require further study. It will also be of interest to see what other quenchers for singlet oxygen can be found.[10]

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[10] G. O. Schenck and K. Gollnick, *Angew. Chem.*, 70, 509 (1958), report nicotine quenches the reactive intermediate (presumably singlet oxygen) in photosensitized oxygenations. See also ref 4 for some other possible cases.

[11] John Simon Guggenheim Fellow, 1967–1968.

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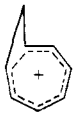
A New Dibenzohomotropylium Cation[1]

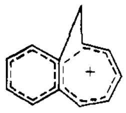
Sir:

The homotropylium cation I, the benzohomotropylium cation II, and the dibenzohomotropylium cation III have been described by Pettit[2,3] and Winstein[4] and their coworkers.

In this communication we wish to report the generation and characterization of a new dibenzohomotropylium ion IV, an isomer of III. The precursors V and VI used for the generation of IV in the strong acid media have been prepared by Nenitzescu and his collaborators during the investigation of the dibenzocycloheptane–dibenzocyclooctane rearrangement.[5,6]



I



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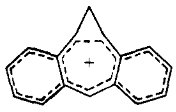
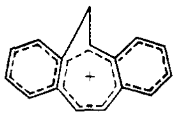
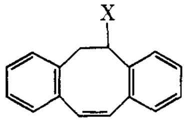


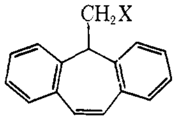
III



IV



V, X = OH



VIa, X = OH
b, X = Cl
c, X = Br
d, X = OTs

When a sulfur dioxide solution of the alcohol V is added with vigorous stirring to a FSO_3H–SbF_5 (1:1) solution in sulfur dioxide at −60° the dibenzohomotropylium cation IV is formed *via* the protonated species VII and the unstable secondary cation VIII. The same cation (IV) is obtained from the primary halides VIb and VIc in SbF_5–SO_2 solution at −60°. The unstable primary cation IX is initially formed but undergoes, with aryl participation, an instantaneous rearrangement to the relatively more stable eight-membered ring secondary cation VIII. The final homoaromatic stabilization to IV is easily accomplished by the participation of the double bond.

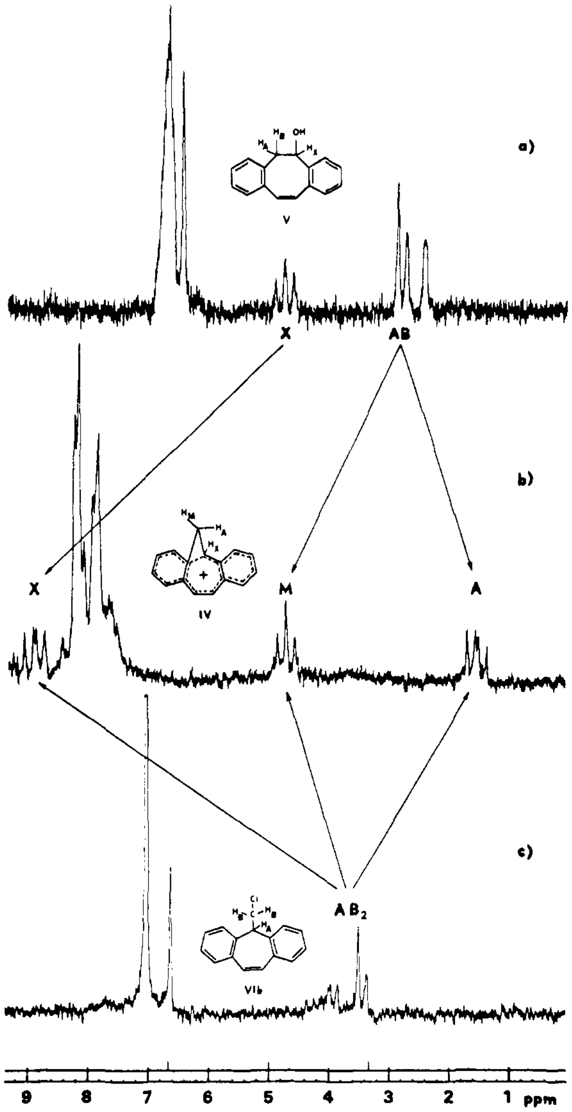


Figure 1. Nmr spectra (60 MHz) of V in liquid SO_2 (a), IV in FSO_3H-SbF_5-SO_2 (b), and VIb in liquid SO_2 (c), all recorded at −60°. No change was observed by raising the temperature to −18°.

Ion IV could also be detected in FSO_3H–SbF_5 solutions of VIa, VIb, VIc, and VId; however, only poor nmr spectra could be obtained probably due to secondary reactions.

The protonation of the dibenzocyclooctatetraene X in FSO_3H–SO_2 also leads to the formation of the dibenzohomotropylium cation IV. Evidence of the homoaromatic nature of the cation IV is provided by its nmr spectrum shown in Figure 1 in comparison with those of the precursors V and VIb. The nmr spectrum of V in liquid sulfur dioxide (Figure 1a) presents a relatively narrow multiplet at δ 6.70 for the eight aromatic protons and a single slightly broadened line at 6.40 for the two olefinic protons. The hydroxylic proton absorbs at δ 2.38. The remaining three protons H_A, H_B, and H_X form an ABX spectrum with an X quadruplet centered at δ 4.70 and an unresolved AB

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[1] (a) Support of the research by the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation is gratefully acknowledged; (b) considered as Stable Carbonium Ions. LXXVII.

[2] J. L. von Rosenberg, Jr., J. E. Mahler, and R. Pettit, *J. Amer. Chem. Soc.*, 84, 2842 (1962).

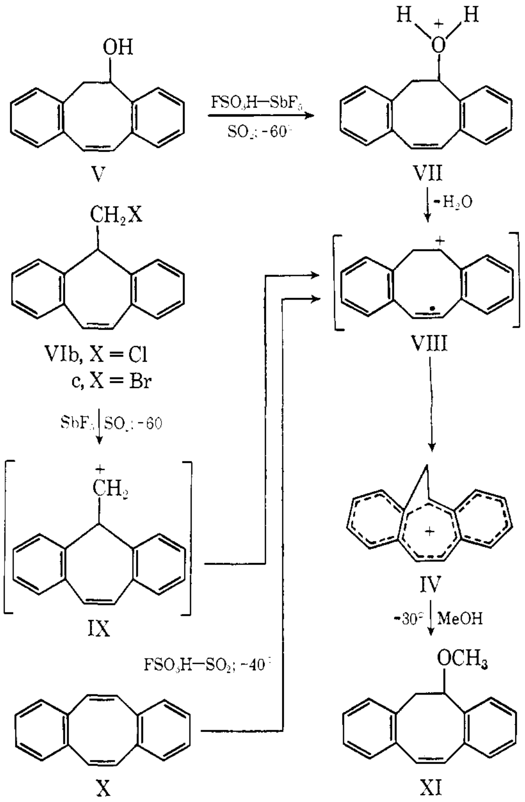
[3] W. Merk and R. Pettit, *ibid.*, 90, 814 (1968), and references cited therein.

[4] R. F. Childs and S. Winstein, *ibid.*, 89, 6348 (1967).

[5] E. Cioranescu, A. Bucur, M. Banciu, and C. D. Nenitzescu, *Rev. Roum. Chim.*, 10, 141 (1965); *Chem. Abstr.*, 63, 11456*g* (1965).

[6] E. Cioranescu, A. Bucur, M. Elian, M. Banciu, M. Voicu, and C. D. Nenitzescu, *Tetrahedron Lett.*, 3845 (1964).

part (two lines) at 2.75 (due to a solvent effect; the nmr spectrum of V in CCl$_4$ shows the typical octet of an AB part). The nmr spectrum of VIb (Figure 1c) emphasizes the symmetry of the molecule; the signals of the aromatic (δ 6.98) and olefinic (δ 6.60) protons are considerably narrower and an AB$_2$ pattern (δ 3.40–4.40) illustrates the equivalence of the two H$_B$ protons. The nmr spectrum of the dibenzohomotropylium cation IV (Figure 1b) exhibits dramatic changes in comparison with the spectra of the precursors. There are three major factors supporting the homotropylic structure: the striking alteration of the ABX and AB$_2$ patterns, the significant modification of the aromatic absorption, and the disappearance of the signals in the olefinic region.



Both ABX (Figure 1a) and AB$_2$ (Figure 1c) patterns become an AMX one in the spectrum of the cation IV. A large chemical shift difference ($\Delta\delta$ = 3.2 ppm) between the protons H$_A$ (δ 1.5) and H$_M$ (δ 4.7) is observed. As already pointed out[1-3] this difference could not be accounted for by the effect of the aromatic rings alone, and the shielding of H$_A$ is mainly caused by the homoaromatic ring current (H$_A$ lies above this ring while H$_M$ is situated in the deshielding zone). The coupling constants (J_{AM} = J_{MX} = 8.6 Hz and J_{AX} = 11.4 Hz) are also in agreement with previous observations.[2] H$_X$ (δ 8.90) experiences a similar deshielding as the corresponding proton in the cation II (δ 7.92).[2] The assignments of the chemical shifts and coupling constants in the AMX system of IV were confirmed by double-resonance experiments. The dissymmetry created in the cation IV and the alteration of the electronic structure results also in the significant diversification of the aromatic lines (δ 7.2–9.3) due to alteration of both shielding and coupling constants. Finally the integration of the signals of the olefinic protons in the deshielded aromatic region strongly supports the homoaromatic character of the central ring.

Quenching of the FSO$_3$H–SbF$_5$–SO$_2$ or SbF$_5$–SO$_2$ solutions of the cation IV with methanol gave a high yield of methyl ether XI. The nmr spectrum of XI is very similar to that of the alcohol V and shows a splitting of the olefinic signal as an effect of the presence of the more anisotropic methoxy group.

[7] Exchange Visitor at Case Western Reserve University, Department of Chemistry, Cleveland, Ohio, 1967–1968.

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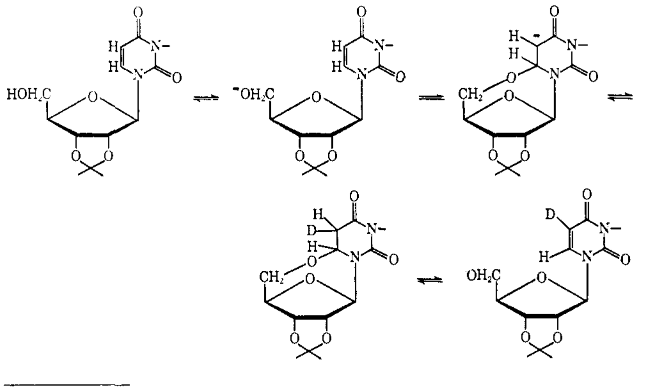
Model Studies of Thymidylate Synthetase. Neighboring-Group Facilitation of Electrophilic Substitution Reactions of Uracil Furanosides

Sir:

We report herein the initial results of our model studies of thymidylate synthetase. This enzyme catalyzes the reductive methylation of 2′-deoxyuridine 5′-monophosphate (dUMP) to give thymidine 5′-monophosphate,[1] and the exchange of the 5-H of dUMP for those of water.[2] We have observed that certain electrophilic reactions of uracil furanosides analogous to those catalyzed by the enzyme proceed exclusively by rate-determining nucleophilic attack of an ionized hydroxyl of the furanoside upon the heterocycle to form transient 6,5′- or 6,2′-anhydro nucleoside intermediates.

We initially observed that when 2′,3′-O-isopropylideneuridine (**1**) is treated with MeONa (0.474 *N*)–MeOD at 60.0°, the 5-H of the pyrimidine is exchanged for deuterium by an apparent first-order process ($t_{1/2}$ = 2.84 hr); in the absence of base no exchange is observed after as long as 2 weeks. Under identical conditions, the 5-H of 5′-deoxy-2′,3′-O-isopropylideneuridine (**2**) and 1-methyluracil (**3**) are stable for as long as 2 weeks. These data suggest that the formation of 2′,3′-O-isopropylideneuridine-5-*d* proceeds by anchimeric assistance of the 5′-oxy anion of **1**, as depicted in Scheme I. The 6,5′-anhydro cyclonucleoside inter-

Scheme I



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[1] M. Friedkin, *Ann. Rev. Biochem.*, **32**, 185 (1963).

[2] M. I. S. Lomax and G. R. Greenberg, *J. Biol. Chem.*, **242**, 1302 (1967).