walls of the reaction vessel.[10] A similar adsorption onto the surface of the resin particles may occur. The difference in activity, illustrated in Figure 6, accounts for the lack of micronuclease activity when initially added to DNA–Sephadex (Figure 4). Hence additional enzyme (five times the original amount) was added after 52 min to each resin preparation. The experiments using deoxyribonuclease-I (Figure 5) were performed in the same way so that an exact comparison could be made.

The results of the experiments using Sephadex-trapped DNA (Figures 4 and 5) indicate that DNA–Sephadex-IV (M_e = 58,000 daltons)[16] is easily permeated by both enzymes. DNA–Sephadex-V (M_e = 23,000 daltons) shows greatly reduced permeability to deoxyribonuclease-I, but only slightly reduced permeability to micrococcal nuclease. For DNA–Sephadex-VI (M_e = 5000 daltons) no detectable activity of deoxyribonuclease-I was observed. Micrococcal nuclease, although somewhat reduced in activity, was still active in degrading trapped DNA.

Discussion

The results obtained for the DNA–Sephadex complexes strongly suggest that the biopolymer has been mechanically trapped by *in situ* cross-linking of the dextran, and that by varying the reaction parameters the degree of entrapment can be varied. In principle one should be able to carry out similar reactions with a variety of large molecules. Since numerous methods are known for producing a three-dimensional matrix (either hydrophilic or hydrophobic), it should be possible to select conditions that do not affect the trapped species. It should be possible, for example, to trap a large catalyst (*e.g.*, an enzyme) which could selectively attack only those substrates small enough to diffuse into the resin. This type of experiment would be the reverse of that described in this work, in which the substrate was trapped and enzymes were selectively allowed to diffuse into the resin. An interesting application of this principle would be the removal of molecules whose size is less than M_e, since in a heterodisperse mixture (with respect to molecular weight) smaller molecules could enter the gel, be degraded to very small size, and thus be easily separated from the mixture.

In these studies a specific example of molecular sieve entrapment has been demonstrated, *viz.*, the assay of nucleases of differing molecular weight. However, other applications of the method should be possible. Among these are the slow, controlled release of vaccines, enzymes, drugs, catalysts, or large molecules into the surrounding environment. The basic consideration is that one or more of the reactants be sufficiently greater in size than the others so that the differentially permeable gel can bring about selectivity in the reaction.

(16) The exclusion limits of the DNA–Sephadex preparations were estimated by use of the following empirical relation, which was derived from product literature of Pharmacia Corporation: $\log M_e = 2.14 \log R + 2.68$, where M_e is the exclusion limit in daltons and R is the water regain.

Communications to the Editor

A Dibenzohomotropylium Ion[1]

Sir:

A considerable number of monohomotropylium-type cations are now recognized.[2] Even the 1-hydroxy-substituted species[2g] is decidedly homoaromatic and is capable of sustaining a large induced ring current. In exploring this phenomenon further, it seemed to us that a homocounterpart of the 2,3,6,7-dibenzotropylium ion[3] (II) would be instructive from the viewpoint of homoaromaticity[2f] since the two benzene rings in I and II dampen considerable the gain in ΔE_π due to cyclic electron delocalization attending formation of a tropylium species.[3b] An additional interest in dibenzohomotropyl derivatives VIII was the comparison of any rate-enhancing effect of the cyclopropane ring in VIII with that of the spirocyclopropyl group in the ionization[4] of IV to the anthrylethyl bridged ion[4b] V.

Cyclopropanation of the olefinic group in dibenzotropyl derivatives proved difficult but was finally accomplished by the action of $C_6H_5HgCBr_3$ on the dibenzotropone. Reduction of the dibromo ketone[5] VII-ketone, mp 177–178°, gave rise to the *cis* alcohol[5] VII-OH, mp 160–161°, which was debrominated by way of the tetrahydropyranyl ether with the aid of *n*-Bu_3SnH. The debrominated *cis*-VIII-OH,[5] mp 143–144°, equilibrated with the *trans*-VIII-OH,[5] mp 135–137°, to an 80.8% *cis*–19.2% *trans* equilibrium composition in acidified 80% aqueous dioxane at 75°. Similarly, the equilibrium between *cis*-VIII-OMe,[5] mp 93.5–94°, and *trans*-VIII-OMe,[5] mp 56–58°, was 56.4% *cis*–43.6% *trans* in MeOH at 65°, and that between *cis*-VIII-OAc,[5] mp 150–151°, and *trans*-VIII-OAc,[5] mp 141–142°, was 46.5% *cis*–53.5% *trans* in Ac_2O at 100°.

Configurations and conformations were assigned to the VIII epimers on the basis of nmr studies.[6] As

(1) Research supported by the National Science Foundation.

(2) (a) J. L. Rosenberg, J. E. Mahler, and R. Pettit, *J. Am. Chem. Soc.*, **84**, 2842 (1962); (b) J. D. Holmes and R. Pettit, *ibid.*, **85**, 2531 (1963); (c) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *ibid.*, **87**, (1965); (d) C. E. Keller and R. Pettit, *ibid.*, **88**, 604 (1966); (e) S. Winstein, C. G. Kreiter, and J. I. Brauman, *ibid.*, **88**, 2047 (1966); (f) S. Winstein, Special Publication No. 21, The Chemical Society, London, 1967; (g) M. Brookhart, M. Ogliaruso, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 1965 (1967); (h) G. Boche, W. Hechtl, H. Huber, and R. Huisgen, *ibid.*, **89**, 3344 (1967).

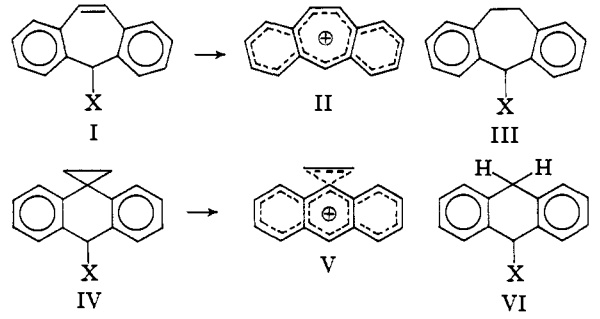
(3) (a) G. Berti, *Gazz. Chim. Ital.*, **87**, 293 (1957); (b) E. Heilbronner, *et al.*, *Helv. Chim. Acta*, **41**, 57 (1958); **33**, 1221 (1960).

(4) (a) R. Leute and S. Winstein, *Tetrahedron Letters*, 2475 (1967); (b) L. Eberson and S. Winstein, *J. Am. Chem. Soc.*, **87**, 3506 (1965).

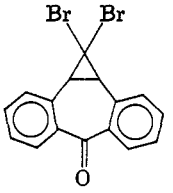
(5) The indicated compounds had satisfactory elemental analyses and appropriate infrared and nmr spectra.

(6) F. A. L. Anet, M. Brown, R. F. Childs, and S. Winstein, unpublished work to be reported separately.

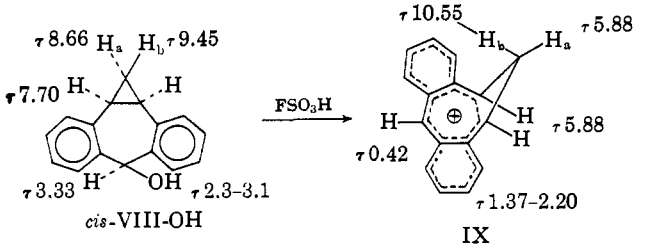
illustrated in X and XI for *trans*- and *cis*-VIII-OMe, respectively, the evidence is that both epimeric VIII derivatives strongly prefer shallow boat conformations with the cyclopropylmethylene group pseudo-equatorial. In these conformations the *trans* epimer has an equatorial H_α and an axial OMe group, while the *cis* epimer has an axial H_α and an equatorial OMe.



I II III IV V VI



VII-ketone



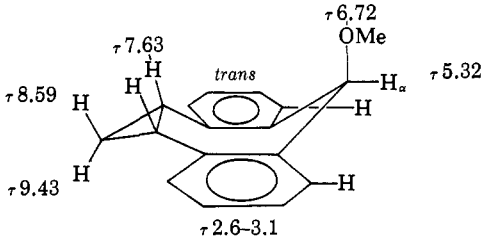
cis-VIII-OH IX

First-order hydrolysis rate constants of the various acetate esters in 80% aqueous acetone summarized in Table I show that any rate-enhancing effect of the cyclopropane ring in the dibenzohomotropyl systems (VIII-OAc) is not large and is apparently less than that of the olefinic group in the dibenzotropyl system I-OAc. However, all the rate enhancements are beclouded by the question of what model compounds to employ. The rate of the unsaturated I-OAc system is some 10^2 times that of the saturated III-OAc system but not appreciably greater than that of VI-OAc[4a] with a methano

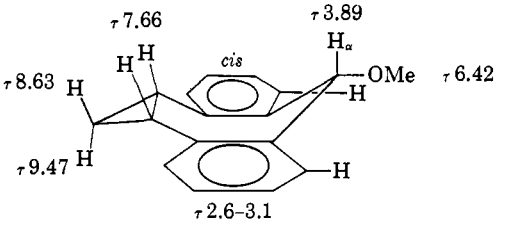
Table I. Solvolysis Rates in 80% Aqueous Acetone

ROAc	Temp, °C	k, sec^{-1}	Rel rate, 25°
trans-VIII-OAc	100.1	$(1.39 \pm 0.02) \times 10^{-5}$	
	75.0	$(9.61 \pm 0.19) \times 10^{-7}$	
	25.0[a]	1.23×10^{-9}	1
cis-VIII-OAc	75.0	$(1.02 \pm 0.01) \times 10^{-4}$	
	50.0	$(6.86 \pm 0.15) \times 10^{-6}$	
	25.0[a]	2.94×10^{-7}	2.4×10^2
I-OAc	25.0	$(5.13 \pm 0.09) \times 10^{-5}$	4.2×10^4
III-OAc	100.1	$(4.00 \pm 0.06) \times 10^{-4}$	
	75.0	$(4.13 \pm 0.09) \times 10^{-5}$	
	25.0[a]	1.45×10^{-7}	1.2×10^2
VI-OAc[4a]	25.0	1.26×10^{-5}	1.0×10^4
IV-OAc[4a]	25.0[b]	1.45×10^{-2}	1.2×10^7

[a] Extrapolated from data at higher temperatures. [b] Estimated from the rate constant in 90% acetone.



X



XI

instead of an ethano group. This illustrates the problem of conformational and substituent effects associated with the model compounds available for comparison.

Of the dibenzohomotropyl acetates, the *cis*-VIII-OAc is some 10^2 times as reactive as the *trans*-VIII-OAc, but even the more rapid *cis* epimer is not appreciably faster than the III-OAc analog without the cyclopropane ring. It is quite evident that the cyclopropane ring in the dibenzohomotropyl system turns out to be less rate enhancing than the spirocyclopropane group[4a] in IV-OAc, the precursor of the anthrylethyl bridged ion V. As regards products of solvolysis, except for some disturbance from some acyl-oxygen cleavage, especially in the case of the slower *trans*-VIII-OAc, kinetic product control gives a *cis*:*trans* product ratio of the order of 10^2 from both *cis*- and *trans*-VIII-OAc (Table II). This ratio is, of course, in line with the *cis*:*trans* reactivity ratio of *ca.* 10^2 and a thermodynamic equilibrium ratio of *ca.* 1.

Extraction of *cis*-VIII-OH from CH_2Cl_2 into FSO_3H at −78° or H_2SO_4 at room temperature gives clean solutions of the dibenzohomotropylium ion whose nmr spectrum is summarized in IX. This spectrum compared to that of the parent *cis*-VIII-OH strongly supports a homoaromatic dibenzohomotropylium structure. On conversion of alcohol to cation, the signal for the "inside" cyclopropane methylene proton H_b (τ 9.45 in alcohol) moves to higher field (τ 10.55), while the signal for the "outside" H_a proton (τ 8.66 in alcohol) moves to lower field (τ 5.88), as does also the signal for the tertiary cyclopropane protons (τ 5.88). The most striking feature of the nmr spectrum of cation IX is the large chemical shift between "inside" and "outside" cyclopropane methylene protons,[2] Δ_{ab} being 4.7 ppm compared to a Δ_{ab} of 0.8 ppm in *cis*-VIII-OH. The Δ_{ab} of 4.7 ppm compares quite favorably with the value of 5.8 ppm in the parent monohomotropylium ion.[2a,c,e] It is thus clearly evident that, in the fully formed dibenzohomotropylium ion IX, the cyclopropane electrons are heavily involved in the electron delocalization of the cationic electronic system and participate in a very substantial homoaromatic ring current in the central ring.[2e,f]

Quenching of the H_2SO_4 solution of IX in methanol gave a high yield of ether containing 94.8% *cis*-VIII-OMe and 5.2% *trans*-VIII-OMe. Allowing for some

Table II. Summary of Solvolysis Products from *cis*- and *trans*-VIII-OAc

VIII-OAc	Solvent	Temp, °C	Products
cis	80% Me_2CO	75	99.4% *cis*-VIII-OH, 0.6% *trans*-VIII-OH
trans	80% Me_2CO	100	83.4% *cis*-VIII-OH, 16.6% *trans*-VIII-OH
cis	MeOH	100	2.9% *cis*-VIII-OH, 97.9% VIII-OMe (98.9% *cis*:1.1% *trans*)
trans	MeOH	100	34.7% *trans*-VIII-OH, 65.3% VIII-OMe (98.7% *cis*:1.3% *trans*)

acid-catalyzed isomerization of the ether product during the quench, the observed product composition is in satisfactory agreement with that observed from kinetic control in acetate methanolysis. While the preference for *cis* stereospecificity in ionization and formation of covalent VIII derivatives is probably for stereoelectronic reasons, we are not yet prepared to discuss this in quantum-mechanical terms.[7]

Acknowledgment. We are grateful to Dr. Richard Leute and Mr. George Levy for assistance in some phases of the above research.

(7) It is pertinent that $NaBH_4$ reduction of VIII-ketone,[5] mp 84–85°, gives 98.8% *cis*- and 1.2% *trans*-VIII-OH.

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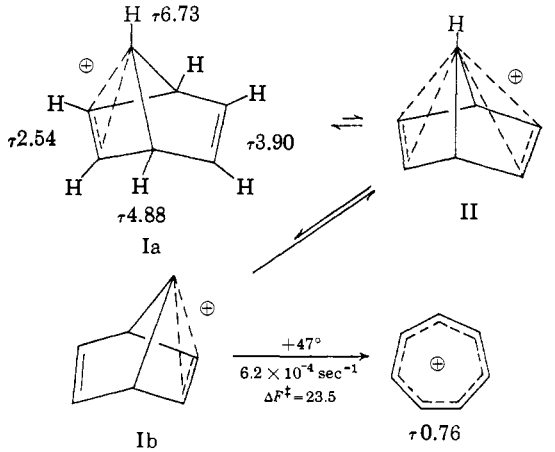
Received September 5, 1967

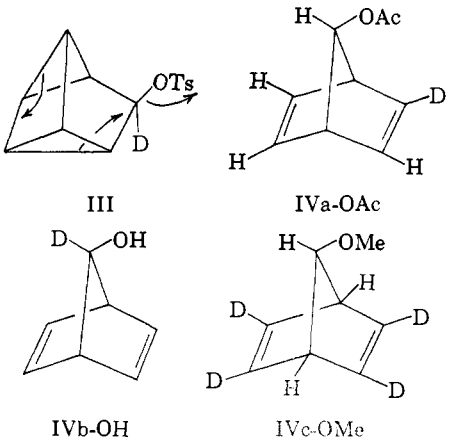
Degenerate Five-Carbon Scrambling in the 7-Norbornadienyl Cation[1]

Sir:

In this communication we describe a novel degenerate rearrangement of the norbornadienyl cation I discovered during a search for "bridge flipping" by this species[2] (Ia ⇌ II ⇌ Ib).



Extraction of 7-norbornadienol from pentane or CH_2Cl_2 into FSO_3H at −78° gave an FSO_3H solution of the 7-norbornadienyl cation I. Warming the solution to +45° caused no noticeable broadening of the nmr signals.[2] The ion decomposes at this temperature, as evidenced by the development ot some broad, undetailed nmr signals, as well as a sharp signal at τ 0.76 for tropylium ion formed in *ca.* 25% yield. Despite very rapid decomposition, the nmr spectrum[3] of ion I could be recorded at 77°. At this temperature the τ 2.54 signal for the "bound" vinyl protons was still sharp with the coupling pattern somewhat collapsed. However, the τ 3.90, 4.88, and 6.73 signals for "unbound" vinyl, bridgehead, and bridge protons were broadened, indicating the onset of an interesting degenerate rearrangement.



To study this rearrangement on a conventional rather than nmr time scale, labeled 7-norbornadienyl precursors were employed. These were IVa-OAc with a *syn*-vinyl deuterium obtained from acetolysis of 7-deuterioquadricyclyl tosylate (III) *via* the Richey–Story rearrangement;[4] IVb-OH with a 7-deuterium obtained from 7-deuterioquadricyclanol; and IVc-OMe with 77% of 4-vinyl deuterium atoms obtained by base-catalyzed exchange[5] of 7-norbornadienyl methyl ether with $LiNDC_6H_{11}$ in $C_6H_{11}ND_2$.

In FSO_3H at −73°, IVa-OAc displayed the four-signal spectrum of I with the intensity of the unbound vinyl signal only half as great as that for the bound vinyl (Ia). When the cation solution was warmed to −47°, a scrambling of the deuterium label was observed with a rate constant of 3×10^{-4} sec^{-1} (Table I). However, the vinyl proton peak intensities did not approach the 1:1 ratio expected for a bridge-flip phenomenon. Rather, the peak intensities approached a 2:1.6:1.6:0.8 ratio for the bound vinyl, unbound vinyl, bridgehead, and bridge protons, respectively (Ie). In other words, deuterium was scrambled to all positions *except* the bound vinyl! The same phenomenon was demonstrated with cations Ib and Ic from IVb and IVc, respectively (Table I). At −60° initially, both Ib and Ic exhibited the same relative peak intensities as their precursors, but, on warming to *ca.* −50°, these intensities approached the ratios expected for a five-carbon scrambling reaction (If and Ig, Table I).

Examination of the nmr signal intensities during scrambling of Ia, Ib, and Ic revealed that deuterium is incorporated sequentially at the different positions. Thus, in the case of Ia and Ic, deuterium is first in-

(1) Research supported by the National Science Foundation.
(2) M. Brookhart, R. K. Lustgarten, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 6352 (1967).
(3) All chemical shifts are based on CH_2Cl_2 as a secondary standard (τ 4.70).
(4) (a) H. G. Richey and N. C. Buckley, *J. Am. Chem. Soc.*, **85**, 3057 (1963); (b) P. R. Story and S. R. Fahrenholtz, *ibid.*, **86**, 527 (1964); **88**, 374 (1966).
(5) A. Streitwieser, Jr., and W. C. Langworthy, *ibid.*, **85**, 1757 (1963); A. Streitwieser, Jr., and J. H. Hammons, *Progr. Phys. Org. Chem.*, **3**, 73 (1965). We are grateful to C. Watts for assistance.