(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 $k_\mathrm{T}/k'_\mathrm{H}$ *vs.* $m_\mathrm{a}/(m_\mathrm{a} + m_\mathrm{d})$ for various values of k'_ϕ/k'_H for olefin yields of 76.0% (**3**) and 24.0% (**4**). Three separate determinations of $m_\mathrm{a}/(m_\mathrm{a} + m_\mathrm{d})$ (using both C-1 and C-2 labeled **1**) gave values of 0.5080, 0.5074, and 0.5060. Under identical conditions, $m_\mathrm{a}/(m_\mathrm{a} + m_\mathrm{d})$ 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 $m_\mathrm{a}/(m_\mathrm{a} + m_\mathrm{d})$ can be no greater than 0.511. We can thus set the following minimum values for our three ratios: $k_\phi/k_\mathrm{H} \geqq 63.5$, $k'_\phi/k'_\mathrm{H} \geqq 200$, and $k_\mathrm{T}/k'_\mathrm{H} \geqq 1200$ (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.

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[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, $k_\mathrm{tol}/k'_\mathrm{H}:k_\phi/k'_\mathrm{H}$ 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 $m_\mathrm{a}/(m_\mathrm{a} + m_\mathrm{d})$ (determined by a computer calculation using yields of 77.0 and 75.0% for **3**).

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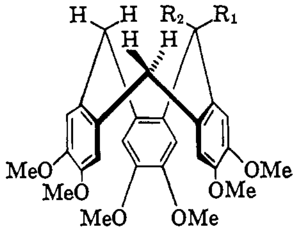
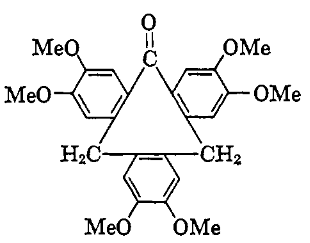
The α- and β-Cyclotriveratrylenols. Isolation of Two Conformational Isomers

Sir:

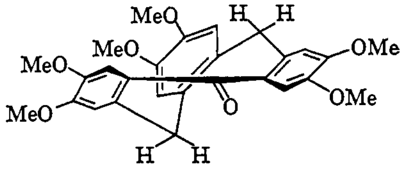
Reduction of the ketone[1] II, derived from cyclotriveratrylene (I) with lithium aluminum hydride followed by a neutral or alkaline workup, gives rise to an alcohol, α-cyclotriveratrylenol (III), whose nmr spectrum in dimethyl sulfoxide shows two one-proton doublets at τ 4.17 and 4.37 (J = 4 cps); on 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).

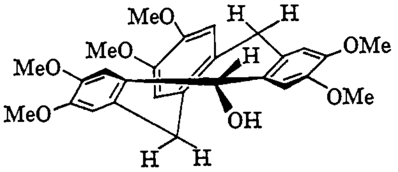
[5] The authors of ref 4a and b appear to have been unaware of the paper by Erdtman[3] in which the same data are presented in fuller form.

Table I. Nmr Spectra of Cyclotriveratrylene Derivatives[a]

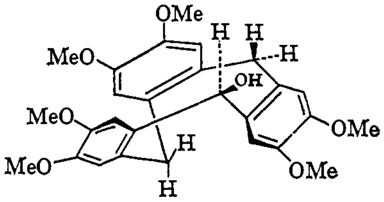
Ia	Ib	Id	III	III, Py[b]	II	II, Py[b]
					2.57 (2) s	
	3.07 (1) s	2.88 (2) s	2.83 (2) s			
3.21 (6) s	3.21 } (6)	3.22 (2) s			3.20 (2) s	
	3.24 }	3.26 (2) s	3.32 (4) s		3.46 (2) s	
		3.59 (1) s				
			3.92 (1) s			
	5.26 (1) OH[g]					
5.36 (2) d[c]	5.35 (2) d[c]	5.29 (2) d[c]		5.53 (2) d[f]		
			5.96[e] }			5.95 (4) s
			} (22)	6.07 (2) d[f]	6.10 (12) s	
6.19 (18) s	6.15 } (18)	6.20 (18) s	6.13 }	6.21 } (18)	6.20 (10) s	6.17 (12) s
	6.18 }		6.24[e] }	6.28 }		6.34 (6) s
		6.46 (2) q[d]				
6.52 (2) d[c]	6.52 (2) d[c]	6.47 (2) d[c]				
		8.71 (3) t[d]				

[a] Figures show, respectively, position in τ (TMS = 10), number of protons, and multiplicity of absorptions (s = singlet, d = doublet, etc.). All spectra were run in deuteriochloroform except where indicated. [b] Py = pyridine solution. [c] AB quartet, J = 14 cps. [d] CH_2 and CH_3 of ethyl group, J = 7 cps. [e] Peaks 1, 2, and 4 of AB quartet visible, J = 15.5 cps. [f] AB quartet, J = 15.5 cps. [g] OH = hydroxyl resonance.

ial), on the basis of its stability and the occurrence of the methylene AB quartet in the nmr spectrum at almost the same position as that in I (see Table I). In the crown conformation of Ia and Ib the geminal coupling of the methylene protons is −14.0 cps (sign assumed), in fair agreement with the dihedral angle, estimated from Dreiding models, between the methylene groups and each adjacent p orbital of the benzene rings (110 ± 5°) after allowance for some opening of the C–CH_2–C angle.[6]



Va



VI

The conformation of the unstable α-cyclotriveratrylenol (III) is still subject to some doubt since two possibilities are open. Either it has the crown conformation Ic with the hydroxyl group "in" (*cf.* axial) (models show this to be an extremely crowded arrangement), or it could have a flexible conformation VI, like V, with the possibility of pseudorotation. Either of these could explain the observed data, but we favor VI as being derived more directly from reduction of V (V → Va → VI) and also on the ease of conversion of III to IV. (Nmr shows no evidence of inversion in cyclotriveratrylene at temperatures up to 200°.)

The sensitivity of the α-alcohol to acid also argues in favor of a flexible conformation; thus after 1 hr in chloroform–30% ethanol with a trace of hydrochloric acid the α-alcohol is converted completely into a mixture of α- and β-cyclotriveratrylenyl ethers (VII and VIII), together with a small amount of IV, whereas after 14 hr under the same conditions the β-alcohol is converted only partially into β-cyclotriveratrylenyl ethyl ether. (The α- and β-ethers exhibit the same behavior as the alcohols, the α being converted into the β form. The nmr spectra indicate that the conformational difference is analagous to that of the two alcohols.)

More conclusive evidence on the conformation of III could be obtained by isolation of a third conformer. We are pursuing this and other aspects of the chemistry of this interesting system.

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[6] M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, **85**, 1899 (1963); J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965).

Anomalous Temperature Dependence in the Electron Spin Resonance Spectrum of Bis(trifluoromethyl) Nitroxide[1]

Sir:

Recently a new stable neutral free radical, bis(trifluoromethyl) nitroxide (I), was prepared by Blackley and Reinhard.[2] They measured its electron spin resonance spectrum in $CFCl_3$ and determined the two hyperfine splittings: a^N = 8.2 gauss and a^F = 9.3 gauss. The unusual feature of this radical is its stability, which Blackley and Reinhard propose is due to the strong electronegative character of the CF_3 groups and possibly some delocalization of the unpaired electron onto the six fluorine atoms. In this note we present evidence which appears to confirm the delocalization mechanism for the fluorine hyperfine splittings. It has been found that both the fluorine and nitrogen hyperfine splittings change in an opposite manner between 163 and 277°K.

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[1] This research was supported in part by the National Science Foundation through Grant No. GP-2836 and by the Graduate School, University of Minnesota.

[2] W. D. Blackley and R. R. Reinhard, *J. Am. Chem. Soc.*, **87**, 802 (1965).