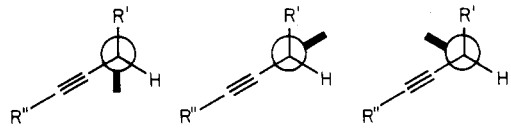
Table I. Circular Dichroism of Benzoates of Propargyl Alcohols

	I			abs		Δε	
	R′	R″	$[\alpha]^{25}_D$	config	ee, %	exptl[a]	calcd
Ia	Me	*n*-Bu	−14.51 (*c* 3.1, ether)	*S*	36.2	+1.8	+0.9
Ib	Et	*n*-Bu	−9.94 (*c* 3.7, hexane)	*S*	64.1	+1.3	
Ic	*i*-Pr	*n*-Bu	−6.43 (*c* 6.3, hexane)	*S*	78.1	+2.3	
Id	*t*-Bu	*n*-Bu	−13.72	*S*	84.8	+1.9	+1.3
Ie	*t*-Bu	H	−2.38	*S*	13.4	+2.2	+1.1
If	*t*-Bu	Br	not determined	*S*	13.4	+3.7	+1.8

[a] Reported to 100% ee.

Chart I



II III IV

positive benzoate Cotton effects are correlated to the absolute *S* configuration of II, the nature of the alkyl group R′ on the asymmetric carbon atom affecting only the intensity values. It is noteworthy that the present assignment of the *S* absolute configuration to the alcohols Ia–f is in agreement with the GLC method proposed by Mori and Akao.[2] The most important aspect of this CD investigation is that the relationship between the absolute configuration and the sign of the benzoate Cotton effect is largely independent of the nature of the substituent on the triple-bond moiety. In fact this will be certainly valid for all the groups which will not change the polarization direction of the allowed transition of the acetylenic group. Therefore substituents like alkyl, acetylenic, and cyano groups and halogen atoms, when present in II, will give rise to a positive Cotton effect for the 230-nm benzoate transition.

In conclusion, a nonempirical rule emerges that correlates the positive sign of the above Cotton effect to the absolute *S* configuration of the alcoholic chiral center. This result is coming from a detailed calculation of the benzoate Cotton effect at 230 nm, by means of the De Voe polarizability model for optical activity. It is then to be noted that the approach used in the present work (formation of chromophoric derivatives of "transparent" molecules for measuring the CD and comparison of the experimental value with the result of calculations) can constitute a general method for assigning absolute configurations. In fact, the use of the De Voe model, which accounts for even alkyl perturbers, provides the opportunity to treat also very simple compounds where the chromophoric group is perturbed by alkyl groups only in contrast to the Harada and Nakanishi rules,[5] and it is therefore of larger applicability.

Experimental Section

All solvents were reagent-grade materials, purified by standard methods, and redistilled before use. Optical rotations were measured on a Perkin-Elmer 142 automatic polarimeter in a 1-dm tube; unless otherwise specified, rotations refer to those of the pure liquid. GLC analyses (Perkin-Elmer 3920 B) on the methoxy(trifluoromethyl)phenylacetates were performed with 2-m Carbowax 20M columns, at 170 °C, nitrogen flow rate 15 mL min^{-1}; ^{19}F NMR (94.1 MHz) spectra were obtained with a Varian XL-100 spectrometer on $CDCl_3$ solutions with Me_4Si as an internal standard. Absorption and CD spectra were obtained by means of JASCO Uvidec-710 spectrophotometer and a JASCO J-500 C spectropolarimeter equipped with a DP-500 N data processor, respectively, using heptane solutions in standard 0.01-cm cylindrical quartz cells.

The optically active carbinols were obtained from the corresponding acetylenic ketones by reducing them with [[(1*S*,2*R*)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl]methyl]aluminum dichloride[6a] (Ia–d) and tris[(*S*)-2-methylbutyl]aluminum (Ie)[6b] according to published procedures.[6] Compound If was obtained from Ie by treatment with bromine in alkaline solution at 0 °C. Both MPTA esters and the benzoates of Ia–f were prepared according to the following representative procedure. (2-Methyl-4-nonyl-3-ol (0.200 g, 1.30 mmol) and distilled (+)-MPTACl or benzoyl chloride (1.55 mmol) were mixed with CCl_4 (1.1 mL) and dry pyridine (1.1 mL) and allowed to stand for 12 h at room temperature; then the mixture was diluted with water and extracted with ether (20 mL), washed with dilute HCl, saturated Na_2CO_3, and water, and dried (Na_2SO_4). Removal of the solvent under vacuum furnished the crude esters. While the MPTA ester was used without any purification, the benzoate was purified by flash-chromatography (hexane/acetone, 90:10).

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Registry No. (*S*)-Ia, 90792-10-2; (*S*)-Ia benzoate, 90792-04-4; Ia MPTA ester, 90792-14-6; (*S*)-Ib, 90792-11-3; (*S*)-Ib benzoate, 90792-05-5; Ib MPTA ester, 90792-15-7; (*S*)-Ic, 87682-11-9; (*S*)-Ic benzoate, 90792-06-6; Ic MPTA ester, 90792-16-8; (*S*)-Id, 90792-12-4; (*S*)-Id benzoate, 90792-07-7; Id MPTA ester, 90792-17-9; (*S*)-Ie, 90865-49-9; (*S*)-Ie benzoate, 90792-08-8; Ie MPTA ester, 90792-18-0; (*S*)-If, 90792-13-5; (*S*)-If benzoate, 90792-09-9; If MPTA ester, 90792-19-1.

Stereochemistry and Mechanisms in Eliminations from Some 1,2-Dihalo-1,2-diphenylethanes Promoted by Potassium *tert*-Butoxide in *tert*-Butyl Alcohol

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In our recent study of hydrogen halide eliminations from 1,2-dihaloacenaphthenes[1] and 2,3-dihalo-2,3-dihydrobenzofurans[2] promoted by *t*-BuOK in *t*-BuOH, we found that fluorine is a better leaving group than chlorine in the syn reactions of compounds where chlorine is the β halogen. This result was interpreted as involving a stepwise elimination through an irreversibly formed carbanion: an $(ElcB)_I$ mechanism.

Since both these investigations have involved cyclic substrates, it seemed of interest to determine whether similar results would be obtained with β-aryl-activated acyclic dihalides. We here report on a kinetic and product study of eliminations from *meso*-1,2-dichloro-1,2-diphenylethane (1), *erythro*-1-chloro-2-fluoro-1,2-diphenyl-

(1) Baciocchi, E.; Ruzziconi, R.; Sebastiani, G. V. *J. Org. Chem.* **1982**, *47*, 3237–3241.
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Table I. Kinetic Data for Syn and Anti Eliminations from 1,2-Dihalo-1,2-diphenylethanes Promoted by t-BuOK in t-BuOH at 30 °C[a]

substrate	leaving group	β-halogen	syn, %	anti, %	syn k_2, M^{-1} s^{-1}	syn k_{Cl}/k_F	anti k_2, M^{-1} s^{-1}	anti k_{Cl}/k_F
1	Cl	Cl	13	87	2.12×10^{-4} [b]	0.1	1.37×10^{-3} [b]	
2	F	Cl	95	5	2.33×10^{-3}		1.27×10^{-4}	11
2	Cl	F	0	100			4.52×10^{-4}	30
3	F	F	32	68	6.95×10^{-6} [b]		1.48×10^{-5} [b]	

[a] The concentration of the base was 0.38 M. [b] Data corrected for the statistical factor.

Table II. Kinetic Data for Syn and Anti Eliminations from 1,2-Dihalo-1,2-diphenylethanes Promoted by t-BuOK in t-BuOH in the Presence of 18-Crown-6 Ether at 30 °C[a]

substrate	leaving group	β-halogen	syn, %	anti, %	syn k_2, M^{-1} s^{-1}	anti k_2, M^{-1} s^{-1}	anti k_{Cl}/k_F
1	Cl	Cl	0	100		2.30[b]	3.0
2	F	Cl	13	87	1.21×10^{-1}	7.64×10^{-1}	
2	Cl	F	0	100		9.23×10^{-2}	12
3	F	F	5	95	3.84×10^{-4}	7.62×10^{-3} [b]	

[a] The concentration of the base was 0.016 M and that of 18-crown-6 was 0.032 M. [b] Data corrected for the statistical factor.

ethane (2), and *meso*-1,2-difluoro-1,2-diphenylethane (3) induced by *t*-BuOK in *t*-BuOH in the presence and in the absence of 18-crown-6 ether.

Results

Treatment of 1 with *t*-BuOK–*t*-BuOH leads to a mixture of (*Z*)- and (*E*)-α-chlorostilbenes (4) (Scheme I), , the latter being the major product (87%). A small amount (~0.5%) of 1,2-diphenylacetylene (5) is also formed. In the presence of 18-crown-6 only the *E* isomer is formed, indicating exclusive anti elimination. From 3 a mixture of (*Z*)- and (*E*)-α-fluorostilbenes 6 is obtained both in *t*-BuOK–*t*-BuOH and *t*-BuOK–*t*-BuOH–18-crown-6. The *E* isomer is the major component (68% in the absence of and 95% in the presence of 18-crown-6). Elimination from 2 in *t*-BuOK–*t*-BuOH leads to 70.6% of (*Z*)-α-chlorostilbene, 4.4% of (*E*)-α-chlorostilbene, 16.3% of (*E*)-α-fluorostilbene, and 8.8% of 1,2-diphenylacetylene. In *t*-BuOK–*t*-BuOH–18-crown-6 these figures become 0.6%, 78.3%, 9.6%, and 11.5%, respectively. Thus HF elimination is the main reaction of 2 in both systems, the stereochemistry being predominantly anti in the presence of 18-crown-6. The elimination of HCl from 2 is exclusively an anti process, only (*E*)-α-fluorostilbene being formed both with and without 18-crown-6. Since blank experiments have shown that, under our conditions, 1,2-diphenylacetylene comes from the reaction of (*Z*)-α-chlorostilbene with the base, the percentages of these two products have been summed to calculate the extent of syn elimination. The elimination processes in *t*-BuOK–*t*-BuOH are shown in Scheme I.

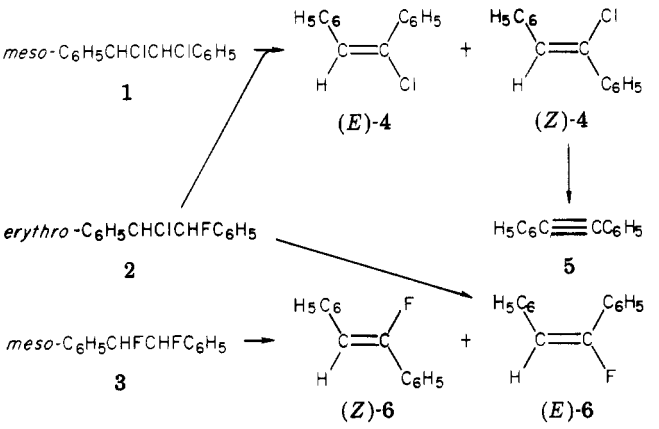
Kinetics were studied by following the formation of the *Z* olefin spectrophotometrically at 284–290 nm. An excess of base was used, and excellent first-order plots were obtained in all cases. For reasons stated in previous studies[1,2] all kinetic experiments were carried out at the same concentration of *t*-BuOK (0.38 M in *t*-BuOH and 0.016 M in *t*-BuOH–18-crown-6). The overall second-order rate constants were dissected on the basis of product analysis to get the rate constants for the individual elimination processes. The stereochemical and kinetic data are collected in Tables I and II.

No incorporation of deuterium in the unreacted starting material was observed in eliminations from 2 and 3 in *t*-BuOK–*t*-BuOH.

Discussion

The observation that a significant proportion (13%) of syn elimination occurs in the reaction of 1 with *t*-BuOK–*t*-BuOH is worth noting since exclusive anti elimination is generally found in eliminations from vicinal dihaloalkanes, unless large steric effects are operating.[3] For example, elimination from 4,5-dichlorooctane in *t*-BuOK–benzene is an anti process, despite the fact that this base–solvent system is more prone than *t*-BuOK–*t*-BuOH to promote syn processes. Thus it appears that the presence of a β-phenyl group in a dihaloalkane increases the propensity of the system toward syn elimination.[4] This conclusion is somewhat surprising since it is reported[3] that a β-phenyl group in an alkyl monohalide decreases the amount of syn elimination. An explanation of this apparent contradiction is offered below.

Scheme I



The proportion of syn elimination increases when fluorine replaces chlorine as the leaving group, as shown by the data for HCl and HF elimination from 1 and 2, in accord with previous observations.[3]

The reaction stereochemistry is also significantly affected by the nature of the halogen that acts as the β substituent. Thus syn elimination is more important when the β halogen is chlorine (HF elimination from 2) than when it is fluorine (HF elimination from 3). As expected,[3] in all cases the addition of 18-crown-6 decreases the proportion of syn elimination (Table II).

The values of the leaving group effect (k_{Cl}/k_F) for the elimination processes are shown in Tables I and II. In-

(3) Bartsch, R. A.; Zavada, J. *Chem. Rev.* **1980**, *80*, 454–494.
(4) Although an α-phenyl group is also present, this structural feature should make the departure of the leaving group easier and consequently should favor an anti process.

terestingly, in *t*-BuOK–*t*-BuOH, when chlorine is the β halogen, the k_{Cl}/k_F value for syn elimination is significantly smaller than unity (0.1). Thus in this process fluorine is a better leaving group than chlorine, as has been observed in the syn eliminations from 1,2-dihaloacenaphthenes (k_{Cl}/k_F = 0.24)[1] and 2,3-dihalo-2,3-dihydrobenzofurans (k_{Cl}/k_F = 0.1).[2] Since an $(ElcB)_I$ mechanism was indicated for the reactions of the latter systems, it is likely that the same pathway is followed in the *t*-BuOK-promoted HCl and HF syn eliminations from **1** and **2**.

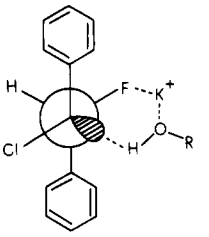
It is worth noting that this finding adds to previous results[1,2,5] in providing evidence against the recent proposal[6] that halides might stabilize a β-halo carbanion by a hyperconjugative effect. Indeed, the hyperconjugative effect would have led to a result, $k_{Cl}/k_F > 1$, opposite to that observed.[6b] Moreover the benzylic carbanion formed from a dihalodiphenylethane should be highly localized and pyramidal.[7] Therefore the absence of a β-halogen hyperconjugative effect cannot be due to a high delocalization of the negative charge into the aromatic ring, which drastically reduces the requirement for the operation of such an effect, as suggested for the planar cyclic carbanions formed in the 1,2-dihaloacenaphthenes, 2,3-dihalo-2,3-dihydrobenzofurans, and fluorenes.[8]

If the similarity between cyclic and acyclic β-aryl-activated dihalides applies to substrates with fluorine as the β substituent, an $(ElcB)_I$ mechanism should hold for the syn HF elimination from **3** in *t*-BuOK–*t*-BuOH since this mechanism has been indicated for the syn eliminations from *trans*-1,2-difluoroacenaphthene and *trans*-2,3-difluoro-2,3-dihydrobenzofuran in the same base–solvent system.[1,2] However, syn elimination of HF from **3** is only 340-fold slower than that from **2**. This factor (the chlorine:fluorine β-halogen effect) is much smaller than that observed (ca. 2- 10^4) for the structural analogues in the $(ElcB)_I$ HF syn eliminations from 1,2-dihaloacenaphthenes and 2,3-dihalo-2,3-dihydrobenzofurans.[1,2] This difference may be related to the different degree of charge delocalization in cyclic and acyclic carbanions, rather than to a different mechanism of elimination, since the capacity of chlorine to stabilize a β-halo carbanion is much greater when the carbanion is planar than when it is pyramidal.[9] Nevertheless, we feel that an E2 mechanism for the eliminations from **3** cannot be excluded at present.

The values of k_{Cl}/k_F are significantly larger than unity in the anti elimination from 1,2-dihalo-1,2-diphenylethanes, as was found in the corresponding reactions of dihaloacenaphthenes (k_{Cl}/k_F between 30 and 56).[10] An E2 mechanism can certainly be suggested, at least for the processes involving loss of HCl.

In the presence of 18-crown-6 (Table II) the anti elimination exhibits a "normal" but small k_{Cl}/k_F value (3.0). An E2 process is again possible for HCl elimination, but an $(ElcB)_I$ mechanism is more probable for HF elimination. Our recent work has shown that the addition of a crown ether can induce an E2 → $(ElcB)_I$ mechanistic shift.[2]

Our reasoning leads to the conclusion that in *t*-BuOK–*t*-BuOH a stepwise process is possible only for syn elimination. This conclusion can be rationalized by assuming that the carbanion involved in the syn process is very stable and has a high energy barrier for decomposition because of (1) the favorable coordination between the base counterion and the leaving group[11] as indicated in structure I



and (2) the lone pair not being conveniently situated for the expulsion of the leaving group. These factors are not present in the carbanion involved in the anti elimination, hence the carbanion has no significant lifetime and the anti process proceeds by a concerted mechanism.

An $(ElcB)_I$ mechanism for the syn elimination from **1** may explain the previously noted different stereochemical behavior of this substrate compared with unactivated dihalides, and account as well for the different effects of a β-phenyl group in a vicinal dihalide and in an alkyl monohalide. Accordingly, the introduction of a β-phenyl group may cause the E2 → $(ElcB)_I$ shift, which promotes syn elimination, only when the substrate is a 1,2-dihalide, where there is a β halogen that can contribute to the stabilization of the negative charge in the intermediate carbanion.

Experimental Section

Melting points were measured with a Buchi 510 electrothermal apparatus and are uncorrected. ^1H NMR spectra were recorded with a JEOL C-60 HL spectrometer. GLC analyses were performed on a Model G1 Carlo Erba gas chromatograph. Kinetic experiments were carried out on a Beckman DB-GT spectrophotometer.

Materials. *trans*-Stilbene, 1,2-diphenylacetylene, and 18-crown-6 ether were commercial materials (Fluka); the last was purified by crystallization from *n*-hexane. *tert*-Butyl alcohol (Erba RPE) was purified and dried as previously described.[1] Solutions of alkoxide were prepared by reacting freshly cut potassium with the alcohol under nitrogen.

***meso*-1,2-Dichloro-1,2-diphenylethane** (**1**) was prepared as described by Cristol and Bly: mp 194–195 °C; (lit.[12] mp 194.5–195.5 °C).

***erythro*-1-Chloro-2-fluoro-1,2-diphenylethane** (**2**) was prepared by reaction of *erythro*-2-fluoro-1,2-diphenylethan-1-ol[13] with $SOCl_2$ as described by Jullien:[14] mp 84–85 °C; ^1H NMR ($CDCl_3$) δ 5.03 (1 H, dd, $^3J_{HF}$ = 14.3, $^3J_{HH}$ = 6.0, ArCHCl) 5.68 (1 H, dd, $^2J_{HF}$ = 45.1, $^3J_{HH}$ = 6.0, ArCHF), 7.3 (10 H, m, Ar H).

***meso*-1,2-Difluoro-1,2-diphenylethane** (**3**) was prepared by following the procedure described by Olah.[15] A mixture of meso and *d,l* difluorides was obtained from which the *meso* isomer was isolated by HPLC chromatography; mp 101–102 °C (lit.[16] mp 98–99 °C).

(*E*)- and (*Z*)-α-Chlorostilbenes (**4**) were prepared by sodium hydroxide induced dehydrochlorination in ethanol of *meso*- and

(5) Corey, E.; More O'Ferral, R. A.; Vernon, N. M. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1581–1586.
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(7) Koch, H. F.; Koch, J. G.; Koch, N. H.; Koch, A. S. *J. Am. Chem. Soc.* **1983**, *105*, 2388–2393.
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(9) Streitwieser, A.; Mares, F. *J. Am. Chem. Soc.* **1968**, *90*, 2444–2445.
(10) Much larger k_{Cl}/k_F values are observed in anti eliminations from *cis*-2,3-dihalo-2,3-dihydrobenzofurans.[2] The reasons for this phenomenon are not clear. It is possible that the reactivity of this system is enhanced by the interaction between the two cis halogens and the lone pair (as also shown by the particularly high anti/syn reactivity ratios) and that this interaction is stronger in the dichloro than in the chlorofluoro compound.
(11) Hunter, D. H.; Shearing, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 8333–8339.
(12) Cristol, S. J.; Bly, R. S., Jr. *J. Am. Chem. Soc.* **1960**, *82*, 142–145.
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(16) Barton, D. H. R.; Hesse, R. H.; Jackman, G. P.; Ogunkoya, L.; Pechet, M. M. *J. Chem. Soc., Perkin Trans. 1* **1974**, 739–742.

d,l-1,2-dichloro-1,2-diphenylethane, respectively. (*E*)-**4**: bp 111–113 °C mp (0.5 mmHg) (lit.[17] bp 97–99 °C (0.25 mmHg)). (*Z*)-**4**: mp 52–53 °C (lit.[17] mp 52–54 °C).

(*E*)- and (*Z*)-Fluorostilbenes (6) were obtained by dehydrofluorination of a mixture of *meso*- and *d,l*-1,2-difluoro-1,2-diphenylethanes with potassium *tert*-butoxide in *tert*-butyl alcohol. The two fluoroolefins were isolated by column chromatography on SiO_2 after elution with petroleum ether and identified by ^1H NMR spectroscopy.[16,18]

Kinetic Study. Kinetic experiments were carried out by following the appearance of the reaction products spectrophotometrically at 284–290 nm and by using the procedure described elsewhere.[1] The concentration of the substrate was in the range of 5.0×10^{-5}–9.0×10^{-5}.

Product analyses were performed by following the procedure previously described. The concentration of the base was the same as in the kinetic studies, and that of the substrate was in the range of 5×10^{-3}–6×10^{-3} M. The reaction products were analyzed by GLC on a 1.0 × 0.002 m column packed with 20% LAC 728 on 60–80-mesh Chromosorb W at 150 °C. The olefins **4** and **6** had the same molar response. The molar response of **5** was 1.05 with respect to that of the olefins. The retention times of (*E*)-**4**, (*Z*)-**4**, (*E*)-**6**, (*Z*)-**6**, and **5** were 29, 88, 13, 50, and 42 min, respectively (N_2 carrier gas at 15 mL/min). Under these conditions no thermal isomerization of the olefins was observed. Moreover, the (*E*)-halostilbenes were recovered unchanged following exposure to the reaction conditions.

H–D Exchange Experiments. *tert*-BuOK in *tert*-BuOD (0.5 mL) was added to a known amount of **2** or **3** (the base:substrate molar ratio was 0.5) and the mixture was analyzed by ^1H NMR. When the reaction was complete the pattern of the aliphatic protons of the starting material was unchanged, thus showing no appreciable deuterium incorporation in the substrate.

Acknowledgment. Thanks are due to the Italian National Council of Research (CNR) and the Ministero della Pubblica Istruzione for financial support.

Registry No. **1**, 15951-99-2; **2**, 39600-82-3; **3**, 14090-31-4; (E)-**4**, 948-98-1; (Z)-**4**, 948-99-2; (E)-**6**, 671-19-2; (Z)-**6**, 671-18-1.

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Structure of Brianthein W, from the Soft Coral *Briareum polyanthes*[1]

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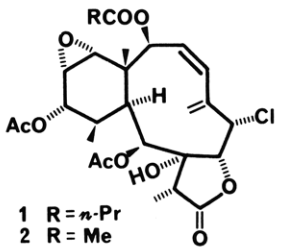
In the course of purifying briantheins Y and Z (**1** and **2**)[2] by HPLC, we encountered a modest amount of a tan



(1) Contribution No. 935 from the Bermuda Biological Station.

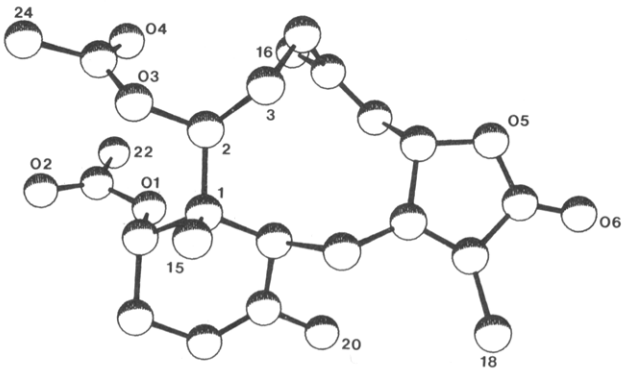


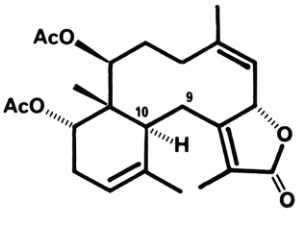
Figure 1. Computer-generated perspective drawing of brianthein W. Hydrogens are omitted for clarity and no absolute configurations is implied.

solid. ^1H NMR analysis of this material suggested an isoprenoid constituent seemingly quite different from the aforementioned diterpenes. Crystallization from either acetone–isooctane or dichloromethane–hexane gave large rectangular prisms, mp 205–209 °C. Additional quantities of this new compound were obtained from the carbon tetrachloride soluble extracts (in all, about 0.4% of the total organic solubles).

High-resolution mass spectrometry established the molecular formula of the new entity as $C_{24}H_{32}O_6$, and major fragments at m/z 356 and 296 were in accord with the two acetate groups expected after examination of the ^1H NMR spectrum. The infrared spectrum indicated the absence of hydroxyl groups, but a carbonyl stretch at 1750 cm^{-1} and λ_{max} 228 nm (ϵ 7500) indicated an α,β-unsaturated γ-lactone, thereby accounting for the remaining oxygen atoms. The ^{13}C NMR spectrum indicated three olefinic bonds, two trisubstituted and the other fully substituted; therefore, two carbocyclic rings had to be incorporated into the structure.

The ^1H NMR spectrum corroborated our initial assessments—two acetates, two olefinic protons, three methines bearing heteroatoms, three vinyl methyls, and a quaternary methyl—but shed no conclusive light on the structure. Almost all the signals were broadened by small couplings and the extensive overlap of signals precluded successful decoupling experiments and assignment of couplings and the associated coupling constants. Decoupling and 2D/*J*-resolved NMR experiments did establish that the protons at δ 2.85, 2.68, and 2.50 were mutually coupled in an AMX array (the protons on C-9 and C-10).

These conclusions and the supposition that we had encountered another compound possessing the briaran skeleton, but one strikingly different from the other briantheins[2] or briarein A,[3] led us to consider structure **3**



3

for this compound, for which we propose the trivial name

(2) (a) Grode, S. H.; James, T. R.; Cardellina, J. H., II. *Tetrahedron Lett., 1983, 24*, 691. (b) Grode, S. H.; James, T. R., Jr.; Cardellina, J. H., II; Onan, K. D. *J. Org. Chem.* **1983**, *48*, 5203.
(3) Burks, J. E.; van der Helm, D.; Chang, C. Y.; Ciereszko, L. S. *Acta Crystallogr., Sect. B.* **1977**, *B33*, 704.

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