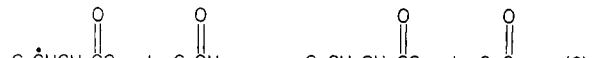
radical formed can add to an olefin, thus leading to branched C_{15} acids or esters as products. These substances were found in trace amounts at all reaction times.

The *tert*-butylperoxy radical was the least reactive and most plentiful radical present in the system.[8] This would make a termination step involving this radical and a heptyl radical a probable reactive pathway, thus accounting for the observed peroxide product. A like termination step involving the *tert*-butoxy radical was not expected since the reactivity of the alkoxy radical would preclude such a step. Consequently, the heptyl *tert*-butyl ether was most likely the result of an S_H2 type reaction.

The heptyl radical was observed to undergo dimerization to yield a trace amount of tetradecane(s).

The olefin, heptene, was not only involved in lower molecular weight products but can be implicated in the higher molecular weight products as well. Heptene can react by the addition of an acyl radical (steps 8 and 9).

(8)



(9)

The resulting ketone (8-pentadecanone) was a minor product at all reaction times but increased slightly as reaction time progressed.

Solvent Products. The major products that were observed from solvent participation are toluene (0.1% at 15 min to 0.3% at 180 min) and *n*-heptylbenzene (0.3% at 15 min to 1.0% at 180 min). No xylenes or other substituted benzenes were found regardless of reaction time.

The yield of toluene was uniformly low at all reaction times. This was in keeping with the low yield of acetone that was observed from the cleavage of *t*-BHP. The methyl radical also arises from this step. The small amounts of methane, ethane, and isomeric methylheptanes would give expectations for low yields of other methyl radical products.

The heptyl radical was generated in greater yield than any other alkyl radical in the system. Consequently, a higher yield was found for *n*-heptylbenzene than for toluene.

Experimental Section

Reagents. *tert*-Butyl hydroperoxide (*t*-BHP) (90%) obtained from Aldrich Chemical Co. was distilled in vacuo to 99.9% purity. Octanal was synthesized and purified likewise to 99+% purity.[12] 1,4-Cyclohexadiene was obtained from Aldrich Chemical Co. and used without further purification.

The benzene solvent (Fisher certified) was refluxed over CaH_2 and distilled.

Method. The reactions were carried out in sealed borosilicate glass tubes. The reagents (typically 0.4 mmol of *t*-BHP and 0.8 mmol of octanal in 0.7 mL of benzene solvent) were weighed into 6-in. long, $^1/_4$-in. o.d. Pyrex tubes closed at one end and fitted at the other with a stainless-steel valve via a Swagelok (teflon ferrules) fitting. The tube was attached to a vacuum system, cooled to −78 °C, and subjected to several freeze–pump–thaw cycles. The tube was then subsequently flame sealed below the valve. The ullage volume (0.30 mL) was kept constant for all runs. The deaerated samples were warmed to room temperature and immersed in a Cole-Parmer fluidized sand bath. The temperature (140 °C) was controlled by a Leeds and Northrup Electromax III temperature controller. The total pressure during each run was estimated to be 5.1 atm. After the reaction period, the sealed tube was cooled to 77 K and opened. The tube was capped and warmed to room temperature, and the internal standards were added. The solution was transferred to a screw cap vial (Teflon capliner) and stored at 0 °C until analysis. Since a typical chromatogram required 60 min, two internal standards were utilized. One, ethyl benzene, afforded quantitation for the peaks with short retention times and a second, 1-phenyldodecane, for the peaks with longer retention times.

Samples were heated for time periods of 15, 30, 60, 120, or 180 min. All tubes were subjected to the same cleaning procedure. They were filled with toluene, cleaned with a nylon brush, rinsed with toluene twice and then with methylene chloride, and dried in air at 150 °C for 8 h. A search of the literature gives a few examples of catalytic behavior with glass systems;[6,13,14] however, when a glass tube was partially filled with crushed Pyrex, thus increasing the surface area, the results at 140 °C for the above time periods were not substantially altered.

The reactions employing the radical scavenger 1,4-cyclohexadiene were run as described except the scavenger was added in 0.05-mmol increments from 0.05 to 0.15 mmol.

The samples were analyzed by two techniques, both based on gas chromatography. Peak identification for both techniques was based on retention time matching with standards and mass spectrometry. In the first, a Varian gas chromatograph Model 3700 with flame ionization detector (FID) and equipped with a 50-m 0.21-mm i.d. wall-coated open tubular (OV-101) fused silica capillary column gave the necessary resolution to distinctly separate the individual components. A 15-m but otherwise identical column was used for octanoic acid analysis. A carrier gas flow of 1 mL/min was combined with an inlet split ratio of 60:1 and a temperature program with an initial hold at 50 °C for 8 min, a ramp of 4 °C/min, and a final temperature of 260 °C.

In the second technique, gases formed during the reaction were analyzed by using a Perkin-Elmer Model Sigma 2 gas chromatograph equipped with a 6 ft. 5A molecular sieve column for CO and CH_4 and a 4 ft. Porapak/S column for CO_2.

In this mode, the column was operated at 55 °C. The chromatogram was recorded and integrated on a Hewlett-Packard Model 3390A reporting integrator. For this procedure, the valve was left on the reaction tube and after the appropriate reaction period the tube valve was connected directly to a GC gas sampling valve via a Swagelok connection. An external standard was used for calibration. A pressure gauge measured the pressure in the sample loop at the time of analysis.

A material balance was assessed for each compound. The principal peaks of the chromatogram account for approximately 88% of the original compounds. The very small peaks account for another 7–8%. The product distribution was repeatable to 2–3% for each component.

Registry No. *t*-BHP, 75-91-2; octanal, 124-13-0.

(12) "Organic Synthesis"; Wiley: New York, 1973; Coll. Vol. V, p 872.

(13) Benson, S. W. *J. Chem. Phys.* **1964**, *40*, 1007.
(14) Kirk, A. D.; Knox, J. H. *Trans. Faraday Soc.* **1960**, *56*, 1296.

An Improved Synthesis of Seven-Membered, Ring-Fused 12-s-Cis Conformationally Locked 11-*cis*-Retinoids

Michael H. Silveira and William H. Okamura*

Department of Chemistry, University of California, Riverside, California 92521

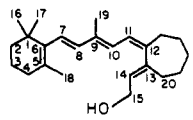
Received December 26, 1984

Retinoids (vitamin A)[1] continue to be substances of interest in a multifarious set of biological processes including those in vision,[2a] energy transduction,[2b] cancer

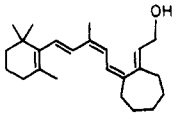
(1) Sporn, M. B.; Roberts, A. B.; Goodman, D. S. "The Retinoids"; Academic Press: New York, 1984; Vol. 1 and 2. For a brief discourse on the problems of retinoid nomenclature, see pages 11–14 and pages 393–412 of Volume 1 of this treatise. For convenience, we have adopted the standard numbering system utilized for retinol as depicted in structure 1 of the text.

0022-3263/85/1950-2390$01.50/0

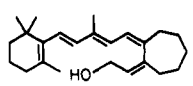
prophylaxis,[2c-f] and the treatment of skin disorders.[2g] Retinoids are also of chemical and spectroscopic interest from the standpoint of their role as model polyene systems.[1] The availability of 12-s-cis-locked retinoids[3] such as 1–4[3b] has provided a means of gaining valuable insight into their electronic spectral characteristics as well as their thermal and photochemical behavior.



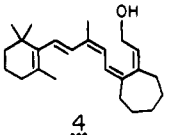
1



2

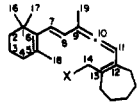


3

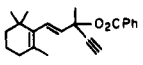


4

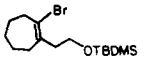
A continuing series of investigations, however, has created a need for an improved synthesis of the sensitive vinylallene[4] precursors to these conformationally locked retinoids.[3] It is the purpose of this paper to describe an operationally more convenient route to the seven-membered, ring-fused systems 1–4,[3b] and it is our supposition that this new route should be generally applicable to other related molecules. In our earlier preparation of 1–4, the key 9,10-allenic retinoid **5a** was obtained by coupling the



5

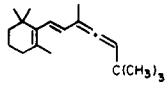


6

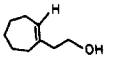


7

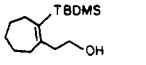
(a, X=$CH_2OTBDMS$; b, X=CH_2OH)



8



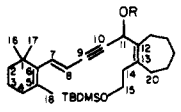
9



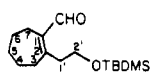
10

benzoate **6** with the vinylcuprate derived from bromo silyl ether **7**.[3b] The capriciousness of this procedure along with the formation of a number of side products such as the allene **8** and the alcohols **9** and **10** prompted the studies leading to the improvements described herein.

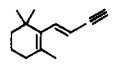
The new route entails the regioselective coupling of a suitable methylcopper species with benzoate **11a** at C-9. The precursors were synthesized as follows. The bromo silyl ether **7** was lithiated with *tert*-butyllithium and quenched with *N,N*-dimethylformamide to give the unsaturated aldehyde **12** which was then condensed with the lithium derivative of dienyne **13**[5] to give alcohol **11b**. The



11



12



13

(a, R=COPh; b, R=H)

latter alcohol was then benzoylated with benzoyl chloride in the presence of pyridine as a base and 4-(dimethylamino)pyridine as a catalyst. The resulting propargylic benzoate **11a** undergoes an S_N2' coupling reaction with CH_3MgBr in the presence of cuprous iodide–lithium bromide as a promoting agent[6] to give 12-s-cis-locked 9,10-allenic retinoid **5a**. Deprotection of **5a** with *n*-Bu_4NF in THF is accompanied by a [1,5]-sigmatropic hydrogen shift to give, after standing at room temperature for an appropriate time interval, a mixture of 1–4. These four 11-*cis*-retinols were identified after preparative HPLC separation by comparing their ^1H NMR data to those of authentic specimens.

The reaction of the methylcopper species with the propargylic benzoate **11a** could have resulted in allylic or propargylic substitution of the S_N2' type at C-13 or C-9, respectively.[7] However, in our case the organocopper reagent prepared by equivalent addition of CH_3MgBr, LiBr, and CuI in THF couples exclusively regioselectivly at C-9 to give the desired 12-s-cis-locked 9,10-allenic retinoid **5a**. This observation should offer a convenient route to other allenic retinoids (e.g., by utilizing variants of aldehyde **12**) needed in our ongoing retinoid structure–activity studies.

Experimental Section

2-[2′-(*tert*-Butyldimethylsiloxy)ethyl]-1-cycloheptenecarboxaldehyde (12). A solution of *tert*-butyllithium (2.03 M in pentane, 3.2 mL, 6.5 mmol) was added dropwise to a cold (−78 °C), stirred solution of the bromo olefin **7** (1.0 g, 3.0 mmol) in dry THF (15 mL) under an atmosphere of nitrogen. The reaction mixture was stirred for 3 h and then DMF (0.66 mL, 9.0 mmol) was added at −78 °C. After being stirred for 2 h at −78 °C, the mixture was quenched with aqueous NH_4Cl solution, allowed to warm to room temperature, and extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated under vacuum. The residual oil was flash chromatographed (silica gel, 85:15 hexanes–ether) to afford 1.66 g (92%) of the aldehyde **12**: ^1H NMR ($CDCl_3$) δ 0.87 (9 H, *tert*-butyl, s), 2.81 (2 H, $H_{1'}$, t, $J \sim 6.5$ Hz), 3.77 (2 H, $H_{2'}$, t, $J \sim 6.5$ Hz), 10.02 (1 H, aldehyde, s); ^{13}C NMR, ($CDCl_3$) δ 190.8, 162.4, 141.6, 60.9, 37.3, 36.5, 32.4, 26.1, 25.8, 25.6, 24.2, 16.2, −5.5; IR (neat film) ν 2750 (m, CHO), 1670 (s, CHO), 1630 (s, C=C) cm^{-1}; MS, exact mass, m/z 282.2019 (calcd for $C_{16}H_{30}O_2Si$, 282.2016); MS, m/z 282 (2, M), 226 (7), 225 (39, M − C_4H_9), 195 (19), 151 (5), 133 (20), 129 (5), 121 (5), 107 (5), 105 (9), 103 (23), 101 (6), 95 (5), 93 (9), 91 (20), 89 (20), 81 (5), 79 (13), 77 (8), 76 (7), 75 (base), 73 (44), 67 (11), 59 (12), 55 (7); ≥5% plus key peak.

(7*E*,12*Z*)-12,20-Tetramethylene-9,10-didehydro-11,14-dihydro-9-demethyl-11-hydroxyretinyl *tert*-Butyldimethylsilyl Ether (11b). A solution of *n*-butyllithium (1.53 M in hexanes, 0.49 mL, 0.75 mmol) was added dropwise to a cold (−78 °C) stirred solution of the dienyne **13** (0.129 g, 0.74 mmol) in anhydrous ether (0.75 mL) under an atmosphere of nitrogen, and the mixture was stirred for 0.5 h. A solution of the aldehyde **12** (0.190 g, 0.67 mmol) in ether (0.75 mL) was then added, and the mixture stirred for 2 h. After the temperature was raised to −45 °C, the reaction

(2) (a) Wald, G. *Science (Washington, D.C.)* **1968**, *162*, 230. (b) Stoeckenius, W. *Sci. Am.* **1975**, 38. (c) Bollag, W. *Cancer Chemother. Rep.* **1971**, *55*, 53. (d) Bollag, W. *Eur. J. Cancer* **1972**, *8*, 689. (e) Sporn, M. B. *Nutr. Rev.* **1977**, *35*, 65. (f) Mayer, H.; Bollag, W.; Hänni, R.; Rüegg, R. *Experientia* **1978**, *34*, 1105. (g) Peck, G. L.; Olsen, T. G.; Yoder, f. W.; Strauss, J. S.; Downing, D.; Pandya, M.; Balkus, D.; Arnand-Baltandier, J. *N. Engl. J. Med.* **1979**, *300*, 329.

(3) (a) Chandraratna, R. A. S; Okamura, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 6114. (b) Chandraratna, R. A. S.; Bayerque, A. L.; Okamura, W. H. *Ibid.* **1983**, *105*, 3588. (c) Chandrarata, R. A. S.; Okamura, W. H. *Tetrahedron Lett.* **1984**, *25*, 1003. (d) Chandraratna, R. A. S.; Birge, R. R.; Okamura, W. H. *Ibid.* **1984**, *25*, 1007.

(4) Besides ref 3, see: (a) Knudsen, C. G.; Carey, S. C.; Okamura, W. H. *J. Am. Chem. Soc.* **1980**, *102*, 6355. (b) Knudsen, C. G.; Chandraratna, R. A. S.; Walkeapää, L. P.; Chauhan, Y. S.; Carey, S. C.; Cooper, T. M.; Birge, R. R.; Okamura, W. H. *Ibid.* **1983**, *105*, 1626. (c) For a review, see: Okamura, W. H. *Acc. Chem. Res.* **1983**, *16*, 81.

(5) Negishi, E.; King, A. O.; Klima, W. L.; Patterson, W.; Silveira, A., Jr. *J. Org. Chem.* **1980**, *45*, 2526.

(6) Macdonald, T. L.; Regan, D. R.; Brinkmeyer, R. S. *J. Org. Chem.* **1980**, *45*, 4740.

(7) (a) Kleijn, H.; Westmijze, H.; Kruithof, K.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 27. (b) Descoins, C.; Henrick, C. A.; Siddall, J. B. *Tetrahedron Lett.* **1972**, 3777.

mixture was stirred for 1 h, quenched with aqueous NH_4Cl solution, allowed to warm to room temperature, and extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated under vacuum to give 0.289 g of residue which could be further purified by reversed-phase HPLC (Whatman Partisil M9 10/50 ODS-2, CH_3CN, 4.0 mL/min). The crude residue was usually directly benzoylated as described in the next section: ^1H NMR ($CDCl_3$) δ 0.06 (6 H, $(CH_3)_2Si$, s), 0.88 (9 H, $(CH_3)_3CSi$, s), 0.98 (6 H, $C_{16,17}$-$2CH_3$, s), 1.68 (C_{18}-CH_3, s), 3.67 (2 H, H_{15}, m), 5.40 (1 H, H_{11}, s), 5.45 (1 H, H_8, d, $J \sim 16.6$ Hz), 6.54 (1 H, H_7, d, $J \sim 16.6$ Hz); ^{13}C NMR ($CDCl_3$) δ 140.8, 138.9, 137.6, 136.9, 131.1, 111.8, 88.8, 84.7, 63.1, 60.9, 39.5, 37.8, 34.7, 33.9, 33.0, 32.6, 29.8, 28.6, 27.4, 26.3, 26.0, 21.5, 19.0, 18.4, -5.5; IR (neat film) ν 3430 (OH, br), 3010 (C=CH), 2230 (C≡C, w), 1470, 1460, 1380, 1360, 1255, 1000, 950, 830 cm^{-1}; exact mass, m/z 438.3321 (calcd for $C_{29}H_{48}O_2Si - H_2O$, 438.3319); MS, m/z 439 (12), 438 (33, M - H_2O), 307 (12), 306 (11), 293 (24), 291 (37), 237 (17), 223 (13), 159 (12), 145 (21), 133 (12), 131 (12), 129 (10), 105 (16) 91 (20), 89 (17), 81 (11), 75 (base) 73 (69), 69 (18), 59 (11), 55 (16); ≳10% plus key peaks.

(7*E*,12*Z*)-12,20-Tetramethylene-9,10-didehydro-11,14-dihydro-9-demethyl-11-(benzoyloxy)retinyl *tert*-Butyldimethylsilyl Ether (11a). A solution of benzoyl chloride (0.095 g, 0.67 mmol) in pyridine (0.24 mL) was added to the crude alcohol **11b** (0.289 g) described above. (Dimethylamino)pyridine (0.010 g) was added, and the reaction mxiture was stirred for 3 h and then extracted with ether. The organic layer was washed with saturated $NaHCO_3$ solution and brine, dried over $MgSO_4$, and evaporated under vacuum. The residual product was subjected to Chromatotron purification (silica gel, 90:10:2, hexanes–ether–pyridine) to afford 0.268 g of the benzoate **11a** in a yield of 71% (based on the aldehyde **12**): ^1H NMR, ($CDCl_3$) δ 0.01 (6 H, $(CH_3)_2Si$, s), 0.81 (9 H, $(CH_3)_3CSi$, s), 0.93 (6 H, $C_{16,17}$-$2CH_3$, s), 1.63 (3 H, C_{18}-CH_3, s), 3.61 (2 H, H_{15}, m), 5.40 (1 H, H_8, d, $J \sim 16.3$ Hz), 6.51 (1 H, H_7, d, $J \sim 16.3$ Hz), 6.58 (1 H, H_{11}, br s), 7.3–7.5 (3H, *m*- and *p*-phenyl, m), 7.99 (2 H, *o*-phenyl, d, $J \sim 7.3$ Hz); IR, (neat film) ν 2930 (s) 2860 (s), 2205 (C≡C, w), 1725 (CO, s), 1605, 1590, 1480, 1460, 1260, 1180 cm^{-1}; exact mass, m/z 438.3313 (calcd for $C_{36}H_{52}O_3Si - C_6H_5COOH$, 438.3319); MS, m/z 439 (8), 438 (21, M - C_6H_5COOH), 307 (10), 306 (22), 304 (6), 293 (13), 292 (6), 291 (26), 237 (9), 181 (6), 179 (8), 159 (6), 147 (7), 145 (15), 143 (6), 133 (8), 122 (19), 77 (12), 75 (base), 73 (11), 56 (7), 55 (7), 44 (11), 43 (6), 41 (21); >5% plus key peaks.

(7*E*)-12,20-Tetramethylene-10,14-*retro*-retinyl *tert*-Butyldimethylsilyl Ether (5a). A solution of CH_3MgBr (2.85 M in ether, 0.46 mL, 1.31 mmol) was added to a well-stirred mixture of LiBr (0.115 g, 1.33 mmol) and CuI (0.253 g, 1.33 mmol) in THF (5.50 mL) at 0 °C, and the solution was stirred for 15 min. The propargylic benzoate **11a** (0.124 g, 0.22 mmol) in THF (1.30 mL) was added dropwise and the reaction mixture stirred for 1 h at 0 °C, quenched with aqueous NH_4Cl, and extracted with ether. The organic layer was washed with aqueous $NaHCO_3$ solution and brine and then dried over $MgSO_4$ and evaporated under vacuum. The residual product was subjected to Chromatotron purification (silica gel, 100:2:2, hexane–ether–pyridine) to give 0.075 g (76%) of the product which had already undergone a considerable amount of rearrangement. This product mixture was normally carried through the next step without further separation.

12,20-Tetramethyleneretinols 1, 2, 3, and 4. A solution of *n*-Bu_4NF (1.0 M in THF, 1.95 mL, 1.95 mmol) was added to partially rearranged vinylallene silyl ether **5a** (0.288 g, 0.65 mmol) from the preceding experiment, and the mixture was stirred under an atmosphere of nitrogen for 2 h. The mixture was then quenched with saturated brine and extracted with ether. The organic layer was washed with saturated $NaHCO_3$ and saturated brine and then dried over anhydrous $MgSO_4$. After concentration under vacuum, the residual product was subjected to Chromatotron purification (silica gel, 2% pyridine/2:2:1 hexane–ether–dichloromethane). Examination of the product at this stage by ^1H NMR and IR indicated that the vinylallene had undergone complete rearrangement to the retinols. The mixture was subjected to preparation HPLC (Whatman Partisil M9 10/50; 15% ethyl acetate/Skellysolve B; 4.0 mL/min) to give a mixture of 11-*cis*-1 and 11-*cis*,13-*cis*-3; 9-*cis*,11-*cis*,13-*cis*-4; and 9-*cis*,11-*cis*-2, respectively. The mixture of 11-*cis*-1 and 11-*cis*-13-*cis*-3, the former eluting first, was separated by HPLC recycling under the same conditions. The four 12,20-tetramethyleneretinols were obtained in the following yields (a 50% mass balance after separation): 11-*cis*-1 (10 mg, 4.5%), 11-*cis*,13-*cis*-3 (26 mg, 12%), 9-*cis*,11-*cis*,13-*cis*-4 (60 mg, 27%), and 9-*cis*,11-*cis*-2 (14 mg, 6.3%).

Acknowledgment. We gratefully acknowledge financial support from the National Institutes of Health (Grant No. EY-02452 and NCI Contract No. CP-05715). We also express our gratitude to BASF (Ludwigshafen) for chemicals.

Registry No. 1, 85236-05-1; 2, 85236-07-3; 3, 85236-09-5; 4, 85236-11-9; 5a, 85236-03-9; 7, 85236-17-5; 11a, 96617-88-8; 11b, 96617-90-2; 12, 96617-89-9; 13, 73395-75-2.

α-^{14}C and ^{34}S Isotope Effects in E2 Reactions of (2-Phenylethyl)dimethylsulfonium Ion[1]

Shune-Long Wu, Ronald T. Hargreaves, and William H. Saunders, Jr.*

Department of Chemistry, University of Rochester, Rochester, New York 14627

Received November 7, 1984

Leaving-group isotope effects have been used by us and by others to probe transition-state structure in bimolecular elimination reactions.[2] The nitrogen isotope effect ($^{14}N/^{15}N$) for the reaction of (2-phenylethyl)trimethylammonium ion with hydroxide ion in Me_2SO–H_2O mixtures at 60 °C changes little as the composition of the solvent changes, ranging from 1.0087 in water to 1.0066 in 57% Me_2SO.[3] The effect essentially levels off above 30% Me_2SO, remaining between 1.0066 and 1.0072 with standard deviations of 0.00001–0.0006. With these results in mind, it is not surprising that the α-^{14}C isotope effect is similarly invariant between 30 and 50% Me_2SO at 1.0269 ± 0.0023.[4] The nitrogen isotope effects correspond to relatively little carbon–nitrogen bond cleavage in the transition state, only 15–20%.[3]

Sulfur isotope effects ($^{32}S/^{34}S$) in E2 reactions of sulfonium salts with hydroxide ion in Me_2SO–H_2O mixtures at 40 °C have been reported to decrease rather precipitously with increasing Me_2SO concentration, from 1.0074 in water to 1.0011 in 20% Me_2SO.[5] In the present paper we report an extension and (in part) correction of these results, as well as ^{14}C isotope effects.

The results are presented in Table I. The earlier result of 1.0011 in 20% Me_2SO[5] is evidently too low, as is probably the result of 1.0038 in 10% Me_2SO,[5] although it was not rechecked. We have no sure reason for the discrepancy, but we point out that the isotopic composition of the original sulfonium salt was determined directly on sulfur dioxide obtained by combustion in the present work, rather than on methyl sulfide obtained by "100%" reaction with base as in the earlier work.[5] Incomplete reaction, or failure to collect all of the "100%" sample of methyl sulfide should lead to a low apparent isotope effect. We also note that

(1) This work was supported by the National Science Foundation.
(2) Melander, L.; Saunders, W. H., Jr. "Reaction Rates of Isotopic Molecules"; Wiley-Interscience: New York, 1980; pp 265–272.
(3) Brown, K. C.; Romano, F. J.; Saunders, W. H., Jr. *J. Org. Chem.* **1981**, *46*, 4242–4246.
(4) Tao, Y.-T.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 3183–3188.
(5) Cockerill, A. F.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1967**, *89*, 4985–4987.

0022-3263/85/1950-2392$01.50/0