Figure 1. Stereoscopic view of 4c.

formulas **4b**, **4c** and **5b**, **5c**, respectively.[8-10] Our subsequent preparation[11] of (−)-13-epirimuane (**8a**) from **4b** and of (−)-rimuane (**8b**) from **4c** by a method which leaves C-5 untouched confirmed the C-8 stereochemistry attributed to **4b** and **4c**, but did not furnish independent proof for the stereochemistry assigned to C-5 since the mode of hydrogenation of (−)-rimuene (**9**), which also furnishes **8b**, is difficult to predict.[12] Nevertheless, it has been generally accepted that H-5 is β.

In a recent publication, ApSimon and co-workers[14] claim that ^{13}C NMR shift data and spin lattice relaxation time measurements require revision of the previously accepted formula **4c** for the γ-lactone from dihydroisopimaric acid (**6**) to **7** with a cis-A/B ring junction, but agree with structure **5c** for the corresponding δ-lactone. Presumably, their conclusions also apply to the γ- and δ-lactones from **2a** and **2b**.[15] It is difficult to imagine how the equilibrium between γ- and δ-lactones can involve epimerization at C-4 if compounds of type **3** can serve as precursors of the γ-lactones.

In view of the mechanistic problem and our interest in cationic rearrangements of diterpenes, we decided to settle the stereochemistry of the γ-lactones once and for all by X-ray crystallography. Our results on the γ-lactone from dihydroisopimaric acid show, contrary to the conclusions reached by the Canadian workers,[14] that this substance possesses structure **4c**, in accordance with the arguments used originally[3,4] to rationalize the rearrangement of **1a**. We infer that the γ-lactones from **2a** and **2b** also possess a trans-A/B ring junction. As a corollary, the hydrogenation of (−)-rimuene results in what appears to be addition of hydrogen from the more hindered β face.[12]

Crystal data for **4c** are listed in the Experimental Section. The crystal contained two independent molecules, in one of which (unprimed), due to thermal motion or disorder, C-16 was not well defined. Figure 1 is a stereoscopic drawing of the second (primed) molecule, which shows that the A/B ring junction is trans, with H-5 β and H-8 α. Tables I and II, containing final atomic and anisotropic thermal parameters, and Tables III, IV, and V, listing bond lengths, bond angles, and selected torsion angles, are available as supplementary material. Since the crystal contained two independent molecules of **4c**, the tables of distances and angles contain two values for each entry.

Experimental Section

Dihydroisopimaric acid was lactonized[16] by a slight modification of the literature method[9] by keeping it with sulfuric acid at −8 °C for 45 min and quenching with water. Extraction with ether, chromatography over silica gel, and elution with benzene gave **4c**, mp 107.5–108 °C, after recrystallization from aqueous methanol. Slow recrystallization from methanol furnished single crystals which were monoclinic, space group $P2_1$, with $a = 11.775$ (1) Å, $b = 12.450$ (1) Å, $c = 12.859$ (2) Å, $\beta = 104.68$ (1)°, and $d_{calcd} = 1.109$ g cm^{-3} for $Z = 4$ ($C_{20}H_{32}O_2$, M_r 304.47). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse height discrimination). A crystal measuring approximately 0.15 × 0.25 × 0.45 mm was used for data collection; the data were not corrected for absorption (μ = 5.4 cm^{-1}). Of the 3851 accessible reflections for θ < 76°, 2763 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by a multiple solution procedure[17] and was refined by block-diagonal least squares in which the matrix was par-

titioned into two blocks. In the final refinement, anisotropic thermal parameters were used for the heavier atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations, but their parameters were not refined. Eleven low θ reflections were strongly affected by extinction and were not included in the refinement. The final discrepancy indices are $R = 0.051$ and $wR = 0.052$ for the remaining 2752 observed reflections. The final difference map has no peaks greater than ±0.2 e Å^{-3}.

Registry No.—**4c**, 59751-40-5; **6**, 5835-26-7.

Supplementary Material Available: Tables I–V listing final atomic and anisotropic thermal parameters, bond lengths, bond angles, and selected torsion angles (7 pages). Ordering information is given on any current masthead page.

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Methyl Effect in Electrophilic Additions. An Open Carbonium Ion Like Rate-Determining Transition State for the Bromination of Styrene

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Whereas bromination of aliphatic alkenes goes through bromonium ions,[1] open carbonium ion like transition states

Table I. Rate Constants (M^{-1} s^{-1}) for Electrophilic Additions to Aliphatic and Aromatic Methyl Substituted Olefins at 25 °C

compd	registry no.	$k_2(Br_2)$ in AcOH[a]	$k_2(Br_2)$ in MeOH[a,f]	$k_2(ArSCl)$ in TCE[b]	$k_2(Ar'SCl)$ in AcOH[c]
$C_6H_5CH{=}CH_2$	100-42-5	8.9^d	1.53×10^3 [i]	62^l	7.5×10^{-4} [n]
$C_6H_5(Me)C{=}CH_2$	98-83-9	3.87×10^3 [e,f]	1.38×10^5 [i]	265^l	4.1×10^{-3} [o]
cis-$C_6H_5CH{=}CH$-Me	766-90-5	$6.4^{e,f}$	7.93×10^2 [j]	43^l	3.4×10^{-4} [n]
$trans$-$C_6H_5CH{=}CH$-Me	873-66-5	$22^{e,f}$	3.23×10^3 [i]	118^l	1.45×10^{-3} [n]
$MeCH{=}CH_2$	115-07-1	17.6^d	4.03×10^2 [k]	205^l	1.5×10^{-3} [p]
$Me_2C{=}CH_2$	115-11-7	1510^g	3.72×10^4 [e]	550^l	4.6×10^{-3} [o]
cis-$MeCH{=}CHMe$	590-18-1	1230^g	2.38×10^4 [k]	1340^l	2.6×10^{-2} [o]
$trans$-$MeCH$-$CHMe$	624-64-6	940^g	1.30×10^4 [k]	434^l	2.9×10^{-3} [o]
t-$BuCH{=}CH_2$	558-37-2	10.2^g	9.57×10^k	95^m	
t-$BuMeC{=}CH_2$	594-56-9	630^h	6.58×10^3 [j]	147^m	
cis-t-$BuCH{=}CHMe$	762-63-0	1020^g	1.11×10^4 [j]	1029^m	
$trans$-t-$BuCH{=}CHMe$	690-08-4	300^g	1.72×10^3 [j]	162^m	

[a] Rate constants for free bromine addition only. [b] TCE = tetrachloroethane, ArSCl-p-ClC$_6$H$_4$SCl. [c] Ar'SCl is 2,4-(NO$_2$)$_2$C$_6$H$_3$SCl. [d] Reference 4. [e] This work. [f] k_{Br_2} is obtained by extrapolation of the function $k_{exp}(1 + K[Br^-])$ to $[Br^-] = 0$ from experimental rate constants k_{exp} measured at several bromide ion concentrations.[7] [g] k_{Br_2} measured directly in absence of bromide ions: A. Modro, G. H. Schmid, and K. Yates, *J. Org. Chem.*, **42**, 3673 (1977). [h] Extrapolated from the relationship between data in methanol and in acetic acid. [i] Reference 14. [j] M. de Ficquelmont, Doctoral Thesis, CNRS No. A08355, Paris, 1973. [k] E. Bienvenue-Goetz and J. E. Dubois, *Tetrahedron*, **34**, 2021 (1978). [l] Reference 6. [m] G. H. Schmid and T. T. Tidwell, *J. Org. Chem.*, **43**, 460 (1978). [n] Reference 9. [o] G. Collin, U. Jahnke, G. Just, G. Lorenz, W. Pritzkow, M. Röllig, and L. Winguth, *J. Prakt. Chem.*, **311**, 238 (1969). [p] Extrapolated from the relationship between data in acetic acid and in tetrachloroethane for sulfenylation.

Table II. Methyl Effects in Electrophilic Additions to Olefins, RCH=CH$_2$ (α-M = $k_{\alpha\text{-Me}}/k_H$, cis-β-M = $k_{cis\text{-}\beta\text{-Me}}/k_H$, $trans$-β-M = $k_{trans\text{-}\beta\text{-Me}}/k_H$)

R	bromination[a] in AcOH α-M	cis-β-M	$trans$-β-M	in MeOH α-M	cis-β-M	$trans$-β-M	sulfenylation[a,f] in TCE α-M	cis-β-M	$trans$-β-M	hydration[b] α-M	cis-β-M	$trans$-β-M
Ph	435^c	0.7^c	2.5^c	90	0.5	2.1	4.27	0.69	1.91	297^e		0.34
Me	86	70	53	92^d	59^d	32^d	2.7	6.5	2.1	7500	1.68	0.71
tBu	62	100	30	69	116	18	1.55	10.8	1.7			

[a] From rate constants of Table I. [b] From ref 6. [c] In ref 6, the values given (60.7, 0.8, and 1.1, respectively) refer to bromination in acetic acid (0.1 M LiBr) where Br$_2$,Br$_3^-$ and Br$_2$, add competitively to olefins. [d] In ref 6, values given (89, 43, and 28, respectively) are for bromination in methanol (0.2 M NaBr). [e] In ref 6, this value is given incorrectly as 1070. [f] For sulfenylation in AcOH, see ref 13.

and intermediates are involved in styrene bromination.[2] This statement is based on two reliable arguments. Identical ρ^+ values[3,4] for ring substituent effects in styrene bromination and in *tert*-cumyl chloride solvolysis demonstrate that the charge distribution in the rate-determining transition state is carbonium ion like. Nonstereospecific bromination of β-methylstyrenes[5] shows that the intermediate is not bridged.

Nevertheless, the kinetic effects of methyl substituents in styrene bromination have recently been considered to more closely resemble those in sulfenylation via bridged intermediates than those in hydration via open cations.[6] Consequently, it is claimed[6] that styrene bromination goes through a bridged rate-determining transition state.

Faced with this contradiction, we have examined an enlarged corpus of data on methyl effects and have corrected previous values.[6] In particular, for bromination in protic solvents, the overall experimental rate constants cannot be used in the interpretation of the methyl effects because they include rate constants for both free bromine and tribromide ion additions. These various rate constants, k_{exp}, k_{Br_2}, and $k_{Br_3^-}$, are interrelated by the equation[7]

$$k_{exp}(1 + K[Br^-]) = k_{Br_2} + Kk_{Br_3^-}[Br^-] \qquad (1)$$

We have therefore measured and will discuss the elementary rate constants for free bromine addition only. Our results are given in Tables I and II.

The kinetic effect of a methyl group measures the charge carried, in the transition state, by the carbon atom to which it is attached. Consequently, the relative values of the α and

β effects, insofar as they indicate the symmetry of the charge distribution, are diagnostic of bridging in the transition state.

Applying this principle to α-M and *trans*-β-M ratios of Table II leads to the following conclusions. In hydration, a large α effect[8] associated with a small β effect shows that the transition state has an open carbonium ion like structure, whatever the substituent R. In sulfenylation,[9] the α and β effects are both small: either the transition state is very early or all the charge is carried by the bridging sulfur atom. In bromination, both α and β effects are large when R is alkyl; the transition states are bromonium ion like, as is already known.[1] On the other hand, when R is phenyl, we find a situation identical to that for hydration with a large α effect[3,4] and a small β effect.[10] Consequently, the transition state for styrene bromination is really carbonium ion like and the methyl effect is not in contradiction with previous kinetic and stereochemical evidence.

The $k_{\alpha\text{-M}}/k_{trans\text{-}\beta\text{-M}}$ ratio for bromination (55) is alleged[6] to be closer to that of sulfenylation (2.2) than that for hydration (3150). However, when the *correct* ratios for bromination (174 or 43 depending on the solvent) and hydration (870) are considered, bromination resembles neither extreme. The difference between sulfenylation and bromination lies simply in the α effects just discussed. Second, the difference between bromination and hydration is not caused by variation in transition state bridging but by a β effect of a different type. In bromination, the β effect (2.1) is slightly greater than unity and corresponds to the normal polar effect of a methyl group in the β position.[10] In hydration, this effect (0.3) is less than

unity, perhaps because of a decrease in hyperconjugative stabilization when a β-hydrogen is replaced by a methyl group.[11]

Moreover, the methyl effects depend on the solvent for sulfenylation[13] and bromination (Table II) and on the acidity for hydration.[8,12] These ratios are also very sensitive to steric factors, as is shown by the effect of a *cis*-β-methyl or a *tert*-butyl group, and this sensitivity depends on the size of the entering electrophile. These observations do not detract from the methyl effect method but underline that strict control of reaction parameters is essential. A critical application of this method, based on a comparison of ring substituent effects on styrene and α-methylstyrene bromination and designed to detect eventual bromine bridging, is in progress.[14]

Experimental Section

Bromination Kinetics. Two different methods both using TFCR-EXSEL conditions (very low concentrations in reagents—salt excess) have been used: couloamperometry[15] for rate constants above 5×10^3 M^{-1} s^{-1} and spectroscopy[16] for rate constants below this limit. In the couloamperometric method, bromine is produced in situ by electrolysis of NaBr; its uptake is followed by the decrease in the bromine diffusion current between two Pt electrodes. Second-order conditions (first order in bromine and in olefin) are used: the bromine concentration is in the range 10^{-5}–10^{-7} M and the initial olefin concentration is approximately half this. In the UV spectroscopic method, bromine (10^{-3}–10^{-4} M overall) is syringed into the reaction cell and its consumption is followed by the absorbance change at a fixed wavelength (280–320 m).

In both methods, reproducibility is within 2%.

Rate Constants for Free Bromine Addition. In acetic acid and in methanol, direct measurement of these constants in the absence of bromide ion is not possible for technical reasons: in couloampero-metry, a bromide salt is necessary to produce bromine; in spectros-copy, the absorption coefficient of free bromine is too small for ac-curate determinations in very dilute solutions. Moreover, bromide ions are produced during the bromination in the reaction pathway leading to solvent incorporated products. These ions give, via the equilibrium

$$Br_2 + Br^- \overset{K}{\rightleftharpoons} Br_3^-$$
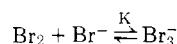
the electrophilic tribromide ions addition which competes with that of free bromine. This time-dependent competition leads to erratic kinetics. Consequently, rate measurements are always made with an excess of bromide ion. Free bromine rate constants are, then, obtained by means of eq 1 from k_{exp} measured at several bromide ion concen-trations. Plotting $k_{exp} (1 + K[Br^-])$ against $[Br^-]$ gives a straight line whose origin is k_{Br_2}.

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Heterocycles from Ketenimines. 12.[1] Pyrrolo[3,2-*b*]pyridines

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The cycloadducts formed from the reactions of pyridine-*N*-imines and 1,3-dipolarphiles usually are unstable and un-dergo rapid dehydrogenation to the aromatic pyrazolopyridine system **2**.[2] We now describe the reaction of pyridine-*N*-imines with triarylketenimines.
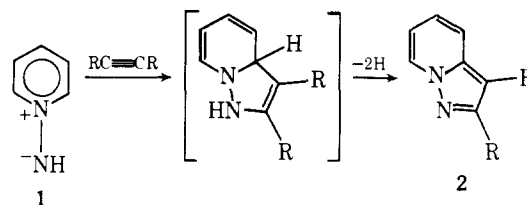
From the reaction of equimolar concentrations of **1** and diphenylketene-*N*-*p*-tolylimine (**3**) was isolated a 54% yield of a bright orange solid **4**. Structural assignment of **4** as 2,3-
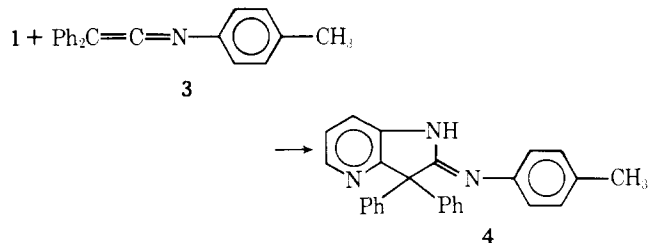
dihydro-3,3-diphenyl-2-(*p*-tolylimino)-1*H*-pyrrolo[3,2-*b*]-pyridine is based on composition: IR absorption at 1590 cm^{-1} (imine stretch); NMR absorptions at δ 2.28 (methyl group) and 7.0–8.5 (the aromatic protons and the amidine N–H); and MS fragments at *m/e* 375 (parent ion), 244 (**5**), and 167 (**6**).
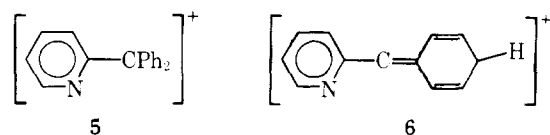
Chemical evidence to support the assigned structure of **4** was obtained from two reactions. Hydrolysis of **4** with hot sulfuric acid gave 3,3-diphenyl-4-azaoxindole (**7**) and *p*-to-luidine. This azaoxindole was identified by IR (absorption at 1665 cm^{-1} for the amide carbonyl), NMR (absorptions from δ 7.0–8.5 for the aromatic and the amide N–H protons),