yield may drop by as much as 1.5 molecules/100 eV.
(16) Such β-hydrogen abstraction by reduced cadmium cations was, however, suggested: M. Kelm, J. Lilie, and A. Henglein, *J. Chem. Soc., Faraday Trans. 1*, **71**, 1132 (1975); M. Freiberg and D. Meyerstein, *ibid.*, **73**, 622 (1977).
(17) This calculation would predict that ~50% of the radicals will encounter the gold aggregate while 50% combine. The results at high dose rate indicate that, under the present experimental conditions, recombination is no more a competing reaction. Probably $[(Au)_c]$ or the diffusion rate constant are underestimated. As expected from these considerations, a decrease in $[(Au)_c]$ by half hardly affected the yield.

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A Convenient One-Step Synthesis of 2,2-Disubstituted Oxetanes from Ketones

Sir:

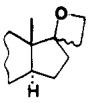
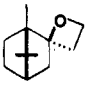
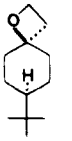
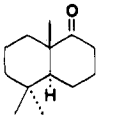
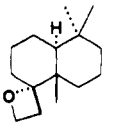
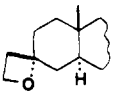
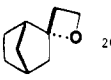
Oxetanes are useful intermediates in organic synthesis which undergo substitution nucleophilic bimolecular ring opening with a variety of good nucleophiles.[1,2] The synthesis and chemistry of oxetanes has been reviewed.[3] The synthesis of 2,2-disubstituted oxetanes from aromatic ketones is accomplished most often by the Paterno-Büchi reaction via a photochemical [2 + 2] cycloaddition reaction.[4] However, the preparation of 2,2-disubstituted oxetanes **4** from aliphatic ketones **1** (Scheme I) normally requires a multistep sequence of reactions employing a Reformatsky reaction ($Zn/BrCH_2CO_2Et$) or Rathke reaction ($LiCH_2CO_2$-*t*-Bu) followed by reduction ($LiAlH_4$), selective esterification (*p*-TsCl or MsCl, pyridine) and base-induced ring closure (NaH or KO-*t*-Bu).[5] Heretofore no simple, straightforward single-step synthesis of oxetanes **4** had been devised or published.

Recently, Johnson and co-workers[6] reported that the sodium anion of dimethyl *N*-(*p*-toluenesulfonyl)sulfoximine (**2**)[7] acts as a nucleophilic methylene-transfer reagent with ketones. According to their general reaction method, depicted in Scheme I, 1.1 equiv of anion **2** are generated by 1.1 equiv of each sodium hydride and the parent sulfoximine[7] in dimethyl sulfoxide (DMSO in Scheme I), followed by the addition of ketone **1** (1 equiv) and stirring at room temperature (20–25 °C) overnight. Under these conditions ketones **1** are smoothly converted into epoxides **3** in good yields. As a matter of fact epoxides **3** with axial carbon-oxygen bonds are formed with a high degree of stereoselectivity in the case of cyclohexanones, both with reagent **2** and with dimethylsulfoxonium methylide in Me_2SO.[8e,9]

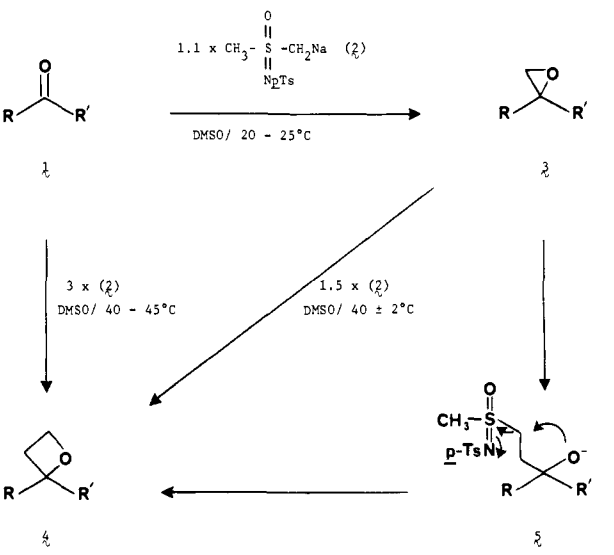
We recently had an occasion to utilize this elegant method on a hindered cyclopentanone intermediate. Estrone 3-methyl ether (**6**) was used as a model for carrying out this methylene-transfer reaction. In an effort to optimize yields, ketone **6** was added to 3 equiv of reagent **2** in Me_2SO and allowed to stir at 45 ± 2 °C for 20 h. After workup and examination of the infrared (IR) and nuclear magnetic resonance (NMR) spectral data of the product, it was apparent that no carbonyl group or epoxide protons were present. However, the NMR spectrum of the product did display a multiplet (overlapping triplets) at δ 4.28 ($-CH_2O-$) and the mass spectrum exhibited a parent ion at M^+/z 312 which is 28 mu greater than the starting ketone. These data, together with the combustion analysis, confirmed the fact that oxetane **6** (actually a 64:36 ratio of β:α C-O bonded diastereomers, respectively; see Table I) was the structure of the product.

Repetition of these experimental conditions with ketones **6**–**20** affords the respective oxetane products cleanly in 46–96% yield (see Table I). Cyclohexanones, such as 4-*tert*-butylcyclohexanone (**8**) and 3-cholestanone (**10**), afford single oxe-

Table I

	Ketone	Oxetane	Reaction time (h)	Conditions temp(°C)	Yields (%) isolated
6 [5g,h]	estrone-3-methyl ether		20	45 ± 2	96
7 [8b]	camphor		16	43 ± 2	59
8 [9]	4-t-butylcyclohexanone		16	40 ± 2	69
9 [8c]			20	45 ± 2	79
10 [9]	3-cholestanone		20	45 ± 2	78
11 [8d]	norcamphor		20	40 ± 2	46
Other Ketones Converted to Oxetanes					
12	bicyclo[3.3.1]non-9-one		20	40 ± 2	68
13 [5d,e]	cyclohexanone		20	40 ± 2	47
14	cycloheptanone		20	45 ± 2	63
15	cyclooctanone		20	45 ± 2	39
16	cyclononanone		20	45 ± 2	65
17	cyclodecanone		20	45 ± 2	61
18	cyclopentadecanone		20	45 ± 2	72
19	2-undecanone		20	45 ± 2	49
20	2-tridecanone		20	45 ± 2	51

Scheme I



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tanes, the stereochemistry of which correlates with observations of Johnson and co-workers in the respective epoxides.[6,9] In fact treatment of the epoxide[9] derived from ketone **8** (prepared via conditions of Johnson and co-workers)[6] with 1.5 equiv of reagent **2** in Me_2SO at 40 ± 2 °C for 20 h affords oxetane **8** in 78% yield, thus confirming the intermediacy of epoxides **3** in the formation of oxetanes **4.** It appears that epoxides **3**[10] are very susceptible to nucleophilic attack and ring opening by excess reagent **2** to intermediates of the type **5** under these reaction conditions. Temperature seems to be of critical importance in the conversion of ketone **8** into the respective oxetane. At 40 ± 2 °C the only product isolated is oxetane **8;** however, at 45 ± 2 °C 2-[4-*tert*-butylcyclohexenyl]ethanol is formed in 17% yield as a side product. Nevertheless oxetanes of the type depicted in structure **4** can now be conveniently prepared by a one-step synthesis from ketones **1** by using 3 equiv of the sodium anion of dimethyl *N*-(*p*-toluenesulfonyl)sulfoximine (**2**) in Me_2SO at 40-45 °C for 16 to 20 h. Further experiments on the synthesis, stereochemistry, and utilization of 2,2-disubstituted oxetanes are in progress.

Acknowledgment. We thank the Robert A. Welch Foundation for the funds (Grants No. E-518) to support this research.

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(8) The anions of dimethyl *N*-(*p*-toluenesulfonyl)sulfoximine and dimethylsufoxonium methylide generally give the same or similar stereochemical results; therefore, the stereochemical assignments of oxetanes **7, 9,** and **11** are made in conjunction with the known or similar stereochemistry of the respective epoxides: (a) Jones, J. B.; Graysham, R. *Chem. Commun.* **1970,** 741-742. (b) Coxon, J. M.; Dansted, E.; Hartshorn, M. P.; Richards, K. E. *Tetrahedron* **1968,** *24,* 1193-1197. (c) Ireland, R. E.; Dawson, M. I.; Kolwalski, C. J.; Lipinski, D. A.; Marshall, D. R.; Tilley, J. W.; Bordner, J.; Trus, B. L. *J. Org. Chem.* **1975,** *40,* 973-990. (d) Bly, R. S.; DuBoise, C. M., Jr.; Konizer, B. *Ibid.* **1968,** *33,* 2188-2193. (e) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965,** *87,* 1353-1364. (f) Carlson, R. G.; Behn, N. S. *J. Org. Chem.* **1967,** *32,* 1363-1367. (g) Cook, C. E.; Corley, R. C.; Wall, M. E. *Ibid.* **1968,** *33,* 2789-2793.
(9) The stereochemistry of oxetanes **8** and **10** are assigned on the basis of the stereochemical assignments of the known or similar epoxides; see ref 6 and 10.
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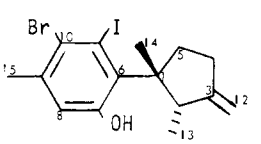
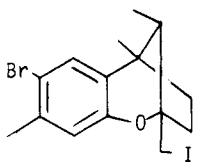
Marine Natural Products. 18. Iodinated Sesquiterpenes from the Red Algal Genus *Laurencia*[1]

Sir:

In recent years a great deal of attention has been focused on the secondary metabolites of marine algae. In particular, the genus *Laurencia* has been found to be a source of bromo and bromochloro nonisoprenoids, sesquiterpenes, and diterpenes.[2] Among these, brominated and nonbrominated aromatic sesquiterpenes have been extensively reported.[3] In this communication we report the isolation of two iodobromo aromatic sesquiterpenes (**1, 2**), the first examples of iodinated sesquiterpenes, and a new compound (**3**) of the laurene type.



(1)



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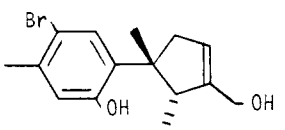
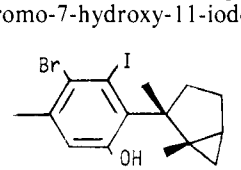


(3)

Laurencia nana Howe, collected at Isla Mujeres, Mexico, was air dried and Soxhlet extracted with dichloromethane. Column chromatography of the crude oil (17.6 g) resulted in the ready identification of filiformin[4] and 10-bromo-7-hydroxylaurene.[4] After storage of the column fractions in hexanes in the freezer, 14 mg of a new metabolite slowly solidified. The ^1H NMR spectrum displayed resonances due to a secondary methyl coupled to an allylic proton, a quaternary methyl, and two exocyclic protons, thus demonstrating a similarity to the ^1H NMR spectrum of the major metabolite, 10-bromo-7-hydroxylaurene. However, the aromatic region of the ^1H NMR spectrum displayed only one resonance and the aromatic methyl resonance was shifted downfield. The infrared and the ultraviolet spectra also supported the idea that this was a hydroxy laurene derivative. Analysis of the low resolution mass spectrum indicated a molecular formula of $C_{15}H_{18}BrIO$ and showed elimination of iodine and iodine + methyl. The ^{13}C NMR spectrum confirmed that the methylenecyclopentane portion was intact and that the iodine was not ortho to the aromatic methyl group.[5,6] Further, comparison with the ^{13}C NMR spectrum of 11-iodolaurinterol[7] (**4**) (see Table I), prepared by iodination of laurinterol using iodine/silver trifluoroacetate in chloroform,[8,9] gave excellent agreement (aromatic ring portion) with the natural compound. Consideration of these data[10] led to the assignment of the structure as that of 10-bromo-7-hydroxy-11-iodolaurene (**1**).



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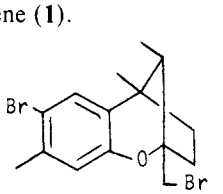

(5)

High performance liquid chromatography (LC) (silica, hexanes) of an early column chromatographic fraction resulted in the isolation of filiformin,[5] α-bromocuparene,[11] bromo ether A (**5**),[12] and a compound whose spectral data were very similar

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