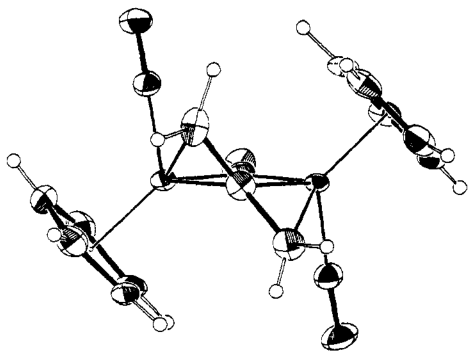
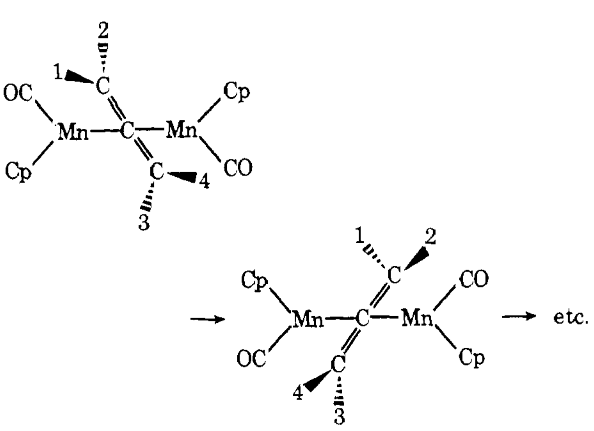


Figure 1. Molecular structure of $(C_5H_5)_2Mn_2(CO)_3(\mu\text{-}\eta^3\text{-}C_3H_4)$. Structural parameters: Mn-CO, 1.775 (5) (terminal); 1.972 (5) (bridge); Mn-CH$_2$, 2.173 (5); Mn-C (allene), 1.976 (5); C-C (allene), 1.393 (8); Mn-Mn, 2.691 (2) Å.

metrical carbonyl bridge between two manganese atoms. The AA′BB′ pattern evident[8] in the ^{1}H NMR spectrum of the allene bridge is due to protons proximal and distal with respect to the Mn—Mn bond. Compound VI, like $Cp_2Mo_2(CO)_4(\mu\text{-}\eta^3\text{-}C_3H_4)$,[10] is thus relatively rigid with respect to the fluxional process shown in eq 4 (μ-CO omitted), presumably because



(4)

the plausible transition state involves major disruption of metal-allene bonding.

This report represents the first synthesis of an allene within the metal coordination sphere. Among synthetic routes to allenes, the formation of a carbon-carbon multiple bond in one step finds precedent only in the Wittig synthesis of allenes from $R_2C{=}C{=}PPh_3$ and OCR'_2. The source (i.e., CO or CH_3I) and ultimate location of the added carbon and hydrogen in VI are currently under investigation as essential preliminaries to any mechanistic proposal for this unusual transformation.

Acknowledgment. This work was supported by the National Science Foundation (CHE 77-10059) and the M. H. Wrubel Computing Center. Mass spectra were recorded at the Michigan State University Mass Spectrometry Facility and $CpMn(CO)_3$ was a gift from the Ethyl Corporation.

Supplementary Material Available: A list of atomic coordinates and thermal parameters for $(C_5H_5)_2Mn_2(CO)_3C_3H_4$ (1 page). Ordering information is given on any current masthead page.

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(3) Addition of HSO_3CF_3 to a benzene solution of I precipitates the corresponding fluorosulfonate salt. This compound, in THF, shows infrared bands at ν 1990 (s, br) and 1980 (sh) cm^{-1}.

(4) Treatment of Ia with excess CF_3CO_2D yields IIa-d_1 in which the intensity of the δ 4.45 resonance decreases over a period of 1 h owing to multiple deuteration. This establishes the time scale of proton transfer from IIa to $CF_3CO_2^-$.

(5) Synthesized from propyne and characterized by mass, (ν_{CO} 1978 (m), 1951 (s), 1925 (s)), and ^{1}H NMR spectroscopy (δ 4.69 (Cp), 4.64 (Cp), 7.02 (CH, q, J = 7 Hz), 2.27 (CH$_3$, d, J = 7 Hz), all in CD_2Cl_2).

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(7) Addition of 2 equiv of $LiEt_3BH$ at 0–20 °C results in the appearance of carbonyl stretching bands at ν 1920, 1878, 1855, 1828, and 1610 cm^{-1}.

(8) The mass spectrum shows this parent ion as well as fragments formed by loss of CO and C_3H_4. IR (hexane): 1910 (s), 1760 cm^{-1}. ^{1}H NMR (C_6D_6): δ 3.70 (Cp, 10 H), 3.79 (=CH, 2 H, "triplet" with a 2-Hz spacing), 2.71 (=CH, 2 H, 2-Hz "triplet").

(9) Crystallographic data (−176 °C): a = 13.253 (5) Å, b = 15.768 (7) Å, c = 7.376 (3) Å, cos β = −0.4352 (3) °, V = 1387 Å^3, Z = 4, in space group $P2_1/a$; $R(F)$ = 0.0547, $R_w(F)$ = 0.0773 for 2316 observed ($F_o^2 > \sigma(F_o^2)$) reflections using anisotropic thermal parameters for all nonhydrogen atoms; all hydrogen atoms were refined isotropically.

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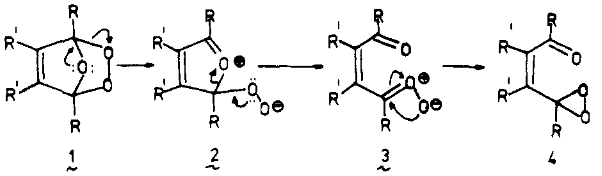
Received August 8, 1979

Oxygen Atom Transfer by Furan Endoperoxides[1]

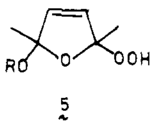
Sir:

A recent communication[2] that carbonyl oxides of nonozonolytic origin can epoxidize olefins prompts us to report our own observations that furan endoperoxides **1** are capable of oxidizing (a) tetramethylethylene to its epoxide, (b) diphenyl sulfide to its sulfoxide, and (c) adamantanone to its lactone. We suspected that the oxygen-atom-transferring species was either the unusual carbonyl oxide **3** or the novel dioxirane **4**, both thought to be derived from the dipolar species **2** by ring opening of the endoperoxide **1** (eq 1). A similar mechanism has been suggested for the singlet oxygenation of tetraphenylpyrrole.[3]



(1)

This attractive mechanistic hypothesis, if experimentally verifiable, would permit rationalization of a number of apparently isolated, but related, facts concerning the chemical behavior of furan endoperoxides. A few of these include the formation of (i) alkoxy hydroperoxides **5**[4] in alcoholic solvents,



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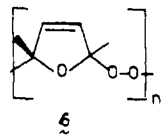

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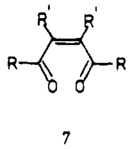

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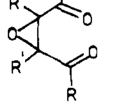

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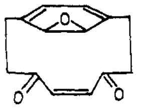

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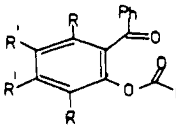

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(ii) polymer **6**[5] in aprotic, polar solvents such as CH_3CN, (iii) 1,2-diacylethylenes **7**[5,6] on thermolysis in nonprotic, nonpolar solvents, (iv) epoxides **8**[7] and **9**[8] in the thermal decomposition, and (v) keto ester **10**[9] on heating of the corresponding furan endoperoxide. Thus, facts i and ii bespeak the interception of the dipolar species **2,** fact iii suggests that the "missing oxygen

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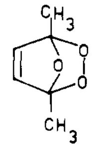
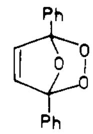
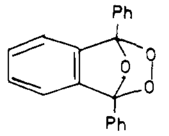
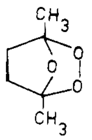
Table I. Yields and Reaction Conditions for Oxygen Atom Transfer

endoperoxide	temp, °C	time, h	epoxide,[a] %	$Ph_2S{=}O$,[b] %
 **1a**	29	12	20.3 ± 0.3	10.9 ± 0.7
 **1b**	29	12	41 ± 3	37 ± 3
 **1c**	60[c]	1	32 ± 0.4	59.5 ± 0.5
 **1d**	60–70	4	93 ± 2	69.6 ± 0.4

[a] Determined on a 6 ft × 1/8 in. stainless steel column packed with 20% Carbowax M on Chromosorb W and operated at a column temperature of 70 °C. [b] Determined on a 6 ft × 1/8 in. stainless steel column packed with 10% SE-30 and operated at a column temperature of 220 °C. [c] In benzene; all others in chloroform.

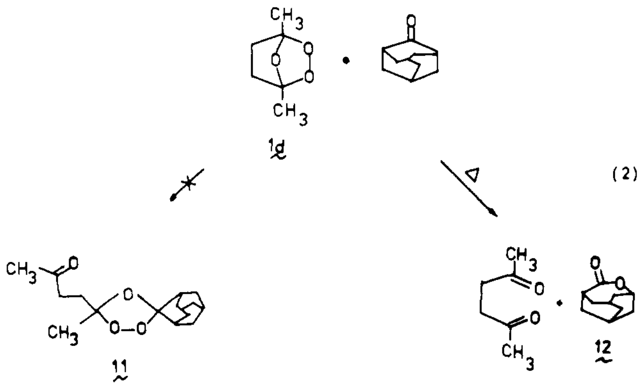
atom" must have been transferred to a suitable acceptor (epoxidation), and facts iv and v imply the intervention of the carbonyl oxide **3** and/or dioxirane **4.**

The furan endoperoxides **1a–d** were made in Freon ($CFCl_3$) at −78 °C by tetraphenylporphyrin-sensitized singlet oxygenation of the respective furans (1.0 mmol) as described previously.[10] After completion of photooxygenation (~2 h), as monitored by ^1H NMR, a solution of either tetramethylethylene (50 mmol) or diphenyl sulfide (10 mmol) in 5 mL of $CFCl_3$ was added at −78 °C and the mixture magnetically stirred while being allowed to warm to the desired temperature. When all endoperoxide **1** had been consumed, as monitored by ^1H NMR, the reaction mixture was analyzed by VPC for tetramethylethylene oxide or diphenyl sulfoxide products. The results are summarized in Table I. The epoxide and sulfoxide were isolated and characterized by comparison of their IR and ^1H NMR spectra with those of the authentic materials.

Control experiments showed that no oxygen atom transfer took place to tetramethylethylene or diphenyl sulfide below 0 °C for **1a–c** and at room temperature for **1d.** In other words, there is no significant direct nucleophilic attack of the oxygen atom acceptor on the endoperoxides. In the case of endoperoxides **1a** and **1b,** we could confirm that the respective epoxides of the 1,2-diacylethylenes **7** were formed in the absence of the oxygen atom acceptor. This, at least in part, explains the much higher yields of tetramethylethylene oxide and diphenyl sulfoxide from the saturated furan endoperoxide **1d.**

Our preliminary results demonstrate that furan endoperoxides **1** are effective oxygen atom donors to suitable acceptors such as olefins and sulfides. However, these results do not sort out whether the intermediary oxidant is the unusual carbonyl oxide **3** or the novel dioxirane **4.** For example, the epoxidizing power of carbonyl oxides is well established,[2] but dioxiranes exhibit similar reactivity, as confirmed in the ketone-catalyzed stereospecific epoxidation of *cis*- and *trans*-cinnamic acid by peroxomonosulfate[12] in which dioxiranes are proposed as reaction intermediates. For this reason we undertook trapping experiments to differentiate between these two mechanistic alternatives especially since it is well established that carbonyl oxides can be captured by reactive carbonyl groups to produce ozonides.[13]

When the endoperoxide **1d** was allowed to decompose in the presence of an excess of adamantanone, an excellent dipolarophile for ketone oxides,[14] instead of the hoped for ozonide **11,** the lactone **12** was isolated in 29% yield (eq 2). Lactone **12** was identical with the authentic substance prepared by Baeyer–Villiger oxidation of adamantanone. Similarly, benzaldehyde and acetaldehyde were oxidized by the furan endoperoxide **1d** to benzoic and acetic acids, respectively. Thus, the oxygen-atom-transferring species derived from the furan endoperoxides **1** prefer to act as Baeyer–Villiger oxidants rather than undergo cycloaddition with the carbonyl dipolarophiles. Since such Baeyer–Villiger behavior has been observed by Story[15] in the ozonolysis of alkenes when aldehydes or ketones were used as solvents, our results imply that the unusual carbonyl oxide **3** is the oxygen atom donor that is derived from the furan endoperoxides **1.** We are persisting in our trapping experiments of the carbonyl oxides **3** by employing still more reactive dipolarophiles.



(2)

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(16) NIH Career Development Awardee, 1975–1980.
(17) Graduate Fellow in the Support for University Biomedical Education (SUBE) program, sponsored under a NIH-MBS training grant.

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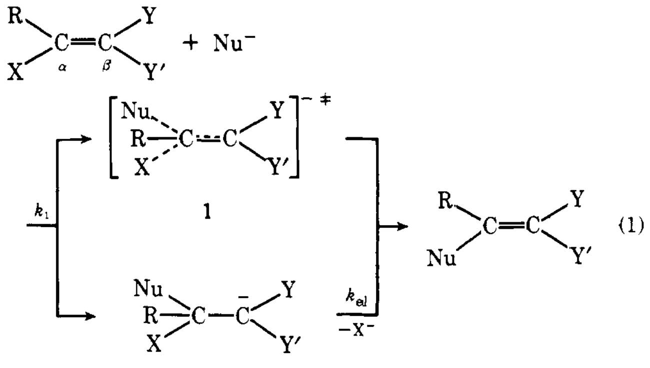
Nucleophilic Attacks on Carbon–Carbon Double Bonds. 26.[1] Stereoconvergence in Nucleophilic Vinylic Substitution of an Activated Nitro Olefin

Sir:

The mechanism of nucleophilic vinylic substitution via addition–elimination[2] continues to be of interest in recent years.[3-6] A main question is whether the substitution is a single-step process with concerted C–Nu bond formation and C–X bond cleavage (transition state **1**) or a multistep process via a carbanionic intermediate **2** when Nu is a negatively charged nucleophile (eq 1) or via a zwitterionic intermediate when Nu is a neutral nucleophile.

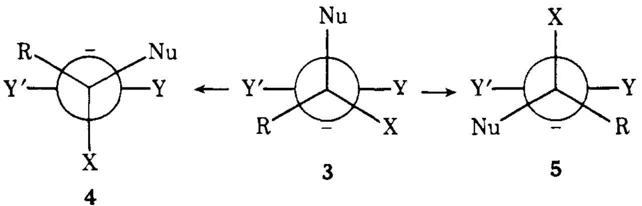


(1)

Y, Y' = activating groups; X = leaving group;
Nu⁻ = nucleophile

When X is a poor leaving group, e.g., F or OR, the evidence for reaction via long-lived carbanions is overwhelming. It includes the isolation of adducts in protic media,[7] stereoconvergence (i.e., formation of the same products from *E* and *Z* precursors),[8] amine catalysis in reaction with amines,[1,9] high $k_{\rm F}/k_{\rm Cl}$ ratios,[8,10] and (*E*)-RX ⇌ *Z*-RX isomerization during the reaction.[11] When X is a good leaving group, e.g., Cl, Br, or I, some authors argue for a single-step process[5,11] based on the preferred or exclusive retention[2-4,6,11] of configuration observed for most (*E*)- and (*Z*)-chloro and bromo olefins as well as on calculations[5b,c] and the reactivity order RBr > RCl > RF found for a small number of unactivated systems.[12] In contrast, the element effects ($k_{\rm Br}/k_{\rm Cl} > 1$, $k_{\rm F}/k_{\rm Cl} \gg 1$),[2,3,8,10,13] the amine catalysis for activated chloro olefins,[9a,13a] the incomplete retention, and the recent calculations which indicate preferred retention for reaction via carbanions[5c,14] argue for a multistep route.

The nucleophilic attack (k_1), the internal rotation in the intermediate or along the reaction coordinate ($k_{\rm rot}$), and leaving group expulsion ($k_{\rm el}$) are concerted in the single-step process. In the multistep process, retention will be observed only if 60° clockwise rotation of the initially formed conformer **3** to give **4** is faster than 120° anticlockwise rotation to give **5** which leads to inversion and if $k_{\rm el} > k_{\rm rot}$, i.e., when **2** is short lived (eq 2). This is likely to occur when most of the charge is localized on C_β, and we therefore predict that, for a highly activated electrophilic olefin, stereoconvergence may be obtained since, for the resulting long-lived carbanion **2**, the condition $k_{\rm rot} > k_{\rm el}$ will be fulfilled.

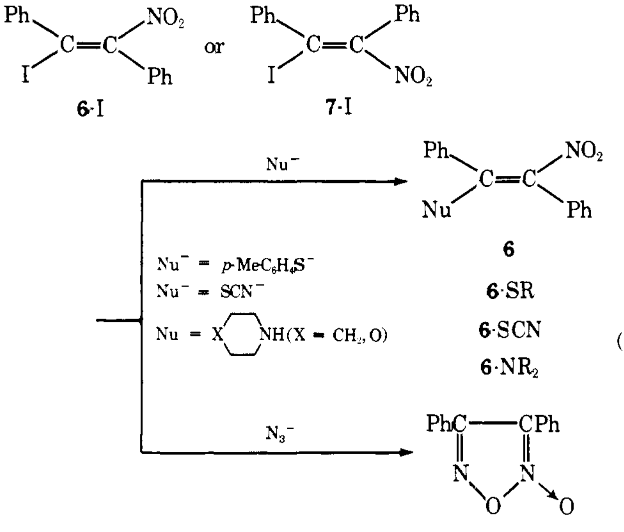


4 **3** **5**

(2)

We chose for study (*E*)- and (*Z*)-α-iodo-β-nitrostilbenes **6**-I and **7**-I,[15] which carry the single most activating nitro group and the fast iodide leaving group but lack hydrogens which may be involved in elimination–addition routes.[2,3]

The reactions of **6**-I and **7**-I with five different nucleophiles are presented in eq 3. The reactions with *p*-toluenethiolate ion in EtOH, with piperidine, morpholine, and SCN⁻ ion in MeCN, and with N_3^- ion in MeOH gave a single, and the same product, from both **6**-I and **7**-I in each case, as shown in Table I.[16] The identity of the products from **6**-I and **7**-I was established by mixture melting point, by the IR spectra, by the identical NMR spectra, and by the retention times on TLC silica plate using 10% acetone–90% petroleum ether. The possibility that the two isomers are obtained in exactly the same ratio from **6**-I and **7**-I seems remote. In all the reactions the observed optical density at infinity under kinetic conditions was identical with the calculated value,[17] even for the reaction of **7**-I with SCN⁻. The yields in the table are lower limits for the stereochemical purity since they are for the isolated material and chromatography gave no indication for the formation of the geometrical isomers. The formation of only a single isomer in each case did not enable an unequivocal structural determination and tentatively we suggest that the products in all the reactions except with N_3^- are the (presumably) more stable *E* isomers **6**. The only product isolated from the reaction with N_3^- is 3,4-diphenylfuroxan (**8**),[18] formed probably via cyclization of the initially formed vinyl azide.



6-I **7**-I

6

6-SR
6-SCN
6-NR₂

8

(3)

The main product from the reaction of SCN⁻ with **7**-I is the vinylic thiocyanate. A second product (mp 85–88 °C; δ ($CDCl_3$) 7.05–7.10 ppm; *m/e* 282 (2%), 178 (50%), 149 (100%)) was isolated in 20% yield. Since it showed no absorption between 2800 and 1600 cm⁻¹, it is not the isomeric **7**-SCN, but may be a cyclization product. This product was not investigated further.

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