It appears that the condensation of citral with olivetol under acidic conditions gives an initial mixture of the Δ^1 isomers (**1** and **4**) which then rearrange to the Δ^6 isomers, with **1** rearranging more readily than **4**. In confirmation of this assumption, we have been able to show that **4** is indeed isomerized by boron trifluoride etherate to **5**; it is known that **1** isomerizes similarly under milder acidic conditions to **3**.[4] Separation of the natural Δ^1-3,4-*trans* isomer (**1**) from the Δ^1-3,4-*cis* isomer (**4**) by chromatography was not possible in our hands; separation by vpc was frustrated by facile thermal isomerization of **1** to **3**. We could show independently that pure **1**[8] was partially converted to **3** after one pass through a vapor phase partition chromatograph (column, 10% GE-SE30 on Diatoport S; gas, helium; oven temperature, 280°). Indeed, in view of this demonstrably facile heat isomerization, it seems possible that the physiological effects attendant upon smoking of hashish, now ascribed to the Δ^1 isomer, may in actuality be due to the Δ^6 isomer.

(8) We are indebted to Professor W. A. Mosher and Mr. R. Hively for a generous sample of pure **1**, isolated from hemp.

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A Method for Relating Rates of Interconversion and Destruction of Classical Carbonium Ions[1]

Sir:

How fast do equilibrating, classical ions interconvert with respect to the rates with which they react with entering groups or eject protons? This question goes to the heart of the debate[2-5] over nonclassical ions. Cram[3] implies, without saying why, that a factor of 100 in favor of phenyl migration would be too great for acetolysis, through classical ions, of *threo*-3-phenyl-2-butyl tosylate. Winstein[2] argues that a factor of 2000 in favor of interconversion of classical norbornyl ions would cause the rate of interconversion to exceed kT/h in the absolute rate equation.

The question is not easily answered, for we seek a ratio of two rates, the absolute values of which are unknown, and which can, conceivably, fluctuate over wide ranges. In addition, a determination of this ratio by ordinary[6] means strains the limits of experimental error for normal polarimetric, stoichiometric, or isotopic tracer techniques.

We attacked the problem first by studying reactions which are known[7] to proceed through equilibrating, classical ions, and outline here an approach which circumvents the need for extraordinary experimental precision.

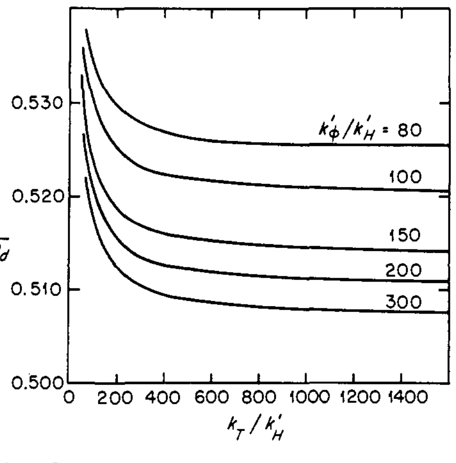
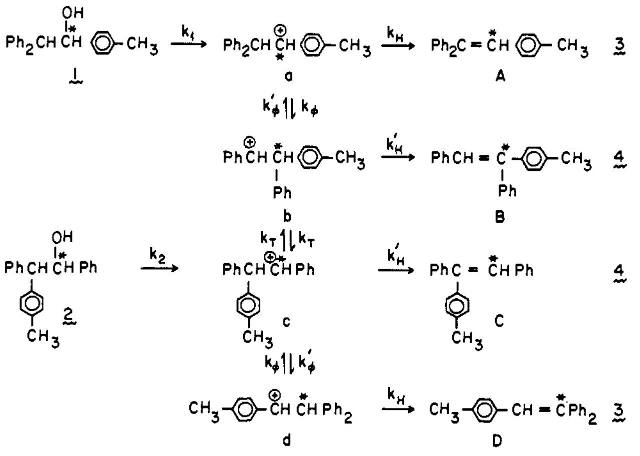


Figure 1. Plot of carbon-14 distribution in **3** *vs.* $k_\mathrm{T}/k'_\mathrm{H}$ (Chart I) in the reaction **1** → **3** (76.0%) and **4** (24.0%).

Chart I



Dehydration of either 1-*p*-tolyl-2,2-diphenylethanol (**1**) or 1,2-diphenyl-2-*p*-tolylethanol (**2**, *erythro* or *threo* forms) in boiling formic acid (containing a trace of *p*-toluenesulfonic acid) produces the olefins **3** and **4** (two geometrical isomers obtained in equal amounts) in yields of 76.0 and 24.0%, respectively. By the use of a carbon-14 label, the four ions a–d (Chart I) can be recognized, and these go irreversibly to olefins **3** and **4** through paths A–D.[8] By a method previously reported,[4] eq 1–4 were derived. These

$$\frac{k_\phi}{k_\mathrm{H}}m_\mathrm{a} + \frac{k_\mathrm{T}}{k'_\mathrm{H}}m_\mathrm{c} = m_\mathrm{b}\left[\frac{k'_\phi}{k'_\mathrm{H}} + \frac{k_\mathrm{T}}{k'_\mathrm{H}} + 1\right] \tag{1}$$

$$\frac{k_\mathrm{T}}{k'_\mathrm{H}}m_\mathrm{b} + \frac{k_\phi}{k_\mathrm{H}}m_\mathrm{d} = m_\mathrm{c}\left[\frac{k_\mathrm{T}}{k'_\mathrm{H}} + \frac{k'_\phi}{k'_\mathrm{H}} + 1\right] \tag{2}$$

$$\frac{k'_\phi}{k'_\mathrm{H}}m_\mathrm{c} = m_\mathrm{d}\left[\frac{k_\phi}{k_\mathrm{H}} + 1\right] \tag{3}$$

$$\frac{k_\phi}{k_\mathrm{H}}(m_\mathrm{a} + m_\mathrm{d}) = (m_\mathrm{b} + m_\mathrm{c})\left[\frac{k'_\phi}{k'_\mathrm{H}} + 1\right] \tag{4}$$

equations exactly describe the mechanism given in Chart I for the dehydration of **1**. Equation 4 relates the ratio $k'_\phi/k'_\mathrm{H}:k_\phi/k_\mathrm{H}$ to the yields of the two olefins, and the extent of carbon-14 rearrangement in **3** and **4** determines the mole fractions m_a, m_b, m_c, m_d

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(1) This research was sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(2) S. Winstein, *J. Am. Chem. Soc.*, **87**, 381 (1965).

(3) D. J. Cram, *ibid.*, **86**, 3767 (1964).

(4) C. J. Collins, B. M. Benjamin, and M. H. Lietzke, *Ann.*, **687**, 150 (1965).

(5) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Am. Chem. Soc.*, **87**, 2137 (1965).

(6) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *ibid.*, **87**, 376 (1965), for example, measured the racemization of *exo*-norbornyl acetate with a precision they state to be within ±0.05%.

(7) C. J. Collins and W. A. Bonner, *ibid.*, **77**, 92, 6725 (1955).

(8) Although the ions a–d yield formate esters reversibly, all functions describing these processes cancel in the derivation of eq 1–4.

(formed through paths A, B, C, and D), as well as the lower limits for k'_ϕ/k'_H and k_ϕ/k_H.

Given in Figure 1 is a plot (obtained by use of a computer program for the IBM 7090) of k_T/k'_H *vs.* $m_a/(m_a + m_d)$ for various values of k'_ϕ/k'_H for olefin yields of 76.0% (**3**) and 24.0% (**4**). Three separate determinations of $m_a/(m_a + m_d)$ (using both C-1 and C-2 labeled **1**) gave values of 0.5080, 0.5074, and 0.5060. Under identical conditions, $m_a/(m_a + m_d)$ after dehydration of **2** was 0.497 (slightly less than 0.500, a finding consistent with the mechanism).[9] The ratio k_T/k'_ϕ can be estimated from several different experiments[10] as 6 or greater. The total error in determining the carbon-14 distribution in **3** is certainly less than ±0.8%, which means that $m_a/(m_a + m_d)$ can be no greater than 0.511. We can thus set the following minimum values for our three ratios: $k_\phi/k_H \geq 63.5$, $k'_\phi/k'_H \geq 200$, and $k_T/k'_H \geq 1200$ (Figure 1).[11]

We are unable at present to relate the rates of proton ejection (k_H and k'_H) to the rates of cation–anion collapse (to yield the formates of **1** and **2**). Since both the olefins and the formates can be isolated from reaction mixtures at lower temperatures, however, we presume that the differences in these rates are not great.

(9) Oxidation of **3** with chromic acid yielded benzophenone and *p*-toluic acid. Olefin **4** upon similar treatment yielded benzoic and *p*-benzoylbenzoic acids. The extent of carbon-14 rearrangements was determined by assay of these degradation fragments. The use of two different labels plus high radiochemical yield reduced error from isotope effects. Yields of the olefins **3** and **4** were determined by integration of the nmr plots to a precision of better than ±1%. The equilibration of label in **4** (from either **1** or **2**) was, within experimental error, complete. Authentic samples of **3** and **4** were stable under the reaction conditions.

(10) We have shown [C. J. Collins, W. T. Rainey, W. B. Smith, and I. A. Kaye, *J. Am. Chem. Soc.*, **81**, 460 (1959), Table II; B. M. Benjamin and C. J. Collins, *ibid.*, **78**, 4332 (1956), Table IV] that the *p*-tolyl/phenyl ratio in compounds similar to **1** and **2** is 6–8 both in cold sulfuric and in formic acids. L. W. Kendrick, Jr., B. M. Benjamin, and C. J. Collins, *ibid.*, **80**, 4057 (1958), Table III, show that the ratio of secondary hydroxyl removal for *erythro*:*threo*-1,2-di-*p*-tolyl-1-phenylethylene-2-^{14}C glycol is 7:1 (sulfuric acid). In formic acid, $k_{tol}/k'_H:k_\phi/k'_H$ for rearrangement of VII and VIII (above reference) is 7.7:1. In the rearrangement in acetic–perchloric acids (0.1–0.86 *N*) of 1-phenyl-2-*p*-tolylethylene-1-^{14}C glycol [B. M. Benjamin, unpublished work] the hydroxyl adjacent to *p*-tolyl is removed in preference to its neighbor in a ratio of 7:1 (*threo* form) and 10:1 (*erythro* form).

(11) If the uncertainty in the yield of olefin **3** is expressed as 76 ± 1%, this corresponds to an error of only ±0.1% in $m_a/(m_a + m_d)$ (determined by a computer calculation using yields of 77.0 and 75.0% for **3**).

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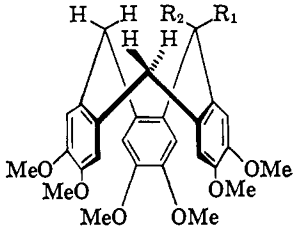
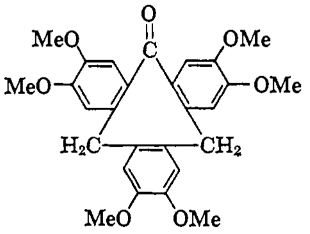
The α- and β-Cyclotriveratrylenols. Isolation of Two Conformational Isomers

Sir:

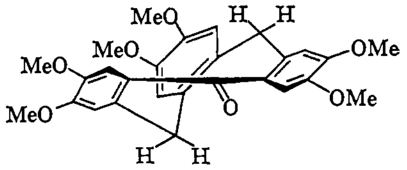
Reduction of the ketone[1] II, derived from cyclotriveratrylene (I) with lithium aluminum hydride followed by a neutral or alkaline workup, gives rise to an alcohol, α-cyclotriveratrylenol (III), whose nmr spectrum in dimethyl sulfoxide shows two one-proton doublets at τ 4.17 and 4.37 (J = 4 cps); on addition of deuterium oxide the signal at higher field disappears and the τ 4.17 signal coalesces to a singlet, as would be expected for a secondary alcohol.[2] Attempted recrystallization of the α-alcohol converts it completely into β-cyclotriveratrylenol (IV), which may also be obtained by lithium aluminum hydride reduction of II followed by an acidic workup. The nmr spectrum of IV in dimethyl sulfoxide also shows two one-proton doublets, this time at τ 3.25 and 4.35 (J = 2.5 cps), and again addition of deuterium oxide causes the higher field signal to vanish and the τ 3.25 doublet to coalesce to a singlet. The nmr spectra of III and IV in deuteriochloroform are quite different (see Table I) although their infrared and ultraviolet spectra are respectively very similar to each other and to those of I. IV gives the correct analysis for $C_{27}H_{30}O_7$ and may be converted to an acetate also showing the expected analytical values and spectral properties. The conversion of III to IV occurs within 24 hr at room temperature or instantly on melting.



Ia, $R_1 = R_2 = H$
b, $R_1 = OH$, $R_2 = H$
c, $R_1 = H$, $R_2 = OH$
d, $R_1 = OEt$, $R_2 = H$



II



V

Thus we have isolated two distinct alcohols of the same structure with no asymmetric center in the molecule, leading us to conclude that they are indeed conformational isomers.

Cyclotriveratrylene has been shown by the work of Lindsey[1] and of Erdtman, *et al.*,[3–5] to possess the "crown" conformation Ia. The ketone II derived from I might also have this conformation, but if it did so, the carbonyl group and the benzene rings would be held rigidly orthogonal. However the ketone has ultraviolet maxima at 238 (log ε 4.50), 284 (4.15), and 326 mμ (4.16) and infrared carbonyl stretch at 1587 cm^{-1}, evidence of strong conjugation. We therefore assign a "flexible" conformation, V, to this ketone (C_2 symmetry), akin to the twist conformation of cyclohexanone. This assignment is confirmed by the nmr spectrum (in pyridine), which shows the methylene protons as a sharp singlet at τ 5.95, as would be expected for a rapidly inverting molecule.

The conformation of the stable β-cyclotriveratrylenol (IV) we assign as being similar to that of I, *i.e.*, "crown" Ib, probably with the hydroxyl group "out" (*cf.* equator-

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(1) A. S. Lindsey, *J. Chem. Soc.*, 1685 (1965); *Chem. Ind.* (London), 823 (1963).

(2) O. L. Chapman and R. W. King, *J. Am. Chem. Soc.*, **86**, 1256 (1964).

(3) H. Erdtman, F. Haglid, and R. Ryhage, *Acta Chem. Scand.*, **18**, 1249 (1964).

(4) (a) A. Goldup, A. B. Morrison, and G. W. Smith, *J. Chem. Soc.*, 3864 (1965); (b) B. Miller and B. D. Gesner, *Tetrahedron Letters*, **38**, 3351 (1965).

(5) The authors of ref 4a and b appear to have been unaware of the paper by Erdtman[3] in which the same data are presented in fuller form.