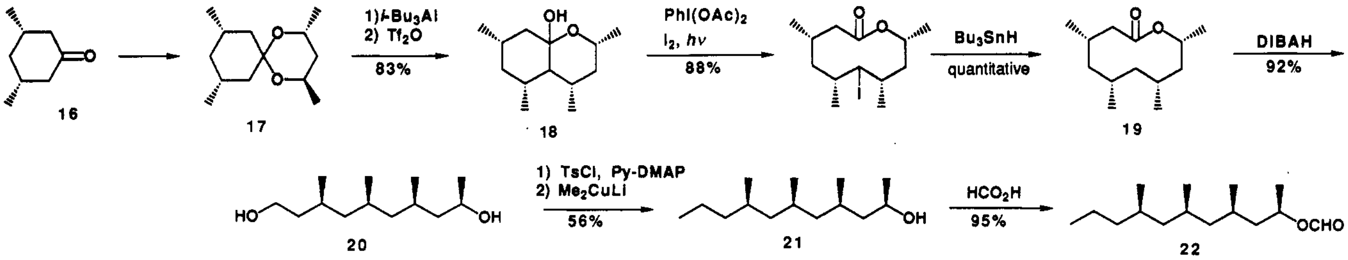
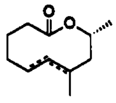
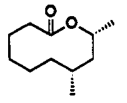
Scheme I



reaction takes place (selectivity: >9:1),[9] thus leading to optically pure hemiacetal after the cyclization process: Addition of triisobutylaluminum to the acetal **8** prepared from prochiral ketone followed by cyclization as above gave hemiacetal **9** (entry 6 of Table I). After one recrystallization of the crude product, all of the chiral centers of the molecule were found to be homogeneous (see also entry 7).

It is presumed that the annulation reaction proceeds through a pure S_N2-like mechanism, namely inversion of stereochemistry at the hydroxy function. Evidence for the complete inversion was obtained upon elimination (with DBU at 90 °C) followed by hydrogenation (Pd/C) from iodo lactone **7**. In this case, it was assumed that hydrogenation should give a mixture of diastereoisomers. Indeed, the crude reaction mixture from hydrogenation of **14** revealed two peaks on GC analysis, while exposure of the iodo lactone with tributyltin hydride–AIBN in THF under reflux furnished quantitatively lactone **15** as a sole product.


14


15

We now demonstrate the effectiveness of this approach starting with simple ketone **16**[10] which can be transformed into (−)-Lardolure (**22**),[11] the aggregation pheromone of the acarid mite, *Lardoglyphus Konoi*, in short steps (Scheme I). Under standard cyclization conditions the hemiacetal **18** was obtained in 83% yeild, mp 78–80 °C, after one recrystallization. Ring opening with iodobenzene diacetate gave the iodo lactone (88%), which was further transformed to lactone **19** quantitatively with tributyltin hydride. Addition of an excess of DIBAH at −78 °C produced the diol **20** (92%). Selective monotosylation (64%; 1.2 equiv of TsCl, pyridine–DMAP at −20 °C) followed by exposure of the monotosylate with excess dimethyl copper lithium in ether gave **21** in 92% yield with the desired carbon framework and desired stereochemistry. Formylation of **21** (95%; formic acid at 65 °C) then led to pheromone **22**,[12] which was identical with the authentic material kindly provided by Professor Kenji Mori.

The synthesis of **22** described herein is straightforward with full stereocontrol. Its brevity stems from the effective dovetailing of new annulation process.

Acknowledgment. A part of this work was financially supported by a Grant-in-Aid for Scientific Study from the Ministry of Education, Science and Culture of the Japanese Government. One of us (K.I.) is also acknowledged for the JSPS Fellowships for Japanese Junior Scientists. We also especially thank Professor Kenji Mori for the authentic sample of (−)-Lardolure.

Supplementary Material Available: Typical procedures and spectral data for new compounds (8 pages). Ordering information in given on any current masthead page.

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(9) Naruse, Y.; Yamamoto, H. *Tetrahedron Lett.* **1986**, *27*, 1363; *Tetrahedron* **1988**, *44*, 6021.

(10) Burman, M. J. F.; Elliott, D. R.; Gordon, M. H.; Robinson, M. J. T. *Tetrahedron Lett.* **1976**, *18*, 1535.

(11) For synthesis of Lardolure, see: Mori, K.; Kuwahara, S. *Tetrahedron* **1986**, *42*, 5539; *Liebigs Ann. Chem.* **1987**, 555. For stereochemistry of Lardolure, see: Mori, K.; Kuwahara, S. *Tetrahedron* **1986**, *42*, 5545.

(12) $[\alpha]^{25}_{D}$ = −3.64° (*c* 7.88, hexane) [lit.[11] $[\alpha]^{23}_{D}$ = −3.4° (*c* 7.86, hexane)]; GC analysis reveals a single peak and identical with an authentic sample;[11] t_R = 66.53 min (OV-101, capillary column at 100 °C), see ref 11.

Photolysis of Alkyl 4-Nitrobenzenesulfenates. A New and Versatile Method for the Generation of Free Radicals

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Summary: The irradiation of alkyl 4-nitrobenzenesulfenates with >300-nm wavelength light in benzene solution results in the homolytic cleavage of the O–S bond. The tertiary alkoxy radicals thus formed undergo β scission to produce carbon-centered free radicals in essentially quantitative yields which react with the arylthiyl radical to produce the alkyl aryl sulfide or dimerize. Primary and secondary alkoxy radicals undergo competitive disproportionation resulting in lower yields of the sulfide product.

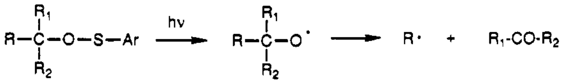
In a study of the regioselectivity of reactions of substituted allyl radicals, it became necessary to find a method for the generation of such radicals in solution from convenient, readily available precursors. The use of peracid and peroxide derivatives and azo compounds did not appear to be an attractive approach due to the difficulty in

Table I. Relative Yields of Products Formed in the Irradiation of the 4-Nitrobenzenesulfenates

sulfenate	sulfide	alcohol	carbonyl compd	dimer
1a	1.00	0.87	0.1-1.2[a]	0.42
1b	1.00	0.87	0.1-1.3[a]	0.60
1c	1.00	-	-	0.42
6a	1.00	1.00	4.8	~0.05[b]
6b	1.00	-	-	-

[a] Yields vary widely. [b] Could not quantitatively determine the amount present.

the preparation of the necessary substituted systems. A potentially attractive route appeared to be the photoinduced homolytic cleavage of the S-O bond of a sulfenate followed by the β scission of the intermediate alkoxy radical (eq 1). A search of the literature revealed only two

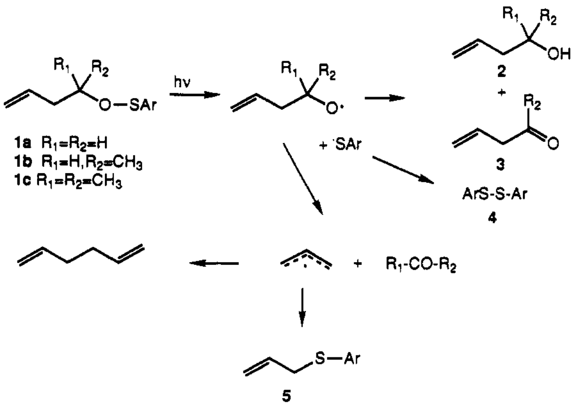


$$R-\overset{R_1}{\underset{R_2}{C}}-O-S-Ar \xrightarrow{hv} R-\overset{R_1}{\underset{R_2}{C}}-O^{\cdot} \longrightarrow R^{\cdot} + R_1\text{-CO-}R_2 \quad (1)$$

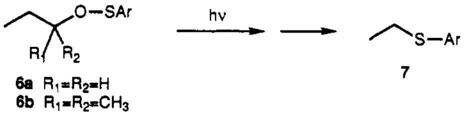
prior reports describing the photolytic cleavage of a sulfenate; one involving the photolytic cleavage of *tert*-butyl methanesulfenate by Kochi and co-workers,[1] the second the photolytic cleavage of a proposed, uncharacterized intermediate formed in the irradiation of a thiochromanone sulfoxide.[2] We report at this time the results of preliminary studies that show that the reaction illustrated in eq 1 is, in fact, an excellent method for the generation of free radicals.

Our initial attempts focused on the photoinduced homolytic cleavage of benzenesulfenates. Alkyl benzenesulfenates undergo photoinduced homolytic cleavage of the S-O bond followed by β scission to produce free radicals as illustrated in eq 1. The benzenesulfenates, however, proved to be somewhat thermally labile, undergoing extensive decomposition on chromatographic purification and on standing, and require light of <300 nm to induce the cleavage of the S-O bond. The 4-nitrobenzenesulfenates are considerably more thermally stable, can be conveniently purified by chromatography on silica gel,[3] and undergo photoinduced S-O bond cleavage by light of >300 nm (λ_{max} of the 4-nitrobenzenesulfenates, ~335 nm).

Irradiation of **1a** in benzene solution,[4] either by a sun lamp or in a Rayonet photochemical reactor, cleanly produces a mixture of the alcohol **2**,[5] carbonyl compound **3**, 1,5-hexadiene, formaldehyde, disulfide **4**,[6] and the allylic sulfide **5**. The relative yields of the products are given in Table I. Irradiation of **1b** produces **2**, **3**, 1,5-hexadiene, acetaldehyde, dissulfide **4**, and allylic sulfide **5**. Irradiation of **1c** produces 1,5-hexadiene, acetone, and **4** and **5** in quantitative yield. In this case the ratio of 1,5-hexadiene to **5** is 30:70.[7]



This procedure works equally well for the generation of saturated alkyl radicals. Irradiation of **6a** produces sulfide **7** and formaldehyde, along with propanol and propanal, and small amounts of butane and disulfide. Irradiation of **6b** cleanly produces only **7** and acetone in essentially quantitative yields.



Continuing investigations are being carried out on the use of this reaction for the generation of substituted allyl radicals and the study of the regioselectivity of their combination reactions and the study of the addition of the allyl and alkyl radicals generated in this photoinduced reaction to substituted alkenes and allenes.

Acknowledgment. This research has been supported by the National Science Foundation, grant no. CHE87-09725.

Supplementary Material Available: ^{1}H and ^{13}C NMR and mass spectra of all new compounds (17 pages). Ordering information is given on any current masthead page.

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[1] Kawamura, T.; Krusic, P. J.; Kochi, J. K. *Tetrahedron Lett.* **1972**, 4075.

[2] Still, I. W. J.; Thomas, M. T. *Tetrahedron Lett.* **1970**, 4225.

[3] The benzene- and 4-nitrobenzenesulfenates are prepared by the reaction of 1 equiv of the alcohol with 1 equiv of benzene- or 4-nitrobenzenesulfenyl chloride in the presence of 2.3 equiv of triethylamine in methylene chloride at -40 °C (Reich, J. H.; Wollowitz, S. *J. Am. Chem. Soc.* **1982**, *104*, 7051). Small amounts of polar side reaction products are formed which can be readily removed from the sulfenate by quick chromatography on silica gel eluting with 3:1 Skelly solve B and methylene chloride. ^{1}H and ^{13}C NMR spectra and high-resolution EIMS have been obtained for all new compounds and are provided in the supplementary material.

[4] Solvents containing easily abstractable hydrogen or chlorine atoms cannot be used; the intermediate alkoxy radicals undergoing more rapid atom abstraction reactions that β scission.

[5] The yield of alcohol **2** varies widely (5-35%) for reasons that are not entirely clear. The relative yields of the other products remain remarkedly constant.

[6] The disulfide **4** precipitates from solution and its yield cannot be quantitatively determined.

[7] The greater tendency for the tertiary alkoxy radical to undergo β scission appears to be due to the more negative $\Delta G°_{(300)}$ for the cleavage of the tertiary alkoxy radical ($R_1 = R_2 = CH_3$, -49.33 kcal mol^{-1}) compared to that for cleavage of the secondary (R_1 = H, $R_2 = CH_3$, -27.68 kcal mol^{-1}) and primary ($R_1 = R_2$ = H, -2.5 kcal mol^{-1}) alkoxy radicals [calculated using group values for ΔH and ΔS of Benson (Benson, S. W. *Thermochemical Kinetics*; John Wiley: New York, 1976)].

Synthetic Studies on Quassinoids: Total Synthesis of (±)-Shinjulactone C

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Summary: The total synthesis of the novel quassinoid Shinjulactone C (**1**) is detailed which proceeds via pentacyclic lactone **3** and features new protocols for elaboration of the ring A 1β-hydroxy-2-oxo-$\Delta^{3,4}$ olefin unit and the C(8), C(11) bridged hemiketal array which are present in **3** and common to numerous quassinoids.

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