; *erythro*-**19b**, 91326-47-5; *threo*-**19b**, 91239-18-8; **20a**, 91239-14-4; *erythro*-**20b**, 91239-15-5; *threo*-**20b**, 91280-05-6; *erythro*-**20c**, 91239-16-6; *threo*-**20c**, 91280-06-7; *n*-$C_5H_{11}CH(OCH_3)_2$, 1599-47-9; $CH_3COC_6H_{13}$-*n*, 111-13-7; octahydro-1-pentalenone, 28569-63-3; *cis*-1-[1-[(trimethylsilyl)oxy]cyclopropyl]-3,3a,4,5,6,6a-hexahydropentalene, 91239-17-7.

Supplementary Material Available: Characterization data for **4**, **5**, **8**, **11**, **12**, **14**, **17**, and **18** (3 pages). Ordering information is given on any current masthead page.

(11) Trost, B. M.; Bogdanowicz, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 5321.
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(13) Brook, M. A.; Chan, T. H. *Synthesis* **1983**, *201*.

Photoinduced Electron Transfer in *meso*-Triphenyltriptycenylporphyrin–Quinones. Restricting Donor–Acceptor Distances and Orientations

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Received April 9, 1984

Porphyrins possessing covalent linkages to quinones have become increasingly important in the study of photoinduced electron-transfer reactions.[1] Most of these models possess flexible linkages

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