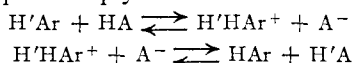


buffer concentration at constant ionic strength ($\mu = 0.100$, $[\text{HOAc}]/[\text{OAc}^-] = 1.00$). No exchange was observed in sodium hydroxide solution during the time required for complete exchange in acid at a hydronium ion concentration comparable to the hydroxide ion concentration. Since acetate ion is a much weaker base than hydroxide ion, the dependence of rate on buffer concentration must be the result of catalysis by acetic acid and not by acetate ion. Preliminary results with other acids indicate compliance with the Brønsted relation; α is near 0.5.

This evidence indicates that, in the rate-determining transition state for aromatic hydrogen exchange catalyzed by weak acids, the proton is not yet completely transferred from acid anion to aromatic. This reaction, therefore, must be a slow proton transfer, and the mechanism can be described quite simply as



We are grateful to Mr. R. P. Bell, F.R.S., for his interest in this work.

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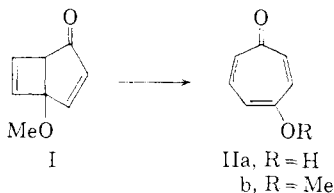
A. J. KRESGE

Y. CHIANG

RECEIVED AUGUST 18, 1959

A NOVEL BASE-CATALYZED ISOMERIZATION OF A BICYCLIC SYSTEM TO A TROPONOID SYSTEM

Sir:
In the course of experiments designed to test the feasibility of anion formation at the bridgehead of photo- γ -tropolone methyl ether (I)¹ (by base-catalyzed exchange of hydrogen for deuterium) it was found that I was rapidly and completely destroyed by 2 *N* aqueous sodium hydroxide with the production of a highly water soluble acidic product. The acidic product was identified quickly as γ -tropolone (IIa) by its characteristic ultra-



violet spectra in neutral solution² and in 0.1 *N* sodium hydroxide.² In dilute base (0.0887 *N* sodium hydroxide) the product initially observed is γ -tropolone methyl ether (IIb, λ_{max} 223 $m\mu$ (19,700) and 333 $m\mu$ (13,000) in aqueous solution³ and in 0.1 *N* sodium hydroxide³). Brief warming of the basic solution gave γ -tropolone anion⁴

(1) O. L. Chapman and D. J. Pasto, *THIS JOURNAL*, **80**, 6685 (1958).

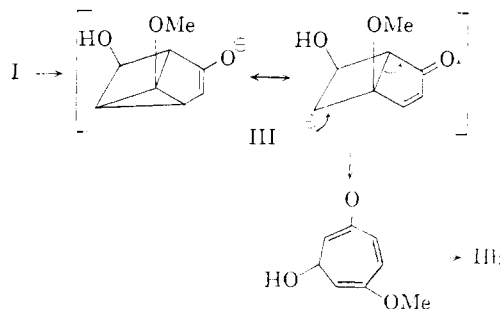
(2) In methanol γ -tropolone shows λ_{max} 228 $m\mu$ (4.27) and 337 $m\mu$ (4.11) and in 0.1 *N* sodium hydroxide 227 $m\mu$ (4.30) and 360 $m\mu$ (4.33); T. Nozoe, T. Mukai, Y. Ikegami and T. Toda, *Chem. and Ind.*, 66 (1955); R. B. Johns, R. S. Coffey and A. W. Johnson, *ibid.*, 658 (1955); J. Meinwald and O. L. Chapman, *THIS JOURNAL*, **78**, 4816 (1956).

(3) Authentic γ -tropolone methyl ether shows exactly this spectrum in either water or 0.1 *N* sodium hydroxide.

(4) This was recognized by its characteristic ultraviolet spectrum.² The hydrolysis of γ -tropolone methyl ether does not proceed at a significant rate in 0.0887 *N* sodium hydroxide at 22°, but in the same concentration of base at 80° it is quite rapid (unpublished rate measurements of O. L. Chapman and D. J. Pasto).

which on acidification gave γ -tropolone. Photo- γ -tropolone methyl ether (I) is quantitatively converted to γ -tropolone methyl ether (IIb) after 110 minutes in 0.0887 *N* sodium hydroxide at 22°. This rapid reaction is in dramatic contrast to the acid-catalyzed opening of I to IIa which does not proceed at a measurable rate in 0.095 *N* sulfuric acid at 22° and which is only 27% complete after 5 hours at 80° in the same acid concentration.⁵ The base-catalyzed isomerization of photo- γ -tropolone methyl ether to IIb is without precedent. The facility of this reaction is no less than astonishing. The base-catalyzed reaction fails for dihydro- and tetrahydrophoto- γ -tropolone methyl ether which, however, do undergo acid-catalyzed ring opening.¹ The isomerization of I to IIb can be induced by bases weaker than hydroxide, but the rate is very considerably reduced. Prolonged refluxing of I in 95% ethanol also effects the conversion of I to IIb. Iodide ion does not catalyze the transformation of I to IIb.

The transformation of I to IIb is best rationalized on the basis of attack by hydroxide ion on the cyclobutene double bond leading to the anion III which can collapse quite simply to IIb. The Michael-type addition depicted is, to the best of our knowledge, without precedent. Interaction



between the non-conjugated double bond and the cyclopentenone system is evident in the ultraviolet spectrum (243 $m\mu$) of I.

Acknowledgment.—The authors wish to acknowledge financial support of this investigation by the Research Corporation through a Frederick Gardner Cottrell grant and by a research grant (CY-4253 PET) from the Cancer Division of the National Institutes of Health, Public Health Service.

(5) The hydrolysis of γ -tropolone methyl ether in 0.095 *N* sulfuric acid at 80° is quite rapid and γ -tropolone is thus the observed product (unpublished rate measurements O. L. Chapman and D. J. Pasto).

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O. L. CHAPMAN
D. J. PASTO

RECEIVED AUGUST 27, 1959

COLINEAR BONDS AT THE OXYGEN ATOM

Sir:

Colinear bonds at the oxygen atom were found first in 1935 by G. R. Levi and G. Peyronel¹ in the pyrophosphate anion, and more recently in $\text{H}_3\text{Si-O-SiH}_3^2$ and in the $(\text{Cl}_5\text{RuORuCl}_5)^{-4}$ an-

(1) G. R. Levi and G. Peyronel, *Z. Krist.*, **92**, 190 (1935).

(2) R. C. Lord, D. W. Robinson and W. C. Schumb, *THIS JOURNAL*, **78**, 1327 (1956).