buffer concentration at constant ionic strength (μ = 0.100, [HOAc]/[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 Brönsted 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

$$H'Ar + HA \rightleftarrows H'HAr^+ + A^-$$

$$H'HAr^+ + A^- \rightleftarrows HAr + H'A$$

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

DEPARTMENT OF CHEMISTRY A. J. KRESGE
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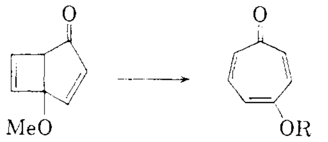
RECEIVED AUGUST 18, 1959

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

Sir:

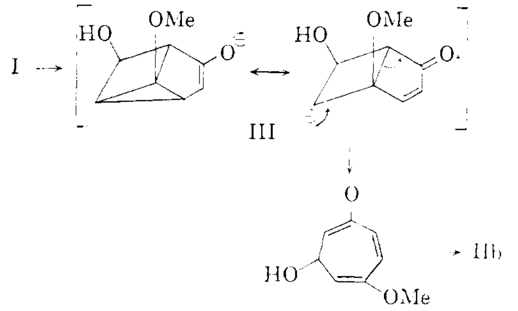
In the course of experiments designed to test the feasibility of anion formation at the bridgehead of photo-γ-tropolone methyl ether (I)[1] (by base-catalyzed exchange of hydrogen for deuterium) it was found that I was rapidly and completely destroyed by 2 *N* aqueous sodium hydroxide with the production of a highly water soluble acidic product. The acidic product was identified quickly as γ-tropolone (IIa) by its characteristic ultraviolet spectra in neutral solution[2] 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 mμ (19,700) and 333 mμ (13,000) in aqueous solution[3] and in 0.1 *N* sodium hydroxide[3]). Brief warming of the basic solution gave γ-tropolone anion[4] 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.



I

IIa, R = H
b, R = Me

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 mμ) 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.

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

[2] In methanol γ-tropolone shows λ_{max} 228 mμ (4.27) and 337 mμ (4.11) and in 0.1 *N* sodium hydroxide 227 mμ (4.30) and 360 mμ (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).

[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).

DEPARTMENT OF CHEMISTRY
IOWA STATE UNIVERSITY O. L. CHAPMAN
AMES, IOWA 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. Peyronel[1] in the pyrophosphate anion, and more recently in H_3Si-O-SiH_3[2] and in the $(Cl_5RuORuCl_5)^{-4}$ an-

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[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).

ion.[3] The strange behavior of oxygen in these compounds has been emphasized recently by P. J. Wheatley[4] and discussed in a review paper by R. J. Gillepsie and R. S. Nyholm.[5]

Surprisingly, in the course of an X-Ray study of $[TiCl_2(C_5H_5)]_2O$[6] we found definite evidence of colinearity of titanium and oxygen atoms. In fact, the crystals of (I), having these unit cell constants: a = 7.47 Å.; b = 9.86 Å.; c = 12.58 Å.; β = 127°56′, space group $P2_1/c$, have only two molecules per unit cell, so that the molecule must be centrosymmetrical.

The colinearity of titanium and oxygen atoms is further confirmed by the Patterson and Fourier syntheses on the ac and bc planes. At the present stage of refinement of the structure (R = 0.20), the fractional coördinates (x, y, z) of the heavy atoms have been assumed to be: Ti: 0.454, 0.132, 0.393; Cl^{I}: 0.767, 0.132, 0.403; Cl^{II}: 0.178, 0.047, 0.187.

It results that: 1, as above said, the Ti-O-Ti atoms are colinear. 2, All the carbon atoms of the cyclopentadiene ring are at the same distance (2.35 ± 0.05 Å.) from the titanium atom. 3, Other relevant interatomic distances are: Ti-O = 1.78 ± 0.03 Å.; Ti-Cl = 2.25 ± 0.04 Å.; $Ti\text{-}C_5H_5$[7] = 2.03 ± 0.05 Å. 4 Relevant bond angles are: O-Ti-Cl = 104° ± 2°; Cl-Ti-Cl = 104° ± 2°; $C_5H_5\text{-}Ti\text{-}Cl$[7] = 112° ± 2°; $C_5H_5\text{-}Ti\text{-}O$[7] = 117° ± 2°. The Ti-O distance is clearly shorter than the one expected for a single bond (1.78 Å. instead of 1.92 Å.),[8] as was the case of the Ru-O[3] distance in the corresponding anion.

Supposing an sp hybridization for the oxygen, and a d^3s hybridization for the titanium atoms, a partial double bond character of the Ti-O bond may arise from donation of electrons from the p_y and p_z filled oxygen orbitals to the $d\gamma$ unfilled titanium orbitals. This fact may in turn stabilize the unusual sp hybridization at the oxygen atom.

We acknowledge the helpful suggestions of Prof. G. Natta, Prof. G. R. Levi and Dr. L. Porri, who also supplied us the sample.

[3] A. McL. Mathieson, D. P. Mellor and N. C. Stephenson, *Acta Cryst.*, **5**, 185 (1952).

[4] P. J. Wheatley, in "Annual Review of Physical Chemistry," **8**, 383 (1957).

[5] R. J. Gillespie and R. S. Nyholm, *Quart. Rev.*, **11**, 339 (1957).

[6] Prepared by boiling in moist air a heptane solution of $TiCl_3$-(C_5H_5). The yellow tabular crystals of $[TiCl_2(C_5H_5)]_2O$, stable in air, may be recrystallized from heptane (private communication of L. Porri).

[7] Referred to the center of the cyclopentadiene π-bonded ring.

[8] Obtained by subtracting from the found Ti-Cl distance (2.25 Å.) the difference between the covalent radii of chlorine and oxygen atoms (0.33 Å.).

DEPARTMENT OF INDUSTRIAL CHEMISTRY
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MILAN (ITALY) GIUSEPPE ALLEGRA

RECEIVED JULY 22, 1959

LARGE SALT EFFECTS IN NON-POLAR SOLVENTS

Sir:

Specific effects of added salts in accelerating rate of ionization of organic substrates such as alkyl toluenesulfonates tend to become quite serious in the less polar solvents, *e.g.*, AcOH.[2] In this Communication we call attention to the large magnitude of such salt effects in the poorest ionizing media and their implications for reaction mechanism.

The rate of ionization of *p*-methoxyneophyl *p*-toluenesulfonate[2b] (I) may be followed in a variety of solvents by titration of generated toluenesulfonic acid, and this is accelerated by inclusion of, *e.g.*, lithium perchlorate. With this salt, the pattern of salt effects in the 0–0.10 M range is the linear[2] one of equation (1) or the more complex one of equation (2), where k and k^0 are first order rate constants with and without added salt, respectively.

$$k = k^0[1 + b(LiClO_4)] \qquad (1)$$

$$k = k^0[1 + b(LiClO_4) + c(LiClO_4)^{3/2}] \qquad (2)$$

As summarized in Table I, such salt effects tend to become quite large in the less ionizing solvents, such as acetone, octanoic acid and ethyl acetate, and enormous in a solvent such as diethyl ether. In the latter medium, ionization rate is increased by a factor of 10^5 by 0.1 M lithium perchlorate.

Because of the large salt effects on ionization illustrated in Table I, inclusion of a salt may drastically alter relative ionizing power of solvents. The comparison between acetic acid and diethyl ether is illustrated in Fig. 1. While rate of ionization of I in acetic acid at 50° in the absence of lithium perchlorate exceeds that in ether by a factor of 2 × 10^4, ether becomes a better ionizing medium than acetic acid at concentrations of lithium perchlorate above 0.036 M. For S_N2 displacement reactions with salts such as lithium chloride, the choice of a relatively poor ionizing solvent may not minimize but instead can promote

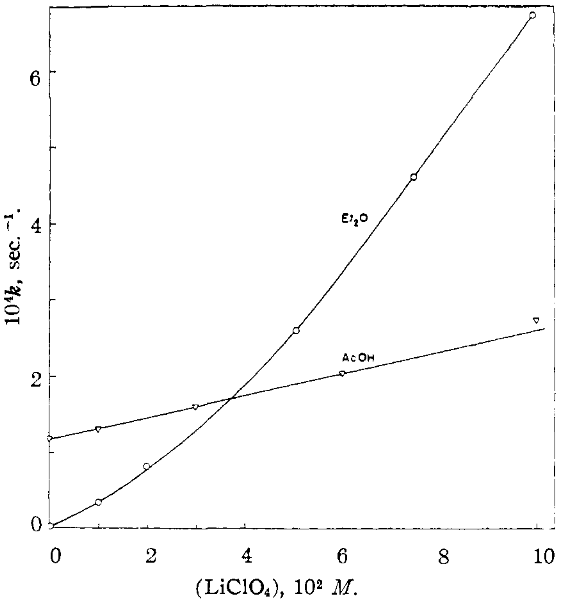

Fig. 1.—Plot of k for I in Et_2O and AcOH at 50.0° *vs.* $[LiClO_4]$.

[1] Research supported by the National Science Foundation.

[2] (a) S. Winstein, *et al.*, THIS JOURNAL, **76**, 2597 (1954); *Chemistry and Industry*, 664 (1954); (b) S. Winstein and A. H. Fainberg, THIS JOURNAL, **78**, 2763 (1956).