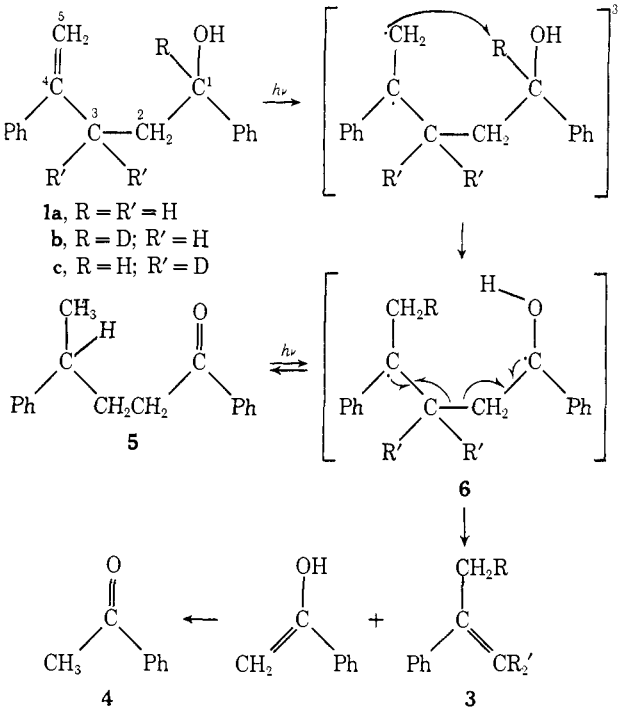
Chart I



and **4** ($\Phi_H/\Phi_D = 5.5 \pm 2$).[14] Analysis of the α-methylstyrene produced, by gc–mass spectroscopy, indicated the presence of one deterium per molecule (parent at 119). A strong peak at 103 (P − 16, loss of monodeuteriomethyl) suggests the location of the deuterium as in **3b**. This was confirmed and carbon **5** was demonstrated to have become the methyl carbon of **3** through the use of **1c** (prepared by a Wittig reaction of α-dideuterated ketone precursor). Analysis by nmr of the α-methylstyrene produced upon irradiation of **1c** revealed the deuterium to be entirely in the vinyl positions, as in **3c**. All of these observations are uniquely consistent with the mechanism outlined in Chart I.

Acknowledgment. The donors of the Petroleum Research Fund, administered by the American Chemical Society, are gratefully acknowledged for support of this research.

(14) Two Pyrex tubes, the first containing **1a** and the second containing **1b**, in equimolar amount, and both containing equimolar amounts of sensitizer (benzophenone), were irradiated in a merry-go-round apparatus to ensure equal absorption of light, then analyzed for the amount of **3** and **4** produced. The low yield of the products and their instability to the reaction conditions limit the accuracy of this experiment.

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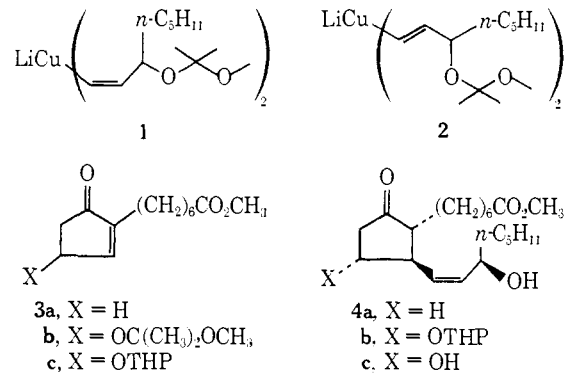
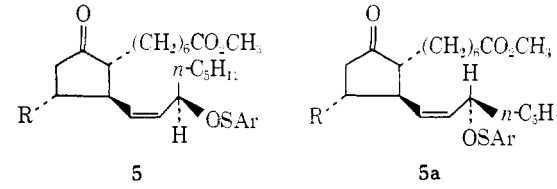
Highly Stereoselective Total Syntheses of Prostaglandins *via* Stereospecific Sulfenate–Sulfoxide Transformations. 13-*cis*-15β-Prostaglandins E_1 to Prostaglandins E_1[1]

Sir:

Recently, we reported highly stereoselective syntheses of 13-*cis*-prostaglandins resulting from the conjugate addition of the *cis*-divinylcuprate (**1**) to the enones (**3a**) and (**3b**).[2] The advantages of using the cis reagent (**1**) over the corresponding trans reagent (**2**)[3] were: (a) higher yields of the addition and (b) the remarkably high degree of stereoselectivity of the reaction (>97%), which led to 13-*cis*-15β-isomers of natural 13-*trans*-15α-prostaglandins. If the 13-*cis*-15β-PGE_1's (**4**) could be converted stereospecifically into PGE_1's, an efficient, nearly stereospecific total synthesis of prostaglandins (E_1, $F_{1\alpha}$, A_1, and B_1) would be achieved.



We now wish to report that the desired transformation of both the chiral and geometric centers can be accomplished concomitantly *via* the sulfenate esters (**5**), which undergo [2,3]sigmatropic rearrangements,[4] giving the sulfoxides (**6**). Treatment of the sulfoxides (**6**) with trimethylphosphite provides the prostaglandins of natural configuration (**7**).[5] The anticipated result of this transformation sequence was based on the prediction that the [2,3]sigmatropic rearrangement of the sulfenate ester (**5**) would be stereospecific with regard to carbon chirality[6] by proceeding through the thermodynamically more stable transition state, which resembles conformer **5a** more than **5** and, thus, would provide the desired geometric and chiral inversions.



Treatment of ketol ester (*dl*-**4a**) in ether with *n*-butyllithium (1 equiv) in hexane at −78°, followed by addition of *p*-toluenesulfenyl chloride gave the *trans*-13α-sulfoxide (*dl*-**6a**): mp 51–52°;[7] ir (KBr) 1730, 1035 (SO), 965 (*trans*-HC=CH) cm^{-1}; uv (MeOH) 250 nm

(1) Publication No. 443 from the Institute of Organic Chemistry. Studies in Prostaglandins No. 40.

(2) A. F. Kluge, K. G. Untch, and J. H. Fried, *J. Amer. Chem. Soc.*, **94**, 9256 (1972).

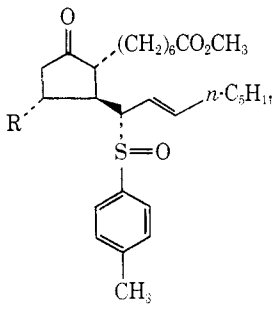
(3) A. F. Kluge, K. G. Untch, and J. H. Fried, *J. Amer. Chem. Soc.*, **94**, 7827 (1972).

(4) (a) P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4869 (1968); (b) J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *Chem. Commun.*, 538 (1968).

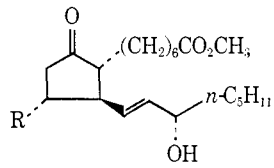
(5) Interceptive cleavage of sulfenate esters to allylic alcohols has been reported by D. J. Abbott and C. J. M. Stirling, *J. Chem. Soc. C*, 818 (1969), using piperidine and, more recently, using other thiophiles, including phosphite, by D. A. Evans, G. C. Andrews, and C. L. Sims, *J. Amer. Chem. Soc.*, **93**, 4956 (1971) and D. A. Evans and G. C. Andrews, *ibid.*, **94**, 3672 (1972). For a recent comprehensive review of the sulfenate–sulfoxide rearrangement, see D. A. Evans and G. C. Andrews, *Accounts Chem. Res.*, 7, 147 (1974).

(6) In this paper we exclude chiral sulfur when using the term stereospecific. All the sulfoxides reported here are diastereomeric due to chirality of the sulfur. All the prostaglandin-like compounds here are epimerically homogeneous at C-15. Both diastereomers of each sulfoxide undergo the [2,3]sigmatropic rearrangement to achiral sulfur sulfenates, which are cleaved.

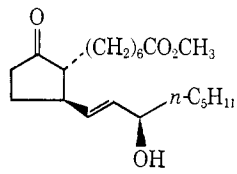
(ε 6100); nmr ($CDCl_3$) δ 2.38 (s, 3, aromatic methyl), 7.1–7.5 (m, 4, aromatic protons); mass spectrum (70 eV) *m/e* 458 ($M^+ - O$), which was converted to *dl*-11-desoxy-PGE_1 methyl ester (*dl*-**7a**),[8] using excess trimethylphosphite in methanol. The two-step sequence (**4a** → **6a** → **7a**) proceeds with complete stereospecificity. None of the 15β-hydroxy epimer (*dl*-**8**) could be detected (direct tlc and glpc comparisons to authentic material[8]).



6a, R = H
b, R = OTHP
c, R = OH



7a, R = H
b, R = OTHP
c, R = OH



8

When the initial reaction (*n*-BuLi–*p*-toluenesulfenyl chloride[9]) was carried out with the 11-substituted ketol (*dl*-**4b**),[10] however, little or none of the desired sulfoxide (*di*-**6b**) could be isolated. Rather, PGA-type products or PGA-type derived products resulted from the strongly basic media. Since it is necessary to avoid strong base for the preparation of PGE_1, the usual method of preformation of the alkoxide anion in obtaining sulfenates had to be circumvented. We found that treatment of *dl*-**4a** in ether containing *ca.* 3 equiv of triethylamine with *p*-toluenesulfenyl chloride (1.4 equiv) at room temperature gave *dl*-**6a** (87%),[11] which was converted to *dl*-**7a** (92%)[11] using excess trimethylphosphite in methanol at room temperature. This same reaction sequence carried out on the 11-protected ketol (*dl*-**4b**) (triethylamine, 3 equiv; *p*-toluenesulfenyl chloride, 1.5 equiv) gave sulfoxide (*dl*-**6b**) (81%):[11] oil;[7] ir (film) 1730, 1035 (SO), 970 (*trans*-CH=CH) cm^{-1}; uv (MeOH) 249 nm (ε 6400); nmr ($CDCl_3$) δ 2.38 (s, 3, aromatic methyl) 7.15–7.6 (m, 4, aromatic protons); mass spectrum (70 eV) *m/e* 434 (M^+ – tolylSOH), which upon treatment with trimethylphosphite in methanol, afforded the ketol (*dl*-**7b**) (88%).[11] Acid hydrolysis (65% acetic acid) of (*dl*-**7b**) gave *dl*-PGE_1 methyl ester (*dl*-**7c**) (90%,[11] identical with an authentic sample[3,8] by tlc, glpc, and nmr).[12,13]

(7) Satisfactory combustion analysis was obtained.
(8) Previously synthesized: F. S. Alvarez, D. Wren, and A. Prince, *J. Amer. Chem. Soc.*, **94**, 7823 (1972).
(9) These are the usual conditions for the formation of a sulfoxide from an allylic alcohol, *i.e.*, prior alkoxide formation. See, for example, ref 4a and D. A. Evans, *et al.*, ref 5.
(10) Prepared *via* conjugate addition of cuprate (1) to enone (*dl*-**3c**), followed by mild acid (20% acetic acid) hydrolysis of the more labile ether at C-15 (45%, based on *dl*-**3c**, unpublished).
(11) Isolated yield.
(12) The two-step conversion applied directly to the unprotected 11-hydroxy ketol (*dl*-**4c**), gave *dl*-PGE_1 methyl ester (an excess, 3.5 equiv, of *p*-toluenesulfenyl chloride was used—not optimum stoichiometry). Selective sulfenate formation of the allylic hydroxyl group probably occurred.

We are continuing our synthetic investigations by utilizing this nearly stereospecific total synthesis for the preparation of prostaglandin analogs and to determine the generality of the sequence.[13a]

Acknowledgment. We are indebted to Mr. B. Amos, Mr. V. Hayashida, Mrs. L. Kurz, Dr. M. Maddox, Mrs. J. Nelson, Mrs. A. Nitzan, Mr. J. Smith, and Mrs. Diane Wong for their assistance with analytical measurements and to Dr. G. F. Cooper for helpful discussions.

(13) Although the above transformations were carried out with *dl* materials, the same results are realized using individual enantiomeric allylic alcohols, *i.e.*, (15*R*)-**4a**[2] and (15*R*)-**4c**[2] give (15*S*)-**7a** and (15*S*)-**7c**, respectively.
(13a) NOTE ADDED IN PROOF. Subsequent investigations (W. K. and K. G. U.) have shown that the 1,4-conjugate addition of **1** to **3b** is not as stereoselective as previously reported;[2] 15-epi-**4a**:**4a**, 2.5:97.5; 15-epi-**4c**:**4c**, 14:86. Independently synthesized 15-epi-**4a** and 15-epi-**4c** were found to be surprisingly nonpolar; rf: **4a** (0.47), 15-epi-**4a** (0.86), **7a** (0.56), **7c** (0.46), **4c** (0.11), 15-epi-**4c** (0.41), hexane:ethyl acetate, 55:45.
(14) Syntex Postdoctoral Fellow, 1972–1973.

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Tribophosphorescence from Nonphotophosphorescent Crystals

Sir:

Recent studies have shown that triboluminescence (TL), the emission of light caused by the application of mechanical stress to crystals, can originate from both spin forbidden[1,2] and spin allowed[3] transitions of molecules in a crystal in contrast with the previously observed ambient gas discharge processes.[4,5] In all of the tribophosphorescent or tribofluorescent crystals for which the excited state origins of the TL have been identified, the corresponding intense photoluminescence spectra were similar to the TL spectra and could be measured at the same temperature as that at which the TL was measured. In this paper we report the first examples of room temperature triboluminescence from crystals which are not photoluminescent at that temperature. (No photophosphorescence could be detected using an Aminco-Keirs spectrophosphorimeter or the apparatus described below.) The TL spectra differ markedly from the corresponding photoluminescence spectra. We also report the first example of simultaneous tribofluorescence and phosphorescence.

The TL spectra of phthalic anhydride and acenaphthene were obtained by grinding 0.5-g samples in glass vials with metal, wood, glass, or Teflon rods. Weak TL excited by the thermal shock of immersing a sample in liquid nitrogen could also be visually observed. The ratio of the intensity of a tribolumines-

(1) J. I. Zink and W. C. Kaska, *J. Amer. Chem. Soc.*, **95**, 7510 (1973).
(2) C. R. Hurt, N. McAvoy, S. Bjorklund, and N. Filipescu, *Nature (London)*, **212**, 179 (1966).
(3) J. I. Zink and W. Klimt, *J. Amer. Chem. Soc.*, **96**, 4690 (1974).
(4) M. C. Hoff and C. E. Boord, *J. Amer. Chem. Soc.*, **72**, 2770 (1950).
(5) P. A. Thiessen and K. Meyer, *Naturwissenschaften*, **57**, 423 (1970).