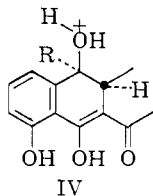


commonly observed<sup>4,6,8</sup> in the tetracycline series requires more than a *trans relationship*<sup>11</sup> of the C.6 oxygen function and the C.5a hydrogen. A logical conclusion is that a transition state such as IV is necessary for the unusually facile elimination observed.



11a-Halo-hemiketals such as III have proven to be of fundamental significance in opening up a new field of tetracycline chemistry, parts of which are described in the accompanying communication.<sup>12</sup>

(11) This conclusion tends to weaken earlier stereochemical arguments in the tetracycline series based solely on dehydration rates (*cf.*: C. W. Waller, B. L. Hutchings, R. W. Broschard, A. A. Goldman, W. J. Stein, C. F. Wolf and J. H. Williams, *J. Am. Chem. Soc.*, **74**, 4981 (1952) and J. R. D. McCormick, P. A. Miller, J. A. Growich, J. Reichenthal, N. O. Sjolander and A. P. Doerschuk, *ibid.*, **80**, 5572 (1958).

(12) R. K. Blackwood, J. J. Beereboom, H. H. Rennhard, M. Schach von Wittenau and C. R. Stephens, *ibid.*, **83**, 2775 (1961).

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#### THE NON-EQUIVALENCY OF METHYLENE RING CARBON ATOMS IN THE SOLVOLYSIS OF CYCLOPROPYLEMETHYL DERIVATIVES

Sir:

In a recent communication<sup>1</sup> we have reported that no isotope effect was observed in the solvolysis of I. It was pointed out that the formation of a non-classical carbonium ion of the bicyclobutonium ion type (II)<sup>2</sup> implies a rehybridization of the carbon-deuterium bonding orbitals and that therefore an isotope effect should occur in the solvolysis of I if such an intermediate was formed in the rate determining process.<sup>3</sup>

This view was criticized<sup>4</sup> on the grounds that carbon-hydrogen bonds in cyclopropane were nearly  $sp^2$  hybridized.<sup>5</sup> Thus, in the process of ionization leading to II the carbon-deuterium bonds on carbon 4 would tend to become more  $sp^2$  but more  $sp^3$  on carbon 3. The sum of these processes is therefore a negligibly small net rehybridization and a lack of an isotope effect in the solvolysis of I should not be surprising even if II is formed in the rate determining process.

In this communication we wish to report some experimental evidence which indicates the correctness of this criticism. The compound III was synthesized and its acetolysis and ethanolysis rate constants determined. An *inverse* isotope effect was found to occur ( $k_H/k_D = 0.962 \pm 0.015$  resp.

(1) S. Borčić, M. Nikoletić and D. E. Sunko, *Chemistry and Industry*, 527 (1960).

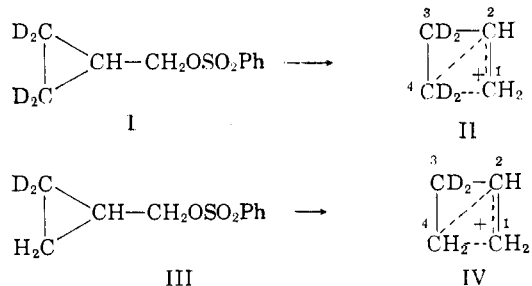
(2) R. H. Mazur, W. N. White, D. A. Semenov, C. C. Lee, M. S. Silver and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 4390 (1959).

(3) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, *ibid.*, **80**, 2326 (1958).

(4) E. F. Cox, M. C. Caserio, M. S. Silver and J. D. Roberts, *ibid.*, **83**, 2719 (1961).

(5) C. A. Coulson and W. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

$0.957 \pm 0.007$ ). These results can be well understood if it is considered that the reaction with III can proceed through a transition state resembling the intermediate IV. The formation of IV is associated with a rehybridization of the carbon-deuterium bonding orbitals toward more p character and represents therefore the reaction path of minimum activation energy.<sup>6</sup> Thus, in the solvolysis of III the energy gained in the above change in hybridization is not compensated by the reverse process as with I, with the result of an over-all rate increase.



The occurrence of an isotope effect in the solvolysis of III and the lack of such an effect in the reaction with I demonstrate in a striking manner the non-equivalency of carbon atoms 3 and 4 in the transition state as implied in the formulation of bicyclobutonium ions.<sup>2</sup>

Full experimental details of this and the previously reported work<sup>1</sup> will be presented in a forthcoming publication.

(6) S. Seltzer, *Chemistry and Industry*, 1313 (1959); D. B. Denney and N. Tunkel, *ibid.*, 1383 (1959).

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#### FERRATE(VI) FORMATION BY HYDROGEN PEROXIDE IN PRESENCE OF ETHYLENEDIAMINETETRAACETATE

Sir:

Recently it was reported<sup>1</sup> that an unidentified purple complex was formed when hydrogen peroxide was added to an alkaline solution of disodium dihydrogen ethylenediaminetetraacetate (EDTA), containing a small amount of suspended  $Fe(OH)_3$  (solid). Our studies with iron chemistry indicate that this complex ion is ferrate ( $FeO_4^{--}$ ), in some solvated form.

We have prepared the complex ion approximately  $1 \times 10^{-3}M$  by addition of an excess of 30%  $H_2O_2$  solution to a cool (ice bath) solution of  $KOH$  (2-7*M*), EDTA ( $>0.02M$ ) and  $Fe(OH)_3$  ( $>2 \times 10^{-3}M$ ). The excess  $Fe(OH)_3$  was removed by filtration through a glass frit and the absorption spectrum was recorded from 3600 to 8000 Å. One broad maximum was observed at 5180 Å. and two minima, one at 4070 and one at 7750 Å. Maximum and minimum absorption therefore was observed at slightly higher wave lengths than usually is noted for ferrate solutions.<sup>2,3</sup> This probably is due to the formation of a somewhat

(1) F. R. Duke and T. W. Haas, *J. Phys. Chem.*, **65**, 304 (1961).

(2) Z. G. Kaufman and J. M. Schreyer, *Chem. Anal.*, **45**, 22 (1956).

(3) R. H. Wood, *J. Am. Chem. Soc.*, **80**, 2038 (1958).

different solvated complex in the presence of EDTA and excess  $\text{H}_2\text{O}_2$ . Indeed, when EDTA was added to a ferrate solution prepared from the dry solid  $\text{K}_2\text{FeO}_4$  in 9M KOH, the minimum usually occurring at 3900Å. was shifted to 4000Å., and the maximum usually occurring at 5000Å. was shifted to approximately 5500Å. These displacements were somewhat dependent on the concentration of EDTA. In determining the  $\text{FeO}_4^{--}$  concentration spectrophotometrically, it was assumed that the molar extinction coefficient for  $\text{FeO}_4^{--}$  at the 5180 Å. maximum was 1070 l. mole<sup>-1</sup> cm.<sup>-1</sup>, the same as determined by Wood<sup>3</sup> and reproduced by us at 5050Å.

Attempts to prepare  $\text{FeO}_4^{--}$  as described above, in the absence of EDTA, were unsuccessful. When solid  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was added to the mixture with no EDTA present, purple flashes of color appeared on the crystals and in the immediate area of the crystals but quickly disappeared.

It has been reported by others,<sup>3,4</sup> and observed by us, that addition of  $\text{H}_2\text{O}_2$  to  $\text{FeO}_4^{--}$  in strong alkaline media causes rapid reduction of  $\text{FeO}_4^{--}$  to  $\text{Fe}(\text{OH})_3$ . Likewise, addition of EDTA to an alkaline  $\text{FeO}_4^{--}$  solution prepared from solid  $\text{K}_2\text{FeO}_4$  results in an increase in the rate of thermal decomposition of this solution. We cannot explain the apparent stabilizing effect of EDTA on the formation of  $\text{FeO}_4^{--}$  with  $\text{H}_2\text{O}_2$ . EDTA generally is considered to be a cation complexing agent, but in this strongly alkaline solution, Fe(VI) as  $\text{FeO}_4^{--}$  and Fe(III) as  $\text{FeO}_2^-$  or  $\text{FeO}_3^{---}$  are anionic species. Moreover, as observed by Duke and Haas,<sup>1</sup> addition of EDTA to a  $\text{Fe}(\text{OH})_3$  precipitate in alkaline medium appears to have no effect on the precipitate.

Thanks are due to H. A. Mahlman and J. W. Boyle for suggesting this phase of the work, and to W. F. Vaughan who assisted in the initial preparation of  $\text{FeO}_4^{--}$  by this method. This work was supported by the Oak Ridge Institute of Nuclear Studies in cooperation with Michigan State University and the Oak Ridge National Laboratory.

(4) O. N. Hinsvark, Master's Thesis, Michigan State University, East Lansing, Michigan, 1952.

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### SPIN-SPIN COUPLING CONSTANTS BETWEEN NON-BONDED $\text{C}^{13}$ AND PROTON. III.<sup>1,2</sup> ANOMALIES IN $J_{\text{C}^{13}-\text{C}-\text{H}}$

Sir:

It has been shown that a direct correlation exists between the magnitude of either  $J_{\text{C}^{13}-\text{H}}$  or  $J_{\text{C}^{13}-\text{C}-\text{H}}$  and the degree of sp hybridization of the  $\text{C}^{13}$  atomic orbitals.<sup>2,3</sup> This finding, coupled with the fact that calculations based on the assump-

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(2) Previous paper, G. J. Karabatsos, J. D. Graham and F. Vane, *J. Phys. Chem.*, in press.

(3) (a) J. N. Shoolery, *J. Chem. Phys.*, **31**, 1427 (1959); (b) N. Muller and D. E. Pritchard, *ibid.*, **31**, 768, 1471 (1959).

TABLE I

Compound	$J_{\text{C}^{13}-\text{C}-\text{H}}$ (c.p.s.)	$J_{\text{H}-\text{C}-\text{H}}$ (c.p.s.)
$(\text{CH}_3\text{CH}_2)_2\text{C}^{13}=\text{O}$	$4.7 \pm 0.1$	$7.5 \pm 0.1$
$\text{CH}_3\text{CH}_2\text{C}^{13}\text{O}_2\text{H}$	$5.5 \pm .2$	$7.4 \pm .1$
$\text{CH}_3\text{CH}_2\text{C}^{13}\text{O}_2\text{CH}_3$	$5.3 \pm .1$	$7.4 \pm .1$
$\text{CH}_3\text{CH}_2\text{C}^{13}\text{D}_2\text{OH}$	$6.4 \pm .2$	$7.3 \pm .2$
$(\text{CH}_3\text{CH}_2)_2\text{C}^{13}\text{DOH}$	$4.0 \pm .2$	$6.8 \pm .3$
$(\text{CH}_3\text{CH}_2)_3\text{C}^{13}\text{OH}$	$4.5 \pm .1$	$7.5 \pm .2$
$\text{CH}_3\text{CH}_2\text{C}^{13}(\text{OH})(\text{CH}_3)_2$	$4.4 \pm .2$	$7.3 \pm .2$
$\text{CH}_3\text{CH}_2\text{C}^{13}(\text{Cl})(\text{CH}_3)_2$	$5.7 \pm .1$	$7.5 \pm .2$
$\alpha\text{CH}_3$   $\text{C}^{13}\text{H}_3-\text{C}(\text{OH})^\beta\text{CH}_2\text{CH}_3$	( $\alpha$ ) $3.2 \pm .2$ ( $\beta$ ) $3.0 \pm .2$	
$\alpha\text{CH}_3$   $\text{C}^{13}\text{H}_3-\text{C}(\text{Cl})^\beta\text{CH}_2\text{CH}_3$	( $\alpha$ ) $4.2 \pm .2$ ( $\beta$ ) $3.2 \pm .2$	

tion that the Fermi contact term is the dominant one predict such a correlation, has led to the conclusion that the contact term is indeed the important term in both  $J_{\text{C}^{13}-\text{H}}$  and  $J_{\text{C}^{13}-\text{C}-\text{H}}$ . We wish to point out that such does not seem to be the case in  $J_{\text{C}^{13}-\text{C}-\text{H}}$ .

Spin-spin coupling constants ( $J_{\text{C}^{13}-\text{C}-\text{H}}$ ) for ten compounds are reported in Table I. The enrichment in the samples varied from 30% to 60% excess  $\text{C}^{13}$ . All spectra were taken with a model V4300D Varian Associates Spectrometer, at 60 Mc.; spin-spin coupling constants were measured by the standard side band technique.<sup>4</sup>

The following observations and conclusions are made: (1)  $J_{\text{C}^{13}-\text{C}-\text{H}}$  varies irregularly and there is no obvious correlation between its magnitude and the hybridization of  $\text{C}^{13}$  atomic orbitals. (2) No correlation is possible involving the electronegativity of the group attached to  $\text{C}^{13}$ . (3) The constancy of the corresponding  $J_{\text{H}-\text{C}-\text{H}}$  excludes the possibility that the variations are due to different populations of rotational isomers; there is no reason to suggest that, in the same compound,  $\text{C}^{13}$  sees the methyl protons in different conformations than the methylene hydrogens do.

Calculations analogous to those reported previously,<sup>2</sup> and based on the assumption that the Fermi contact term is the dominant term, lead to the following results: (1) for  $\text{sp}^3$  hybridized  $\text{C}^{13}$ ,  $J_{\text{C}^{13}-\text{C}-\text{H}} = J_{\text{H}-\text{C}-\text{H}} \times 0.3036$ . (2) For  $\text{sp}^2$  hybridized  $\text{C}^{13}$ ,  $J_{\text{C}^{13}-\text{C}-\text{H}} = J_{\text{H}-\text{C}-\text{H}} \times 0.4046$ . Using the experimental values of  $J_{\text{H}-\text{C}-\text{H}}$  given in Table I, one obtains for  $\text{sp}^3$  hybridized  $\text{C}^{13}$   $J_{\text{C}^{13}-\text{C}-\text{H}} = \sim 2.3$  c.p.s. and for  $\text{sp}^2$  hybridized  $\text{C}^{13}$   $J_{\text{C}^{13}-\text{C}-\text{H}} = \sim 3.0$  c.p.s. The random variation of the experimental  $J_{\text{C}^{13}-\text{C}-\text{H}}$  values suggests that the Fermi contact term is not the only important term. Subtler factors, resulting to higher than predicted values for  $J_{\text{C}^{13}-\text{C}-\text{H}}$ , must be operative. We hope to study the problem further by examining rigid systems where the dihedral angle is fixed, and systematic variations of the hybridization of  $\text{C}^{13}$  and the groups attached to it can be performed.

We wish to comment briefly on the fact that for the same compound  $J_{\text{C}^{13}-\text{C}-\text{H}}$  is occasionally greater than  $J_{\text{C}^{13}-\text{H}}$ . It was shown<sup>2</sup> that  $J_{\text{C}^{13}-\text{H}}$

(4) J. T. Arnold and M. E. Packard, *ibid.*, **19**, 1608 (1951).