(240 °C) showed two peaks 4.35 and 4.65 min in the ratio of about 96:6. Anal. Calcd for $C_{20}H_{34}O_2Si$: C, 71.85; H, 10.17. Found: C, 71.81; H, 9.83.

***trans*-2,3-Dimethyl-3-[2-(*tert*-butyldimethylsiloxy)-4-methylphenyl]cyclopentanone (12).** A solution of alcohol 11 (100 mg, 0.29 mmol) in DMF (1 mL) was vigorously stirred with pyridinium dichromate (225 mg, 0.6 mmol) for 4 h at ambient temperature. At this time TLC indicated that the oxidation was complete. The mixture was diluted with water and extracted with ether. The combined extracts were washed with 10% aqueous NaOH, water, and brine, dried with anhydrous $MgSO_4$, and concentrated. The crude product was chromatographed on a silica gel preparative plate developed with 10% ether in petroleum ether to afford 94 mg of 12 (94% yield): IR 2975–2875, 1740 (C=O), 1620, 1500, 1275, 850 cm^{-1}; NMR δ 7.3–6.7 (3 H, m), 2.8–1.9 (4 H, m), 2.2 (CH_3, s), 1.25 (CH_3, s), 1.0 (9 H, s), 0.75 (3 H, d, J = 7 Hz), 0.3 (6 H, s). Anal. Calcd for $C_{20}H_{32}O_2Si$: C, 72.28; H, 9.63. Found: C, 72.41; H, 10.02.

***trans*-2,3-Dimethyl-3-[5-bromo-2-(*tert*-butyldimethylsiloxy)-4-methylphenyl]cyclopentanone (14).** Bromine (13 μL, 0.25 mmol) was added to a solution of the ketone 12 (85 mg, 0.25 mmol) in propylene oxide (2 mL). After 5 min the entire reaction mixture was chromatographed on a silica gel preparative plate developed with 13% ether in petroleum ether to afford 102 mg of 14 (80% yield) as a viscous liquid. We were unable to induce this material to crystallize. 14: IR 2990–2860, 1740 (C=O), 1600, 1500, 1400, 1310, 850; NMR δ 7.15 (1 H, s), 6.55 (1 H, s), 2.3–1.9 (4 H, m), 2.2 (CH_3, s), 1.25 (CH_3, s), 1.0 (9 H, s), 0.72 (3 H, d), J = 7 Hz), 0.3 (6 H, s). Anal. Calcd for $C_{20}H_{31}BrO_2Si$: C, 58.39; H, 7.54. Found: C, 58.16; H, 7.41.

Allolaurinterol *tert*-Butyldimethylsilyl Ether (16). The methylenation procedure of Nozaki[11] was employed. To a suspension of powdered zinc (81 mg, 1.25 mmol) in THF (1 mL) was added CH_2Br_2 (88 μL, 1.25 mmol) and $TiCl_4$ (137 μL, 1.25 mmol). A vigorous, exothermic reaction took place with formation of a dark-blue color. After 20 min the bromo ketone 14 (100 mg, 0.25 mmol) was added in 2 mL THF. The reaction was allowed to proceed for 6 h and then poured into water and extracted with ether. The combined extracts were washed with 10% aqueous NaOH, water and brine, dried with anhydrous Na_2SO_4, and concentrated. The crude product was chromatographed on a silica gel preparative plate developed with 1% ether in petroleum ether to afford 85 mg of 16 (84% yield) as a pale-yellow oil): IR 3080–2850, 1650, 1600, 1350, 1250, 870, 840 cm^{-1}; NMR δ 7.25 (1 H, s), 6.65 (1 H, s), 4.85 (2 H, s), 3.1 (1 H, q), 2.2 (CH_3, s), 1.25 (CH_3, s), 1.0 (H, s), 0.72 (3 H, d, J = 7 Hz), 0.3 (6 H, s).

(±)-Allolaurinterol (1). The silyl ether of 16 (85 mg, 0.20 mmol) was cleaved by treatment with a solution of *n*-Bu_4NF (431 μL, 1 M, 0.43 mmol) in THF (1 mL) for 2 min at room temperature. The reaction mixture was then diluted with water and extracted with ether. The combined extracts were washed with water and brine, dried with anhydrous Na_2SO_4, and concentrated. The crude product was chromatographed on a silica gel preparative plate developed with 8% ether in petroleum ether to afford 57 mg of 1 (93% yield): IR 3550, 30580–2880, 1655, 1618, 1495, 1450, 1255, 1075, 880 cm^{-1}; NMR δ 7.25 (1 H, s), 6.5 (1 H, s), 4.95 (1 H, s), 4.85 (1 H, s), 4.6 (1 H, s), 2.95 (1 H, q), 2.5–1.8 (4 H, m), 2.22 (CH_3, s), 1.18 (CH_3, s), 0.72 (3 H, d, J = 7 Hz). Anal. Calcd for $C_{15}H_{18}BrO$: C, 61.01; H, 6.44. Found: C, 60.85; H, 6.47. This material was spectrally identical with (–)-allolaurinterol.[1]

Acknowledgment. We thank the Research Corp., the Washington State University Research Fund, and the National Institutes of Health for their support of this work. We also thank THE BOEING CO. for their support for purchase of the 200-MHz NMR spectrometer. The generous support of Trihuvan Univeristy, Katmandu, Nepal, and the International Institute of Education for a Fulbright-Hays fellowship for M.B.G. is gratefully acknowledged.

Registry No. 1, 81624-20-6; 5, 63023-33-6; 6, 63023-34-7; 7, 63023-36-9; 8, 81328-66-7; 10, 81603-53-4; 10a, 81603-54-5; 11, 81603-55-6; 12, 81603-56-7; 14, 81603-57-8; 16, 81603-58-9; 3-(methoxymethoxy)toluene, 57234-27-2; 5-chloro-5-methyl-2-cyclopenten-1-one, 63023-31-4.

Kinetic Studies and Stereochemical Considerations for the Rearrangement of 1-(*o*-Chlorophenyl)-2-bromo-2-chloro-1-propyl Trifluoroacetate

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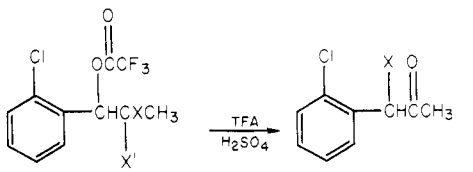
Received October 27, 1981

Neighboring group participation long has been considered a basic tenet of organic chemistry.[2] Demonstration of anchimeric assistance during the course of a reaction has come from rearrangement, rate acceleration, and stereochemical studies. Today a substantial number of groups and atoms are known to serve as important neighboring groups. For example, in a now classic publication Winstein et al.[3] invoked halogen participation and concomitant halonium ion formation to explain the rates of solvolysis of *cis*- and *trans*-2-halocyclohexyl esters. Like most investigations which followed, these authors examined the bridging capabilities of the individual halogens using similar but separate compounds containing iodine, bromine, or chlorine. Subsequently, it was necessary to show that the overall rate enhancement was a function of participation while allowing for the elements of induction, solvent influence, and the way the carbocation center was generated. For example, in Winstein's system the inductive effects of halogen was shown by calculation to result in substantial rate deceleration by as much as 10 000.[4]

Recent investigations[5] in our laboratories directed toward the rearrangement of aryldihalopropanols have utilized a similar approach. In previous experiments, NMR kinetic studies were conducted with 2,2-dichloro- and 2,2-dibromo-1-(*o*-chlorophenyl)-1-propyl trifluoroacetates in a trifluoroacetic acid–sulfuric acid mixture under identical conditions. A comparison of this type revealed a significant rate acceleration owing to halogen participation when the bromine-containing compound was compared with the analogous chloro derivative. This, as well as leaving group effects, implicated a halonium ion intermediate in the rearrangement of 1 to an α-halo ketone 2 (eq 1).



(1)

1a, X = X' = Cl
b, X = X' = Br
c, X = Br, X' = Cl

2a, X = Cl
b, X = Br

In our most recent system, the rearrangement of 1-(*o*-chlorophenyl)-2-bromo-2-chloro-1-propyl trifluoroacetate

(1) Taken, in part, from a thesis by J. Jewett-Bronson in partial fulfillment of the requirements for the M.S. degree in organic chemistry, University of Maine at Orono, Orono, ME.

(2) (a) J. M. Harris and C. C. Wamser, "Fundamentals of Organic Reaction Mechanisms", Wiley, New York, 1976, pp 160–179; (b) J. M. Harris, *Prog. Phys. Org. Chem.*, *11*, 90 (1974); (c) T. H. Lowry and K. S. Richardson, "Mechanism and Theory in Organic Chemistry", 2nd ed, Harper & Row, New York, 1981, Chapter 5.

(3) S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Am. Chem. Soc.*, *70*, 821 (1948); *73*, 5458 (1951).

(4) A. Streitwieser, *J. Am. Chem. Soc. 78*, 4935 (1956).

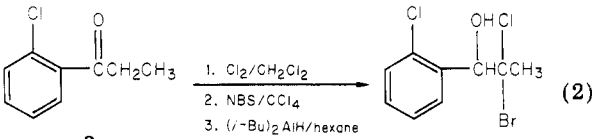
(5) (a) B. L. Jensen and P. E. Peterson, *J. Org. Chem. 42*, 4052 (1977); (b) B. L. Jensen, S. E. Burke, and S. E. Thomas, *Tetrahedron 34*, 1627 (1978); (c) B. L. Jensen, S. E. Burke, S. E. Thomas, and W. H. Klausmeier, *Tetrahedron Lett.*, 2639 (1977); (d) B. L. Jensen and R. E. Counsell, *J. Org. Chem.*, *38*, 835 (1973).

0022-3263/82/1947-2795$01.25/0

by this unusual mechanism offered a unique model to study several aspects of anchimerically assisted rearrangements involving halogen. First, solvolysis of **1c** conceivably could lead to a direct internal competition for participation between chlorine and bromine. While it has long been recognized that bridging by bromine is more facile than for chlorine, few studies have been conducted where two different halogens can compete for an adjacent carbocationic center by neighboring group participation.[6] Secondly, kinetic data from the solvolysis of **1a–c** could provide information on the extent of inductive influence that chlorine and/or bromine has on the rate of reaction. Finally, it could be possible to probe the steric and stereochemical influences which occur during the course of rearrangement by following the rate of reaction for the two pair of diastereomers that make up **1c**. We report here the findings of our most recent study.

Results and Discussion

1-(*o*-Chlorophenyl)-2-bromo-2-chloro-1-propanol was prepared from 1-(*o*-chlorophenyl)-1-propanone (**3**) in a three-step sequence. Monochlorination of **3** was carried out in methylene chloride with an equimolar amount of chlorine. The reaction was monitored via NMR and upon appearance of a singlet at 2.3 ppm the reaction was quenched. Traces of starting material and the dichloro ketone were removed by spinning-band distillation. Preparation of the bromo chloro ketone was accomplished by treating the monochloro ketone with *N*-bromosuccinimide in refluxing carbon tetrachloride under illumination from a 300-W tungsten lamp. NMR and analytical data confirmed the authenticity of this compound. Conversion to **4** was completed by electrophilic reduction of the bromo chloro ketone with diisobutylaluminum hydride in hexane. For purposes of solvolysis, **4** was converted to its trifluoroacetate ester by reaction with trifluoroacetic anhydride in anhydrous ether (eq 2).



(2)

3 4

Kinetic studies were carried out by following the course of reaction with proton magnetic resonance spectroscopy. Rate constants were determined as the negative slope of plots of ln $(1 - A_p/A_t)$ vs. time, where A_p and A_t are areas for the methyl singlets (or benzylic hydrogens) of the product and the total area (product plus reactant). Good first-order plots were obtained for all compounds up to 3-4 half-lives, using the methyl group singlets. However, the signal-to-noise ratio in the benzylic region of the NMR substantially reduced the accuracy of the measurements. Solvolysis products were identified by comparison of their NMR spectra and GLC chromatograms with those of authentic samples that had been prepared previously.[5]

Solvolysis of **1c** was performed with 0.2 M samples in 0.46 M sulfuric acid dissolved in trifluoroacetic acid at 57 °C. From the onset of reaction it was clearly apparent that the set of enantiomers with benzylic protons at 6.86 ppm and methyl protons at 2.35 ppm was undergoing rearrangement more rapidly than the pair of enantiomers having a benzylic absorption at 7.00 ppm and a methyl peak at 2.30 ppm. After 5 h, the nearly completed reaction showed only a single benzylic absorption at 6.10 ppm and a single methyl absorption at 2.45 ppm. The reaction was allowed to proceed for 22 h to insure total conversion of both pairs of diastereomers. At this time the reaction was quenched with water and the product extracted into methylene chloride. In turn, the extract was subjected to capillary gas chromatography, using a fused silica column. Both NMR and GLC analyses confirmed that the bromo ketone **2b** was the exclusive product of rearrangement with the chloro ketone **2a** being found in only trace amounts.[7]

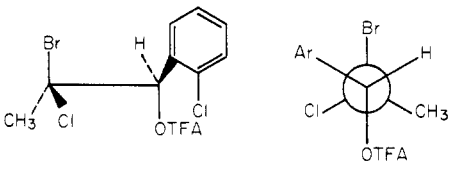


Figure 1.

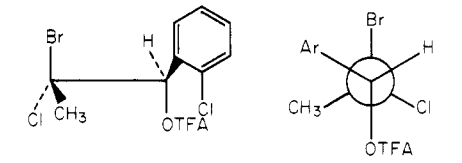


Figure 2.

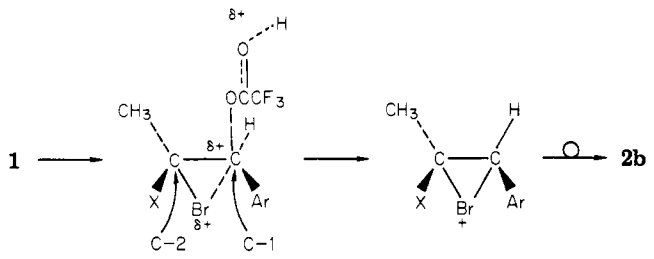
Of the several contributing factors which could most readily influence this reaction, intergroup interactions in the reactant and transition state appear to play a major role. Examination of three-dimensional models revealed that of the six pairs of intergroup interactions in the two sets of conformers that make up **1c**, the aryl–methyl interaction may be the dominant factor. As shown in Figure 1, when the bromine atom and trifluoroacetate group assume an antiperiplanar arrangement prior to neighboring group participation by bromine in the *R,S* conformer (and *S,R* conformer), the terminal methyl group projects away from the aromatic moiety. Furthermore, dipole and steric factors appear to be minimized since the *o*-chlorophenyl, halogens, and trifluoroacetate groups occupy rather spacious positions. Only a small unfavorable ortho hydrogen interaction can arise in these conformations. In contrast, an appreciable interaction develops between the methyl group and aromatic ring in the *R,R* and *S,S* conformers (Figure 2).

That severe intergroup interactions can play a major role in this reaction and obscure smaller contributions, such as differential inductive effects, is also evidenced by a comparison of the rates of reaction for the sets of diastereomers of **1c**, the dichloro trifluoroacetate **1a**, and the dibromo trifluoroacetate **1b**. Under identical conditions, **1a** solvolyzed very slowly at a rate of 1.8×10^{-5} s^{-1} with an approximate half-life of 690 min. In contrast, the dibromo analogue **1b** solvolyzed rapidly at a rate of 2.4×10^{-4} s^{-1} with a half-life of about 48 min. The solvolysis rates for the separate diastereomers of **1c** were distinctly different, as would be expected on the basis of the vastly different group interactions. The *R,S* conformer (and enantiomer) reacted at nearly the same rate as the dibromo compound with a rate of approximately 1.7×10^{-4} s^{-1} and a half-life of 60–80 min. The *R,R* conformer (and enantiomer) reacted about 3 times more slowly than the other set of diastereomers with a rate of approximately 5.8×10^{-5} s^{-1} and a half-life of 180–210 min. A slightly lower rate of reaction for **1c** compared to that of **1b** is to be expected

(6) P. B. D. de la Mare, P. G. Naylor, and D. L. H. Williams, *J. Chem. Soc.*, 443 (1962).

(7) The small amount of **2a** found in the rearrangement mixture is within experimental limits of the purification procedures used to remove the dichloro ketone from the first step of the reaction sequence and is less than 2%.

Scheme I[a]



[a] X = Cl or Br.

on the basis of differing inductive influences by chlorine and bromine. During the transition state leading to the formation of the three-membered ring halonium ion, the developing positive charge acquired by carbon-1 will be influenced by the groups remaining at carbon-2.[8] For **1c**, the remaining halogen is chlorine and for **1b** the remaining halogen is bromine. Because the inductive electron-withdrawing ability of chlorine (σ_I = 0.47) is slightly greater than for bromine (σ_I = 0.45),[9] the transition state leading to the bromonium ion intermediate is slightly destabilized for **1c** in comparison to **1b**. Accordingly, the overall rate of reaction for **1c** is slower than **1b** (Scheme I). However, any inductive effect which is operative here must apply to both sets of compounds making up **1c**. Consequently, the fact that the rates of reaction are considerably different for each set of diastereomers means that the interactions between groups are the major force controlling the course of reaction.

The formation of less than 2% of chlorine shift product is somewhat surprising since the reaction of **1c** would be expected to yield approximately 10% of **2a**, based on the dichloro and dibromo trifluoroacetate rates of solvolysis. However, intergroup interactions and the noncompetitive nature of the chlorine atom would explain this result. In order for chlorine to participate in this reaction, it would be necessary for the *R,R* conformer (and *S,S* conformer) shown in Figure 2 to undergo carbon–carbon bond rotation of 120° to bring the chlorine atom and trifluoroacetate group into a trans coplanar arrangement. While the methyl–aryl interaction is relieved, this same rotation brings the bulky bromine atom into an unfavorable juxtaposition with the aromatic ring. In fact, there would be little, if any, steric relief provided by such a rotation since the bromine atom and methyl group are of approximately equal size.[10] Thus it would appear that while the conformation shown in Figure 2 is not an ideal arrangement of groups, it is better than the analogous one having a chlorine anti to the trifluoroacetate function. Moreover, our finding that chlorine competes to a nearly insignificant degree with bromine is consistent with the results of de la Mare et al.[6] These authors found that when hypobromous acid was added to allyl chloride, no greater than 0.8% of the product distribution arose by chlorine competing with bromine for an adjacent electron-deficient carbon.

Experimental Section

Melting points were obtained with a Thomas-Hoover apparatus and are uncorrected. Quantitative analyses of the kinetic runs and additional NMR spectra were recorded on a Hitachi Perkin-Elmer R20-B spectrometer. Kinetic experiments were conducted from a single batch of TFA–H_2SO_4 with a capillary of Me_4Si as the standard. All other NMR spectra were taken in $CDCl_3$ with Me_4Si as an internal standard. Infrared spectra were determined on a Perkin-Elmer 457 spectrophotometer. Distillations were performed with a Büchi/Brinkman Kugelrohrofen microdistillation oven or with a B/R Instrument Corp. Model 800 spinning-band distillation unit and boiling points were uncorrected. Vapor phase chromatography was done by using a Hewelett-Packard 5731A instrument with a 25-m SE-30 capillary column. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

1-(*o*-Chlorophenyl)-2-chloro-1-propanone. 1-(*o*-Chlorophenyl)-1-propanone[11] (27.0 g, 0.16 mol) was dissolved in methylene chloride (400 mL) and cooled in an ice bath. Chlorine (12.8 g, 0.18 mol), dissolved in ice-cold methylene chloride (200 mL), was added dropwise with stirring over a period of 1 h. After the addition, hydrogen chloride gas was bubbled through the solution for 15 s. The mixture was allowed to warm to room temperature and stirring was continued overnight. During this period the reaction was monitored by NMR spectroscopy and upon the appearance of a singlet at 2.30 ppm the mixture was poured into cold water. The solvent layer was washed with water, 5% aqueous sodium bicarbonate, and water before drying over sodium sulfate. Evaporation of the solvent and spinning-band distillation of the residue afforded 31.0 g (94%) of the monochloro ketone as a light-yellow liquid: bp 77–79 °C (0.25 mm); IR (film) 3080, 3000, 1710, 1590, 1470, 1200 cm^{-1}; NMR ($CDCl_3$) δ 7.35 (m, 4, Ar H), 5.15 (q, 1, CH), 1.70 (d, 3, CH_3).

1-(*o*-Chlorophenyl)-2-bromo-2-chloro-1-propanone. The monochloro ketone (18.3 g, 90 mmol) and *N*-bromosuccinimide (16.0 g, 90 mmol) were refluxed in carbon tetrachloride (200 mL) under illumination from a 300-W tungsten lamp. The reaction was complete after 6 h, when the orange color of the solution had disappeared. The solution was filtered, and the solvent evaporated. Spinning-band distillation of the residue gave 21.0 g (84%) of the product: bp 80–85 °C (0.2 mm); IR (film) 3080, 3000, 1720, 1590, 1220, 1050, 750 cm^{-1}; NMR ($CDCl_3$) δ 7.35 (m, 4, Ar H), 2.48 (s, 3, CH_3).

Anal. Calcd for $C_9H_7Cl_2BrO$: C, 38.34; H, 2.50; Br, 28.34. Found: C, 38.65; H, 2.76; Br, 28.70.

1-(*o*-Chlorophenyl)-2-bromo-2-chloro-1-propanol (4). To a solution of the bromo chloro ketone (2.1 g, 7.5 mmol), under a nitrogen atmosphere and in dry hexane (30 mL), was added fresh diisobutylaluminum hydride (10 mL, 20% in hexane) dropwise via syringe over a period of 5 min. The solution was stirred at room temperature for 2 h and then cooled to 0 °C in an ice bath. Water (10 mL) was added dropwise and the resulting precipitate was removed by filtration. The precipitate was washed with hexane. The hexane layers were combined, washed with brine, and dried over sodium sulfate. The solvent was evaporated to afford 1.9 g (90%) of **4** as a pure colorless liquid. Distillation was carried out at 120–121 °C (0.1 mm). **4**: IR (film) 3450, 1050 cm^{-1} (acetate, IR (film) 1750, 1220 cm^{-1}); NMR ($CDCl_3$) δ 7.3 (m, 4, Ar H), 5.45 (d, 1/2, CH), 5.60 (d, 1/2, CH), 3.80 (d, 1, OH), 2.20 (s, 3, CH_3).

Anal. Calcd for $C_9H_9Cl_2BrO$: C, 38.06; H, 3.19. Found: C, 38.47; H, 3.42.

1-(*o*-Chlorophenyl)-2-bromo-2-chloro-1-propanol Trifluoroacetate (1c). To a solution of **4** (0.8 g, 2.8 mmol) in anhydrous ether (50 mL) was added trifluoroacetic anhydride (2 mL) in ether (2 mL). The solution was stirred at room temperature for 18 h and then cooled to 0 °C. Ice water (10 mL) was added dropwise and the aqueous layer separated. The ethereal layer was washed with water, 5% aqueous sodium bicarbonate, and water before drying over sodium sulfate. Evaporation of the solvent afforded **1c** as a colorless heat-sensitive liquid: 1.1 g (99%); IR (film) 1800, 1150 cm^{-1}; NMR ($CDCl_3$) δ 7.60 (m, 4, Ar H), 6.90 (s, 1/2, CH), 6.76 (s, 1/2, CH), 2.32 (s, 3, CH_3).

Kinetic Procedures. Reaction rates were determined by NMR spectroscopy. Solutions (0.20–0.21 M) were prepared with a single batch of trifluoroacetic acid–sulfuric acid. Rate determinations were based on relative peak heights of the methyl group singlets and benzylic hydrogen singlets. First-order rate constants

(8) P. E. Peterson, *Acc. Chem. Res.*, *4*, 407 (1971).
(9) (a) R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.*, *80*, 2436 (1958); *81*, 5343 (1959); (b) C. D. Ritchie and W. F. Sager, *Prog. Phys. Org. Chem.*, *2*, 337 (1964).
(10) R. W. Taft, "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, 1956, Chapter 13.
(11) Reference 5b, p 1629.

were determined as the negative slope of plots of ln $(1 - A_p/A_t)$ vs. time, where A_p and A_t are areas of the product and total area, respectively. Good first-order rate plots were obtained to 75% reaction using the methyl groups and are comparable in quality to those of earlier studies. The data taken from the benzylic region of the NMR was subject to greater experimental error because of the signal-to-noise ratio. However, the data are representative of the gross overall changes which occurred during the reaction. Products were identified by comparison of their NMR spectra and GLC retention times with those of authentic materials previously prepared.[5]

Acknowledgment. We thank Professor Paul E. Peterson for his interest and valuable suggestions regarding this problem.

Registry No. 1c (isomer 1), 81671-52-5; 1c (isomer 2), 81671-53-6; 3, 6323-18-8; 4, 81671-54-7; 1-(*o*-chlorophenyl)-2-chloro-1-propanone, 81671-55-8; 1-(*o*-chlorophenyl)-2-bromo-2-chloro-1-propanone, 81671-56-9.

Structure of Goyazensolide and Its Congeners[1]

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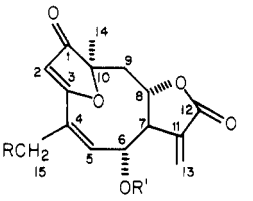
Received February 2, 1982

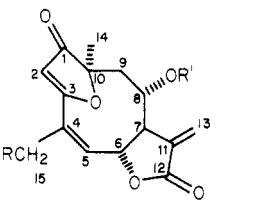
At the time of their discovery[2] the heliangolides goyazensolide and 15-deoxygoyazensolide were assigned formulas **1a** and **1b** (Chart I) rather than **2a** and **2b** for two reasons. (1) Chemical shifts and coupling constants involving H-6, H-7, H-8, and H-9 differed significantly from those exhibited by calaxin,[3] ciliarin,[3] and budlein A[4] which were then believed to possess structures **2b**, **2g**, and **2c**, respectively. (2) H-8 near 4.5 ppm was identified with the hydrogen on carbon carrying the lactone oxygen and H-6 near 5.3 ppm with the hydrogen on carbon carrying the ester group since lactone hydrogens at C-6 or C-8 of sesquiterpene lactones generally resonate at higher fields than C-6 or C-8 hydrogens under ester moieties.

In the interval the first of these arguments has been rendered invalid by the demonstration[5,6] that calaxin, ciliarin, and budlein A actually possess structures **3a–c**.[7] Moreover, goyazensolide, 15-deoxygoyazensolide, and several similar compounds to which structures **1c–f** were assigned by analogy have since been isolated from other plant sources where they are generally accompanied by substances whose lactone ring is invariably closed toward C-6.[8] In particular, goyazensolide and its analogues are

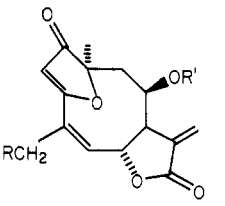
Chart I



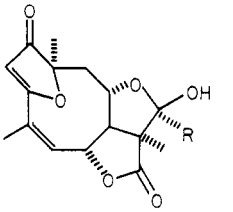
1a, R = OH; R′ = MeAcr
b, R = H; R′ = MeAcr
c, R = OH; R′ = Ang
d, R = H; R′ = Ang
e, R = H; R′ = Epoxyang
f, R = H; R′ = Tigl
g, R = H; R′ = *i*-Bu



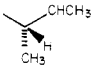
2a, R = OH; R′ = MeAcr
b, R = H; R′ = MeAcr
c, R = OH; R′ = Ang
d, R = H; R′ = Ang
e, R = H; R′ = Epoxyang
f, R = H; R′ = Tigl
g, R = H; R′ = *i*-Bu



3a, R = H; R′ = MeAcr
b, R = H; R′ = *i*-Bu
c, R = OH; R′ = Ang

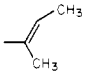


4a, R = *i*-Pr



b, R =

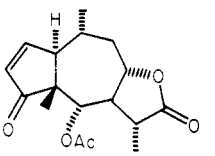
c, R =



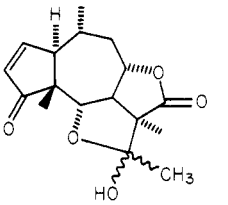
d, R =

e, R =

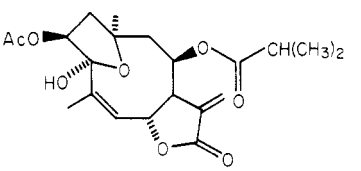
f, R =



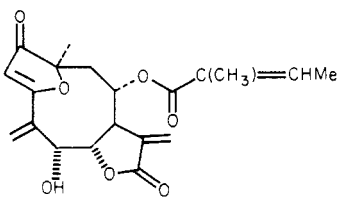
5



6



7



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(1) Supported in part by a grant (CA-13121) from the U.S. Public Health Service through the National Cancer Institute.

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