commonly observed^{5,6,8} in the tetracycline series requires *more than* a *trans relationship*¹¹ 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.¹²

(11) This conclusion tends to weaken earlier stereochemical arguments in the tetracycline series based solely on dehydration rates (c/;
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THE NON-EQUIVALENCY OF METHYLENE RING CARBON ATOMS IN THE SOLVOLYSIS OF CYCLOPROPYLMETHYL DERIVATIVES

Sir:

In a recent communication¹ 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 $(II)^2$ 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.³

This view was criticized⁴ on the grounds that carbon-hydrogen bonds in cyclopropane were nearly sp² hybridized.⁵ Thus, in the process of ionization leading to II the carbon-deuterium bonds on carbon 4 would tend to become more sp² but more sp³ 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 $(k_{\rm H}/k_{\rm D} = 0.962 \pm 0.015$ resp.

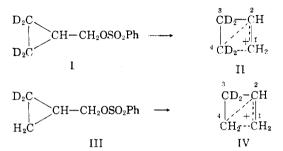
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- (2) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, J. Am. Chem. Soc., 81, 4390 (1959).
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 0.957 ± 0.007). These results can be well understood if it is considered 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 carbondeuterium bonding orbitals toward more p character and represents therefore the reaction path of nuinimum activation energy.⁶ 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.²

Full experimental details of this and the previously reported work¹ will be presented in a forthcoming publication.

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> er Bošković Stanko Borčić avia Dionis E. Sunko Received April 25, 1961

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



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Recently it was reported¹ 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 $1 \times 10^{-8}M$ by addition of an excess of 30% H₂O₂ solution to a cool (ice bath) solution of KOH (2-7*M*), EDTA (>0.02*M*) and Fe(OH)₃ (>2 × 10⁻⁸*M*). The excess Fe(OH)₈ was removed by filtration through a glass frit and the absorption spectrum was recorded from 3600 to 8000Å. One broad maximum was observed at 5180Å. and two minima, one at 4070 and one at 7750Å. Maximum and minimum absorption therefore was observed at slightly higher wave lengths than usually is noted for ferrate solutions.^{2,3} This probably is due to the formation of a somewhat

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