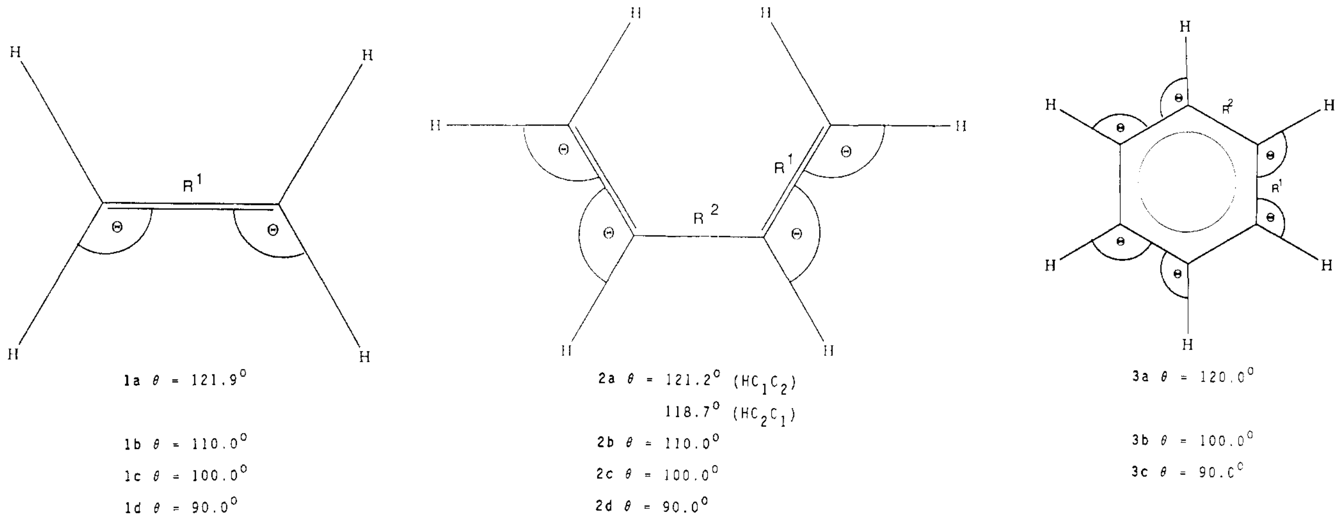

Figure 1. Bond angles used in the calculations of 1–3.

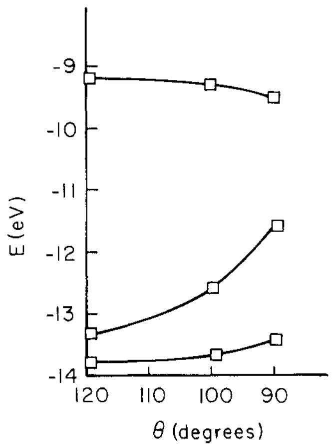

Figure 2. The changes in the energies of the HOMO (top curve), HOMO-1 (center curve), and HOMO-2 (bottom curve) in **3a–c**.

interactions and mixing of the C_{2s} orbital due to rehybridization) but destabilized for larger deviations from the optimal θ value.

How does the same distortion affect benzene? The geometry and energy change in a fashion that is analogous to that observed for **1** and **2** (Table I). Thus, as θ deviates from 120°, R^1 lengthens, R^2 shortens, and the total energy is raised substantially. The molecular orbitals, however, behave very differently when compared to those in **1** and **2** (Table II, Figure 2). The doubly degenerate HOMO's (which are of π type) lower in energy when going from **3a** to **3b** and **3c**, by 2.1 and 6.8 kcal mol^{-1}, respectively. The other occupied π orbital (HOMO-2) is destabilized by about the same respective amount (2.4 and 9.1 kcal mol^{-1}, see Table II). Therefore, although the total energy is raised by 145.8 kcal mol^{-1} along the series, *the π energy is lowered by 4.5 kcal mol^{-1}*. On the other hand, HOMO-1, a doubly degenerate σ orbital is substantially destabilized (16.6 and 40.1 kcal mol^{-1}, respectively) during this procedure, acting as if it were the HOMO according to Walsh's postulate.[17]

The structure of **3c** was optimized also at the HF/6-31G* and MP2/3-21G levels of theory. The results (Table III) indicate that the observed bond alternation is not an artefact of an inflexible basis set or insufficient correlation interaction.

In summary, our results are in agreement with Shaik's understanding of the system, which regards a symmetrical π structure as being imposed by the σ frame. In addition, the much discussed Mills–Nixon effect[18] is confirmed by these calculations, implying that the bond fixation present in the central ring of the angular phenylenes must originate, at least partly, from the bond-angle distortion imposed by the attached four-membered rings.

Acknowledgment. We thank Professor Y. Apeloig for helpful discussions and the National Institutes of Health (Grant CA-20713) and the National Science Foundation (through the SDSC CRAY facility) for financial support. A.S. is a Dr. Chaim Weizmann postdoctoral fellow (1985–1987).

Registry No. 1, 74-85-1; 2, 106-99-0; 3, 71-43-2.

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Received April 19, 1988

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[17] At the suggestion of a referee, similar calculations were carried out (MNDO) on benzene, freezing the CC bonds lengths. As might be expected, the relevant orbital changes corresponding to those in Table II are much smaller, HOMO and HOMO-2 staying practically invariant, HOMO-1 increasing in energy by increments that are about half of those in Table II.

[18] See: Hiberty, P. C.; Ohanessian, G.; Delbecq, F. *J. Am. Chem. Soc.* 1985, *107*, 3095 and references therein.

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Accelerating Effect of a Remote Cationic Center on the Cope Rearrangement. Evidence of σ-Participation by a Norbornane C–C Bond in a Novel Tetracyclic Framework[†]

Summary: The first observation of acceleration of [3,3]-sigmatropic (Cope) rearrangement, by a remote cationic center, in a novel tetracyclic framework embodying a norbornyl moiety, is described.

[†] Dedicated with respect and affection to Prof. M. V. George on his 60th birthday.

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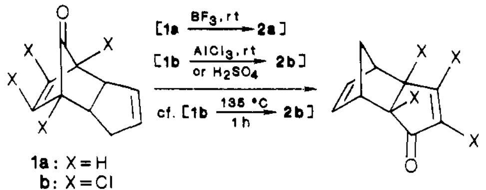
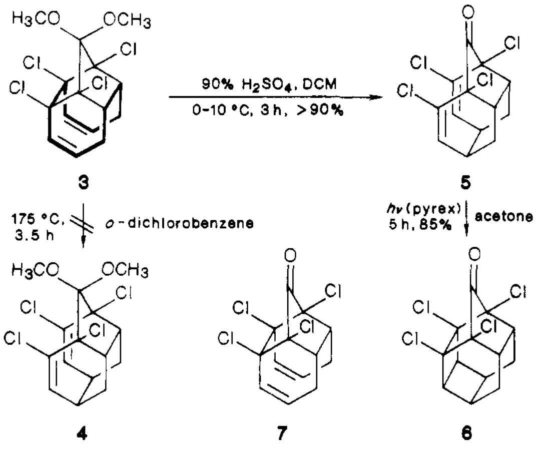
Sir: In 1960, Yates[1a] and Cookson[1b] were the first to observe the acceleration of Cope rearrangement **1a,b** → **2a,b** under the influence of protic and Lewis acids. Subsequently, several examples have been reported[1c,d] wherein a cationic center attached to the 1,5-diene unit of the Cope system catalyzes the reaction through the mutual delocalization of the charge and the six electrons of the Cope transition state (Scheme I). Herein, we wish to record the first observation of the accelerating effect of a cationic center, remote from the Cope system, on the rate of rearrangement. More significantly, such an effect originates through the participation of a norbornyl σ-bond.



1a: X = H
b: X = Cl

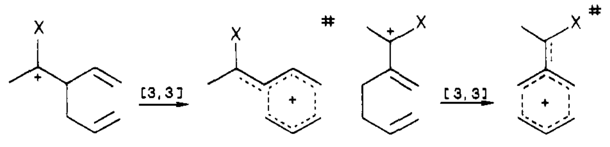
2a: X = H
b: X = Cl

In connection with a synthetic objective, we recently described[2] the synthesis of a novel, tetracyclic compound **3**, in which endo positions C_2–C_6 and C_3–C_5 of the norbornane moiety present in it are locked through two symmetrical 3-carbon (propenyl)bridges. The resulting *cis,-cis*-1,5-cyclodecadiene ring (heavy line) in **3** is firmly constrained in a boatlike geometry for a facile [3,3]-sigmatropic rearrangement to **4**, a compound of intrinsic synthetic interest to us. However, tetracycle **3** proved to be passive to thermal activation and was recovered unchanged (~95%) when subjected to standard Cope rearrangement regimen (175 °C, 4 h, *o*-dichlorobenzene).[3] But, exposure of **3** to 90% H_2SO_4 (0–10 °C, 3 h), conditions routinely employed for the deprotection of α-halogenated 7-oxonorbornane acetals,[2,4] led to its conversion to the rearranged tetracyclic ketone **5**[5] in near quantitative yield. During this reaction, neither the anticipated deacetalized ketone **7** nor the rearranged acetal **4** could be detected. The structure of rearranged ketone **5** was further secured through its intramolecular (2 + 2)-photocycloaddition to the known hexacyclic ketone **6**.[2]



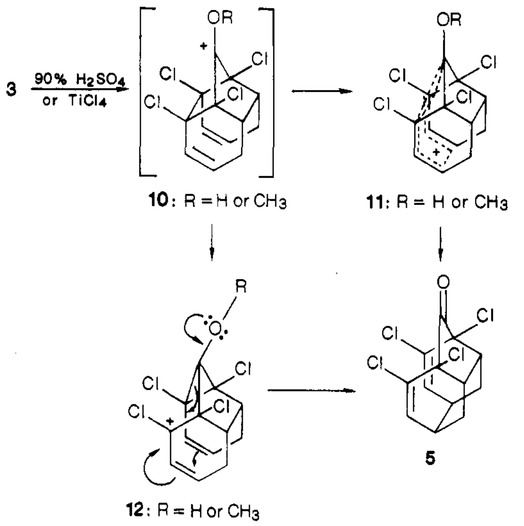
Reaction of **3** with Lewis acids was also investigated. When exposed to $TiCl_4$ or BF_3–etherate in dichloromethane under ambient conditions (28 °C, 6 h, ~80%), **3** underwent acetal cleavage and rearrangement to **5**. This response of acetal **3** to $TiCl_4$ is in marked contrast with that of related polycyclic acetals **8a**[4c] and **9a**,[2] which under identical conditions do not furnish the carbonyl compounds but lead to **8b**[5] and **9b**,[5] respectively, in high yield.

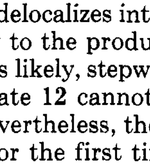
Scheme I^a



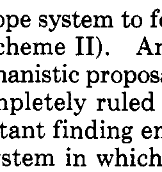
^a X = H, C, O, etc.

Scheme II





8a: R = R_1 = OCH_3
b: R = OCH_3; R_1=Cl



9a: R = R_1 = OCH_3
b: R = OCH_3; R_1 =Cl

The striking acceleration of the **3** → **5** rearrangement by protic and Lewis acids can be explained through the initial rate-determining formation of the oxacarbonium ion **10**, which delocalizes into the Cope system to form the ion **11** on way to the product **5** (Scheme II). An alternate, though less likely, stepwise mechanistic proposal involving intermediate **12** cannot be completely ruled out at this stage. Nevertheless, the important finding emerges that we have for the first time a system in which the 7-norbornyl cation moiety present in **10** elicits definite response

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(5) All new compounds were characterized on the basis of their spectral and microanalytical data. Compound **5**: mp 250–1 °C dec; IR (KBr) 3050, 1760, 1620, 730 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 6.0–5.84 (2 H, m), 3.36–3.16 (4 H, m), 1.85 (4 H, AB q with st, J_{AB} = 10 Hz). On storage and in DMSO, **5** readily forms a hydrate: ^1H NMR (100 MHz, DMSO-d_6) δ 6.24–6.1 (2 H, m), 3.34 (4 H, s), 1.88 (4 H, AB q, J_{AB} = 12 Hz); ^{13}C NMR (25.0 MHz, DMSO-d_6) δ 143.1, 133.6, 108.8, 68.7, 32.4, 22.6, 19.7. **8b**: mp >240 °C; IR (KBr) 2950, 1440, 1210, 730 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 3.8 (3 H, s), 3.05 (2 H, br s), 2.92 (2 H, br s), 1.94 (4 H, br s), 1.8 (4 H, br s). **9b**: mp 228–31 °C; IR (KBr) 3050, 1210, 740 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 6.2–5.8 (4 H, m), 3.82 (3 H, s), 3.72–3.6 (2 H, m), 3.52–3.4 (2 H, m). The stereochemistry of **8b** and **9b** should be regarded as tentative.

from the C_2–C_3 σ-bond. Further experiments are planned to adduce support for this unusual observation.

Acknowledgment. We thank University Grants Commission, New Delhi, for support under the Special Assistance Programme and COSIST programme. One of us (S.P.) thanks CSIR for a research fellowship.

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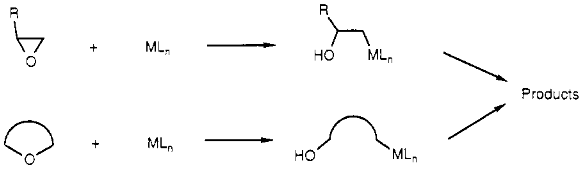
Regioselective Opening of Epoxides and Ethers by (Trialkylsilyl)manganese Pentacarbonyl Complexes. A General Strategy for the Synthesis of Spiroketal Lactone and Cyclopentenone Derivatives

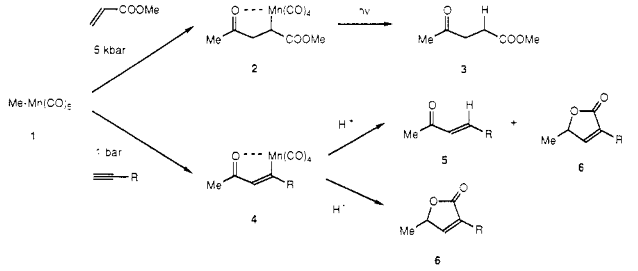
Summary: (Trialkylsilyl)manganese pentacarbonyl reagents react with epoxides and cyclic ethers in a regioselective manner to furnish functionalized alkylmanganese pentacarbonyl complexes. These complexes undergo subsequent sequential insertion with either alkenes or alkynes to afford manganacycles. Photodemetalation of the alkene-derived manganacycles give either aldol-like products or spiroketal lactone derivatives. Acid-catalyzed demetalation of alkyne adducts affords cyclopentenone derivatives by a Nazarov cyclization sequence.

Sir: Preparation of functionalized organotransition metal complexes remains as one of the major hurdles to the application of transition metal based reagents for organic synthesis.[1] On the other hand, a myriad of methods are available in the organic arsenal for the stereoselective synthesis of epoxides,[2] and epoxides should be ideal substrates for the synthesis of transition metal reagents if effective ring cleavage strategies could be effected. As outlined in Scheme I, the nucleophilic opening of an epoxide by a nucleophilic metal complex to afford a β-alkoxy complex should be a viable method of producing functionalized organotransition metal complexes for further elaboration in organic synthesis. In addition, this strategy could be extended to cyclic ethers with the expectation that regioselective ring scission would yield novel complexes poised to serve as intermediates in a wide variety of subsequent transformations (see Scheme I).

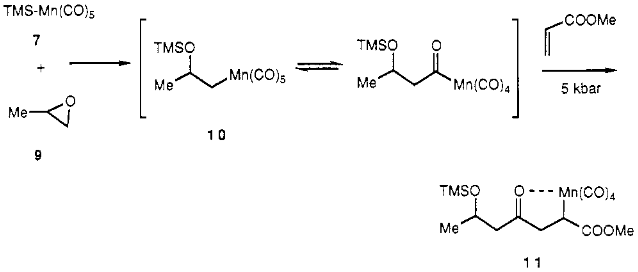
Scheme I



Scheme II



Scheme III



Our laboratory has recently demonstrated that alkylmanganese pentacarbonyl complexes (1) undergo sequential insertion reactions with either alkenes or alkynes to furnish unique manganese complexes (manganacycles) 2 and 4, respectively (Scheme II). Photoinitiated demetalation of manganacycle 2 gave the 1,4-dicarbonyl derivative 3, whereas manganacycle 4 underwent demetalation to afford either enone 5 or butenolide 6, depending upon the specific demetalation conditions employed.[3]

A previous investigation by Gladysz had shown that TMS complex 7 reacted with epoxides and ethers to yield the corresponding (silyloxy)manganese derivatives; however, subsequent reactions of these complexes were not reported.[4,5] In this paper we report that epoxides and cyclic ethers react with (trimethylsilyl)manganese pentacarbonyl (7) or (*tert*-butyldimethylsilyl)manganese pentacarbonyl (8) to afford [(silyloxy)alkyl]manganese complexes, which are competent in the sequential insertion reactions indicated in Scheme II and furnish functionalized manganacycle derivatives. Subsequent transformations of these manganacycles lead to the production of β-hydroxycarbonyl, spiroketal lactone, and cyclopentenone derivatives.

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