cally labile, since our main product, $H_2Ru_4(CO)_{13}$, does not contain hydrocarbon ligands.

The details of the mechanism of the light-induced chemistry are still under study, but for now the principal finding is that catalytic chemistry of olefins can be induced at lower temperatures than needed thermally. Previous studies[6-8] show that $H_4Ru_4(CO)_{12}$ and its substituted derivatives are thermal catalysts for alkene isomerization and hydrogenation, but the temperatures used are at least in the 70–80 °C range; we find no thermal chemistry on the same time scale as our photoreactions at 25 °C. We find an initial *trans-* to *cis*-2-pentene ratio from 1-pentene to be near that found thermally,[6a] and the principal formation of 1-pentene from 1-pentyne and *cis*-2-pentene from 2-pentyne at low extent conversion parallels findings from the thermal catalysis.[6b] Thus, it would appear that the same catalyst is involved thermally and photochemically. Finally, the effect of added CO is to suppress both thermal[6] and photochemical olefin reactions. On these grounds and the photosubstitution chemistry of $H_4Ru_4(CO)_{12}$ we assert that photoinduced ejection of CO is contributory to achieving the catalytically active species, as is proposed in the thermal chemistry.[6] These data do not yet constitute unequivocal proof that the Ru_4 core remains intact during catalysis, since small amounts of very active mononuclear catalysts may yet be present. However, the photosubstitution does take the system a step closer to the catalyst at lower temperatures than ordinarily needed. The $H_4Os_4(CO)_{12}$ photochemistry in the presence of alkenes is clearly related to our work[4] and has led to isolable, apparently inert, Os_4 species that may be the result of CO ejection from $H_4Os_4(CO)_{12}$, but loss of hydrogen also occurs and it is not clear how this happens.

Preliminary results show that $H_2Os_3(CO)_{10}$, $H_3Mn_3(CO)_{12}$, and $H_4Re_4(CO)_{12}$ can also effect stoichiometric reduction of olefins when irradiated at 25 °C. We do not imply that the metal core necessarily remains intact in these instances,[22] but rather we mention these as examples to illustrate that other polynuclear hydrides aside from $H_4Ru_4(CO)_{12}$ yield reactive reducing agents when irradiated.

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(21) $H_2Ru_4(CO)_{13}$ is a known thermal catalyst for 1-pentene isomerization at ~70 °C: Vaglio, G. A.; Osella, D.; Valle, M. *Transition Met. Chem.* **1977**, *2*, 94. We find slow 25 °C, catalytic isomerization that can be accelerated by near-UV irradiation. We detect no thermal conversion to *n*-pentane at 25 °C.

(22) Indeed, recent results show that $H_3Mn_3(CO)_{12}$ is declusterified by light.[16]

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Convenient Method for Regiospecific Carbon–Carbon Bond Formation at the γ Position of Allylic Halides

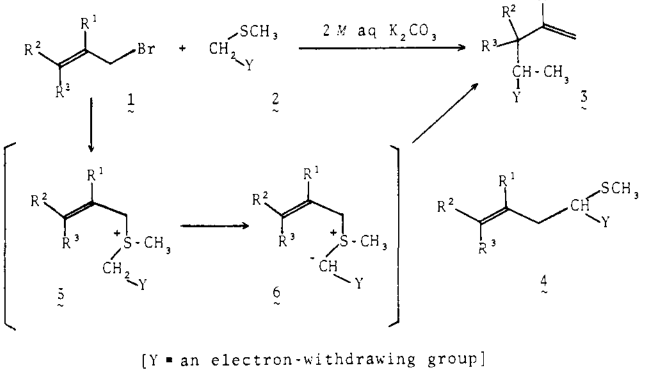
Sir:

We here disclose a new synthetic reaction for the regiospecific formation of a carbon–carbon bond at the γ position of an allylic bromide (**1**). The method simply involves stirring **1** and the α-methylthio ketone (**2**, Y = COR) in the presence of 2 M aqueous K_2CO_3 to give exclusively a substitution product (**3**, Y = COR) of the S_N2' type without contamination of any of its regioisomers (**4**, Y = COR) (Scheme I).

A typical procedure is as follows. To a mixture of 1 equiv of **2** and 1.6 equiv of **1** was added 2 equiv of 2 M aqueous K_2CO_3. This mixture was stirred for several days (see Table I) and extracted with CH_2Cl_2; the dried extract was evaporated; and the residue was column chromatographed (silica gel) or distilled to provide **3**.[1,3] It is noteworthy that, in every case, **4** was not detected by an NMR analysis of the reaction mixture.[4] The yields of **3** obtained by the reaction of (methylthio)acetone (**2**, Y = $COCH_3$) and ω-(methylthio)acetophenone (**2**, Y = COPh) with a variety of allylic bromides are shown in Table I.

For the present reaction, the mechanism involving nucleophilic attack of the carbanion of **2** on the γ position of **1** seems unfeasible by the following reasons: (i) The acidity of **2** is too low to be deprotonated by K_2CO_3; (ii) even if the carbanion

Scheme I



[Y = an electron-withdrawing group]

Table I. Yields of **3**[a,b]

R^1	R^2	R^3	% yield Y = COPh[c]	COCH$_3$[c]	CONH$_2$	COOEt	SOCH$_3$[c]	$CH_2(SPh)COCH_3$
H	H	H	69 (3)	63 (4)	36 (3)[d]		69–93 (2–4.5)	21 (7)
H	CH$_3$	H	94 (2)	82 (2)	95 (2)		47–62 (2–4)	57 (2)
CH$_3$	H	H	78 (11)	71 (9.5)	45 (5)[d]		63–75 (3–5.5)	
H	n-C$_4$H$_9$	H	89 (5)	56 (6)	64 (6)[d]	78 (3)[e]	52 (9)	
-(CH$_2$)$_4$-		H	89 (5)	66 (4)	92 (2)	83 (3)[e,f]	39 (4)	58 (7)
H	CH$_3$	CH$_3$	96 (2)	90 (3)	67 (2)[g]	91 (5)[e]	0 (5)	

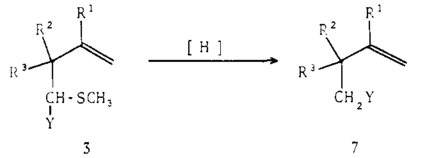
[a] By stirring 1 equiv of **2** and 1.6 equiv of **1** in the presence of 2 M aqueous K_2CO_3. [b] The value in the parentheses indicates reaction time (day unit). [c] 3-Bromocyclohexene reacted with **2** (Y = COPh or COCH$_3$) to give the corresponding substitution product in 48 or 68% yield, respectively. However, **2** (Y = SOCH$_3$) did not afford the expected product. [d] The diallylated product was formed. [e] The yields obtained by the reaction of **1** with **2** in the presence of solid potassium carbonate in DMF. [f] The yield was 28% when the reaction was carried out under the similar conditions described in *a*. [g] 93% yield based on the consumed **2** (Y = CONH$_2$).

of **2** would form in an equilibrium state, the regiospecificity shown here cannot be expected because sodiomalonic ester reacts with crotyl halides to give the S_N2-type product exclusively;[5] (iii) it was observed that the sodio derivative of **2** (Y = COPh) prepared by the action of NaH in tetrahydrofuran afforded **3** (Y = COPh) and **4** (Y = COPh) in the ratio of 58:42 (68% total yield).[6]

The reasonable mechanism is outlined in Scheme I. This is a two-phase reaction and initiated by the formation of sulfonium salt (**5**) at the α position of **1** in the organic phase. Then, **5** transports into the aqueous layer (or to the interface) and undergoes deprotonation by K_2CO_3 to afford the corresponding ylide (**6**), followed by the [2.3] sigmatropic rearrangement to yield **3**.[7,8] The mechanism involving the formation of the sulfonium salt (**5**) is in accord with the facts that **3** was also produced in 40–73% yield when ω-(allylthio)acetophenone was stirred along with methyl iodide (3–8 equiv) and 2 M aqueous K_2CO_3 and that (phenylthio)acetone undergoes this type reaction more slowly and in a lower yield (see Table I).[9]

The easy transformation of **5** into **6** with a weak base (e.g., K_2CO_3) seems to be due to the presence of another electron-withdrawing group such as an acyl group. This consideration led us to examine the reaction of **1** with **2** having other electron-withdrawing groups as Y. We have found that **2** having carbamoyl or methylsulfinyl group gave the corresponding **3** in the reaction with **1** under the similar conditions mentioned above. The results are summarized in Table I. When ethyl (methylthio)acetate (**2**, Y = COOEt) was subjected to this reaction, the expected product **3** (Y = COOEt) was obtained in a low yield.[10] This could be overcome by carrying out the reaction in DMF. When **1** and **2** (Y = COOEt) was stirred in DMF in the presence of solid K_2CO_3 at room temperature, a smooth reaction took place and **3** (Y = COOEt) was produced in a high yield.[11] The reaction using **2** (Y = COOEt) can be compared with the ortho-Claisen reaction with respect to the type of products, its regiospecificity, and the convenience of handling.[12] However, the present reaction is much more widely applicable and a variety of products can be obtained.

Finally, we demonstrate that the thus-obtained products are useful for organic syntheses. By reductive desulfurization, **3** can be converted into the compound formulated as **7**. Thus, the treatment of **3** ($R^1 = R^2 = H$; $R^3 = H$ or CH_3; Y = COPh) with sodium methanethiolate in refluxing methanol afforded **7** ($R^1 = R^2 = H$; $R^3 = H$ or CH_3; Y = COPh) in 76 or 78% yield. The pyrolytic distillation of **3** ($R^1 = R^2 = R^3 = H$; Y = SOCH$_3$) under reduced pressure (~20 mm) at 120 °C (bath temperature) gave 1-methylthio-1,3-butadiene (**8**, $R^1 = R^2 = H$), along with dimethyl disulfide and methyl thiomethanesulfonate, and the yield of **8** ($R^1 = R^2 = H$) was calculated by an NMR analysis to be quantitative. A pure sample of **8** ($R^1 = R^2 = H$) was obtained by redistillation [bp 48–57 °C (37 mm), lit.[13] bp 58–59 °C (38 mm)]. Furthermore, the treatment of **3** (R^3 = H; Y = SOCH$_3$) with an acid afforded an α,β-unsaturated aldehyde (**9**) by the hydrolysis of the dithioacetal *S*-oxide with the concomitant migration of the carbon–carbon double bond. Thus, when **3** ($R^1 = R^2 = R^3 = H$; Y = SOCH$_3$) was treated with a small amount of sulfuric acid in ethanol at room temperature for 4 days, 2-butenal was isolated in 79% yield.[14]



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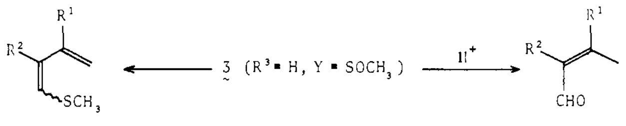

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Supplementary Material Available: Physical data of the new compounds reported herein (12 pages). Ordering information is given on any current masthead page.

References and Notes

(1) It is generally recognized that an allylic halide (**1**) is very labile and rearranged even at room temperature to an equllibrium mixture with a small amount of its regioisomer ($CH_2{=}CR^1CR^2R^3Br$).[2] Therefore we used **1** as the equilibrium mixture in the present experiments. The exclusive formation of **3** indicated that the nucleophilic substitution by **2** proceeded much faster with **1** than with its regioisomer, which was in dynamic equillbrium with 1, to form solely a sulfonium salt **5** (vide infra).

(2) Young, W. G.; Richards, L.; Azorlosa, J. *J. Am. Chem. Soc.* **1939,** *61*, 3070.

(3) All new compounds reported herein were characterized by satisfactory elemental analyses and acceptable spectral (IR and NMR) data.

(4) A GLC analysls also indlcated that the reactlon mixture obtained from 1 ($R^1 = R^3 = H$; $R^2 = CH_3$) and **2** (Y = COPh) contained the corresponding **4** in less <0.5% yleld, even if it existed.

(5) Kepner, R. E.; Winstein, S.; Young, W. G. *J. Am. Chem. Soc.* **1949,** *71*, 115, and the references cited therein.

(6) It was also found that the lithio derivative of **2** (Y = SOCH$_3$) reacted with crotyl bromide in tetrahydrofuran to give **4** ($R^1 = R^3 = H$; $R^2 = CH_3$; Y = SOCH$_3$) and the formation of **3** ($R^1 = R^3 = H$; $R^2 = CH_3$; Y = SOCH$_3$) was not observed by an NMR analysis.

(7) The similar transformations of allylsulfonium methylides were well known. For example, Trost, B. M.; LaRochelle, R. *Tetrahedron Lett.* **1968,** 3327. Bates, R. B.; Feld, D. *Ibid.* **1968, 417**. Blackburn, G. M.; Ollis, W.; Plackett, J. D.; Smith, C.; Sutherland, I. O. *Chem. Commun.* **1968,** 186. Baldwin, J. E.; Hackler, R. W.; Kelly, D. P. *Ibid.* **1968,** 537.

(8) Recently, Reich and his co-worker reported the [2.3] sigmatropic rearrangement of selenium and sulfur ylides In connection with their study on the prenylation of seleno- and thio-substituted ketones: Reich, H. J.; Cohen, M. L. *J. Am. Chem. Soc.* **1979,** *101*, 1307.

(9) In general, it is well known that methylthio group forms the corresponding sulfonium salt more easily than phenylthio group.

(10) The low yield may be ascribed to the partial hydrolysis of the ester group and/or the poor reactivity of **2** (Y = COOEt).

(11) Not only allylic bromides but also allylic chlorides can be used to this reaction. Thus, the reaction of prenyl chloride with **2** (Y = COOEt) in DMF

in the presence of solid K_2CO_3 and a catalytic amount of NaI afforded **3** (R^1 = H, R^2 = R^3 = CH_3; Y = COOEt) in 80% yield.

(12) Johnson, W. S.; Werthemann, L.; Bartlett, W. R.; Brocksom, T. J.; Li, T.-t.; Faulkner, D. J.; Petersen, M. R. *J. Am. Chem. Soc.* **1970,** *92,* 741.

(13) Braun, H.; Mayer, N.; Kresze, G. *Justus Liebigs Ann. Chem.* **1972,** *762,* 111.

(14) This aldehyde was trapped as its 2,4-dinitrophenylhydrazone which was purified by column chromatography on silica gel.

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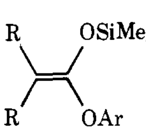
Singlet Oxygenation of Ketene Acetals: Formation of 1,2-Dioxetanes and Their Thermal Rearrangement to α-Peroxy Esters

Sir:

Recently we reported[1] that the photosensitized singlet oxygenation of ketene methyl trimethylsilyl acetals gave the corresponding methyl α-trimethylsilylperoxy esters in high yield. However, when we applied this convenient synthetic utilization of singlet oxygen for the preparation of aryl α-hydroperoxy esters to the corresponding ketene acetals **1**, besides



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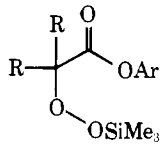

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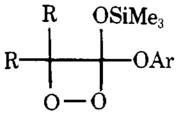

3

the expected α-trimethylsilylperoxy esters **2**, the 1,2-dioxetanes **3** were formed as well.[2] These unexpected results implied the intervention of an intermediate as product branching point in the singlet oxygenation of such electron-rich substrates, a suggestion for which recent evidence has been documented.[3] Still more unusual and mechanistically significant was our observation that the 3-aryloxy-3-trimethylsilyloxy-1,2-dioxetanes **3** rearranged into the α-trimethylsilylperoxy esters **2** on heating. This unprecedented thermal transformation of 1,2-dioxetanes in preserving the peroxide bond is rationalized in terms of heterolytic cleavage of the dioxetane ring at the carbon-oxygen bond leading to a 1,4-dipolar intermediate, which subsequently rearranges via trimethylsilyl migration to afford **2.** The following experimental results substantiate our mechanistic supposition: (i) electron-donating substituents increase while electron-withdrawing substituents decrease the proportion of **3** → **2** rearrangement; (ii) polar solvents enhance rearrangement of dioxetane **3** into α-silylperoxy ester **2** vs. fragmentation into carbonyl products. The experimental results are detailed below.

On tetraphenylporphyrin-sensitized photooxygenation of a 0.05 M solution of *tert*-butylketene phenyl trimethylsilyl acetal (**1a**) in CH_2Cl_2 at −78 °C, irradiating with a 150-W sodium lamp, gave, besides the expected phenyl α-trimethylsilylperoxy-α-*tert*-butylacetate (**2a**) product (characteristic ^1H NMR resonance at δ 4.10 ppm for the α proton), a thermally labile product, exhibiting a characteristic dioxetanyl proton at δ 4.70 ppm. Low-temperature (−78 °C) silylated silica gel chromatography eluting with pentane afforded a 20% yield[4] of the 1,2-dioxetane **3a:** 99% peroxide titer by iodometry; correct elemental composition by combustion analysis; ^1H NMR (CCl_4, Me_4Si) δ (ppm) 0.10 (9 H, s, Me_3Si), 1.15 (9 H, s, *t*-Bu), 4.70 (1 H, s, dioxetanyl), 6.6–7.2 (5 H, m, Ph); no carbonyl absorption in the IR.

Table I. Product Data of the Thermolysis of 1,2-Dioxetanes **3**[a]

dioxetane	solvent	% cleavage[b]	% rearrangement[c]	ratio[d]
3a (H)	C_6H_6	30.4 ± 3.7	69.6 ± 1.0	2.29 ± 0.29
3a (H)	$CDCl_3$	11.8 ± 1.6	88.2 ± 1.0	7.45 ± 0.40
3b (*p*-MeO)	C_6H_6	12.9 ± 1.0	87.0 ± 3.0	6.72 ± 0.23
3c (*p*-Br)	C_6H_6	58.2 ± 4.6	41.8 ± 0.8	0.72 ± 0.10

[a] [3], ~ 0.4 M at 80 °C. [b] *t*-BuCHO product by ^1H NMR integration. [c] α-Silylperoxy esters **2** by ^1H NMR integration. [d] Rearrangement vs. cleavage product ratio for 100% decomposition of the 1,2-dioxetanes **3.**

On heating at 89 °C the dioxetane **3a** decomposed with light emission into the expected *tert*-butylcarboxaldehyde and presumably phenyl trimethylsilyl carbonate (not characterized); however, the major product was the α-peroxy ester **2a** (Table I), isolated by silylated silica gel chromatography at −50 °C and purified by vacuum distillation (bp 75 °C at 0.07 Torr, $n^{25}{}_D$ 1.4735): 99% peroxide titer by iodometry; correct elemental composition by combustion analysis; ^1H NMR (CCl_4, Me_4Si) δ (ppm) 0.25 (9 H, s, Me_3Si), 1.10 (9 H, s, *t*-Bu), 4.10 (1 H, s, α proton), 6.6–7.2 (5 H, m, Ph); 1780 and 1760 cm^{-1} carbonyl bands in the IR (CCl_4). Methanolysis of the α-peroxy ester **2a** or dioxetane **3a** afforded a 79% yield of phenyl α-*tert*-butyl-α-hydroperoxyacetate: mp 91–93 °C (from hexane); >99% peroxide titer by iodometry; correct elemental composition by combustion analysis; ^1H NMR (CCl_4, Me_4Si) δ (ppm) 1.0 (9 H, s, *t*-Bu), 4.40 (1 H, s, α proton), 6.9–7.3 (5 H, m, Ph), 4.70 (1 H, s, OOH); IR (CCl_4) ν (cm^{-1}) 3550–3200 (OOH), 1780 (C=O), 1385 and 1375 (*gem*-dimethyl).

The rearrangement of dioxetane **3a** into α-silylperoxy ester **2a** represents the first example of a peroxide bond preserving transformation of 1,2-dioxetanes. Usually such energy-rich molecules suffer peroxide bond cleavage to afford electronically excited carbonyl fragments on thermal activation.[5] It was, therefore, surprising that the latter event was the minor course in the thermolysis of the 1,2-dioxetane **3a.** The fact that the rearrangement **3a** → **2a** outweighs the usually facile dioxetane cleavage process intrigued us sufficiently to elucidate the mechanism of this unprecedented reaction.

For this purpose we prepared the *p*-methoxy (**3b**) and *p*-bromo (**3c**) derivatives via singlet oxygenation of the respective ketene acetals. Their isolation, purification, and characterization followed the same procedure as outlined for the parent system **3a.**[6] As with the parent system so also these dioxetanes rearrange into the respective α-silylperoxy esters and cleave into *t*-BuCHO, but the relative amounts depend on the electronic nature of the substituent (Table I). For example, the rearrangement *vs.* cleavage product ratio increases with the electron-donating ability of the para substituent on the aryloxy moiety, i.e., *p*-MeO > H > *p*-Br. In fact, a Hammett plot of the product ratio vs. σ gave a negative ρ (−1.94 ± 0.08), indicating buildup of positive charge at the ketal carbon. These results are rationalized in terms of the 1,4-dipolar intermediate **4** shown in Scheme I.

Additional evidence for the unexpected heterolytic ring opening of the 1,2-dioxetane **3** comes from solvent effects. As Table I reveals, for the dioxetane **3a** in the more polar $CDCl_3$ the rearrangement outweighs the cleavage process by ca. threefold compared with benzene. Consequently, a dipolar transition state is being stabilized by the polar solvent. Attempts to use more polar solvents such as CH_3CN, Me_2SO, or DMF (aprotic) and CH_3OH (protic) were thwarted owing to competing and complex side reactions. The trimethylsilyl-1,2-dioxetanes are extremely susceptible to hydrolysis even by adventitious moisture.

Since 1,4-dipolar intermediates, produced by [2 + 2] cy-

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