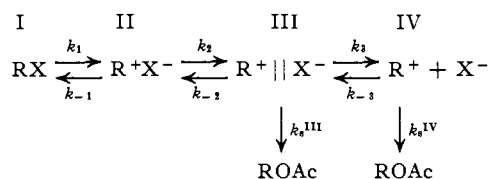


partial measure of ion pair return, is indicated in Table I by the ratio (k_{ext}^0/k_t^0) .

The large effect of solvent change on the relative importance of ion pairs and dissociated carbonium ions is disclosed by common-ion rate depression studies. In acetic acid solvent, no common-ion rate depression due to developing HOBS^{2d} or added LiOBS^{2d} or Bu₄NOBs can be detected. Using the symbolism of the solvolysis scheme with two varieties of ion pairs,^{2,4} II and III, and dissociated carbonium ion, IV, the absence of common-ion rate depression in AcOH was shown^{2a,d} to indicate that dissociation of the product-forming ion pair III (k_3) does not compete with its solvolysis (k_s^{III}). As acetic anhydride is added to the acetic acid solvent, common-ion rate depression becomes more and more important. As Bu₄NOBs is added in each binary solvent mixture, there is an upper limit to the amount of depression it is possible to achieve before the very shallow normal rate acceleration sets in. Such a limit is exactly what is expected from a solvolysis scheme where I-OAc may arise from ion pairs as well as dissociated carbonium ions. The amount of depression possible is indicated in Table I by the ratio, k_t^0/k_t^d , between undepressed and fully depressed rate constants. Thus, the fully depressed rate constant, k_t^d , is 42% of k_t^0 in 50% AcOH-Ac₂O, and only 8% of k_t^0 in Ac₂O. The depression of rate by common-ion Bu₄NOBs salt is very efficient and this is indicated by the low salt concentrations required to introduce half of the achievable depression, symbolized by $(\text{Bu}_4\text{NOBs})_{0.5}$.



The increasing importance of common-ion rate depression as the solvent varies corresponds to increasing ratios of dissociation to solvolysis rate constants of ion pair III, (k_3/k_s^{III}) . From a kinetic analysis of the solvolysis scheme, eq. 1 may be derived for evaluating the (k_3/k_s^{III}) ratios, and these are listed in Table I. These ratios permit one to calculate the percentage of I-OAc product arising from ion pair and that from dissociated carbonium ion when the solvolysis is undepressed (see Table).

$$(k_3/k_s^{\text{III}}) = (k_{\text{ext}}^0/k_t^d) [(k_t^0 - k_t^d)/(k_{\text{ext}}^0 - k_t^0)] \quad (1)$$

$$k_{-3} = 1.13 \times 10^{10} \Lambda_0/D \quad (2)$$

The increasing (k_3/k_s^{III}) values and growing importance of dissociated carbonium ions as the solvent varies may be discussed in terms of the separate k_3 and k_s^{III} values. The order of magnitude of k_3 can be estimated, since it is equal to $k_{-3}K$, where K represents the ion-pair dissociation constant of ion pair III. For a rough calculation, one can employ the K^5 for Bu₄NOTs and a k_{-3} estimated from Debye's expression⁶ for the rate constant for diffusion-controlled

association of two oppositely charged univalent ions. As was first pointed out to us by Dr. Ernest Grunwald some years ago, Debye's expression at 25.0° may be put in the form of eq. 2, where D and Λ_0 are dielectric constant and limiting equivalent conductance, respectively. On this basis in AcOH ($D = 6$), K ,⁵ k_{-3} , and k_3 are 10^{-6} , 6.3×10^{10} l. mole⁻¹ sec.⁻¹, and 6×10^4 sec.⁻¹, respectively. Since k_3 does not compete with k_s^{III} , the latter must exceed 10^6 sec.⁻¹. In Ac₂O ($D = 20.7$), K for Bu₄NOTs is not available, but we might use the K and Λ_0 values in acetone⁵ ($D = 20.7$) for this purpose. On this basis, K , k_{-3} , and k_3 turn out to be 2.5×10^{-3} , 8.5×10^{10} l. mole⁻¹ sec.⁻¹, and 2.1×10^8 sec.⁻¹, respectively. From the (k_3/k_s^{III}) value in Ac₂O, k_s^{III} is thus estimated at 6×10^6 sec.⁻¹.

We see from the above estimates of rate constants that the large increase in the importance of dissociated carbonium ions as the solvent varies in acetolysis of I-OBs is associated with a *ca.* 3500-fold increase in k_3 , an ion-pair dissociation rate constant. The present results and general treatment furnish considerable added insight into the effect of solvent on the roles of ion pairs and dissociated ions in solvolysis and related reactions.

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The Photochemical Isomerization of B-Nor-1-dehydrotestosterone Acetate in Dioxane Solution¹

Sir:

Dehydrogenation of the known B-nortestosterone acetate² with dichlorodicyano-*p*-benzoquinone in boiling dioxane gave the 1-dehydro derivative **1**, m.p. 142° ($[\alpha]_D -43^\circ$ (*c* 0.55, CHCl₃); $\lambda_{\text{max}}^{\text{EtOH}}$ 245 m μ (ϵ 16,800); $\nu_{\text{max}}^{\text{CHCl}_3}$ 1722, 1657, 1625, 1592, and 1250 cm.⁻¹).³ This dienone (**1**) was converted to a single isomer **2** (Scheme I), m.p. 196–198°, ($[\alpha]_D +20^\circ$ (*c* 0.57, CHCl₃); $\lambda_{\text{max}}^{\text{EtOH}}$ 299 m μ (ϵ 14,500); $\nu_{\text{max}}^{\text{CHCl}_3}$ 1720, 1700, 1674, 1583, and 1260 cm.⁻¹, on irradiation of a 0.032 *M* dioxane solution at room temperature, using a low-pressure mercury lamp.⁴ A *ca.* 68% conversion of **1** to **2** was observed after a 2-hr. irradiation period.⁵ Partial hydrogenation of **2** over Raney nickel in ethanol gave rise to the dihydro derivative **4**, m.p. 187–189°, ($[\alpha]_D +114^\circ$ (*c* 0.25, CHCl₃); $\lambda_{\text{max}}^{\text{EtOH}}$ 236 m μ (ϵ 16,500); $\nu_{\text{max}}^{\text{KBr}}$ 1730, 1704, 1670, 1620, and 1250 cm.⁻¹. Complete saturation either of the photoketone, **2**, or of the dihydro derivative, **4**, furnished the tetrahydro acetoxy ketone, **5** (17-OAc), m.p. 113°, ($[\alpha]_D +98^\circ$ (*c* 0.25, CHCl₃); $\nu_{\text{max}}^{\text{CHCl}_3}$ 1727 (broad), 1255 cm.⁻¹. Hydrolysis of **5** with ethanolic potassium carbonate at room temperature gave the corresponding hydroxy ketone **5** (17-OH), m.p. 125°, ($[\alpha]_D +113^\circ$ (*c* 0.17, CHCl₃). In the latter the presence of a cyclopentanone

(1) Photochemical Reactions, Part 27; Part 26: *Helv. Chim. Acta*, **47**, 637 (1964).

(2) J. Joska, J. Fajkoš, and F. Sorm, *Collection Czech. Chem. Commun.*, **25**, 1086 (1960).

(3) Satisfactory mass spectra of the new compounds have been obtained.

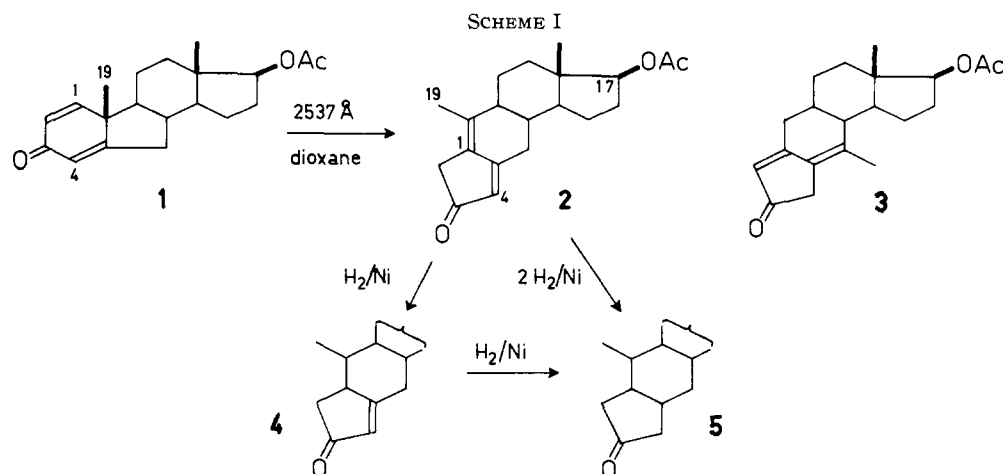
(4) NK 6/20, Quarzlampen GmbH, Hanau (*ca.* 90% emission at 2537 Å.).

(5) Estimated from the ultraviolet absorption of the crude reaction mixture composed of isomers **1** and **2**.

(4) H. L. Goering and J. F. Levy, *J. Am. Chem. Soc.*, **86**, 120 (1964).

(5) P. Klinedinst, S. Smith, and L. Savedoff, unpublished work.

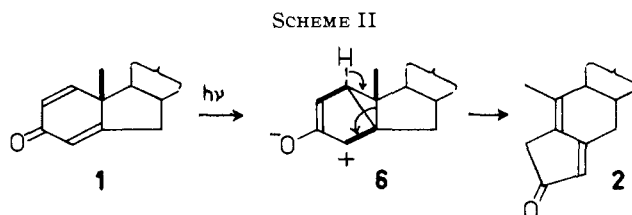
(6) (a) P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942); H. Eyring and E. M. Eyring, "Modern Chemical Kinetics," Reinhold Publishing Corp., New York, N. Y., 1963, Chapter 6.



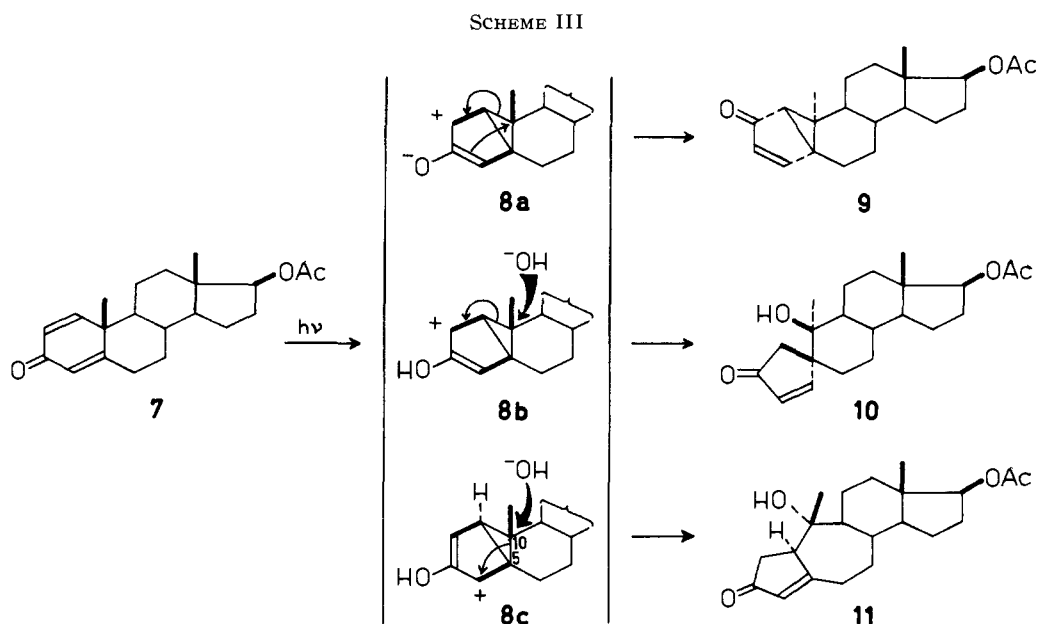
moiety is demonstrated by its characteristic infrared carbonyl absorption at 1735 cm^{-1} (in CHCl_3). The reactions and spectroscopic data described above are compatible with the partial formulas 4 and 5 for the

above δ 4.7. In the spectra of both compounds, 4 and 5, the 19-methyl group appears as a doublet ($J = 7\text{ c.p.s.}$) at δ 0.68 and 0.90 (3H each), respectively.

On the basis of the available experimental evidence no distinction can be made between the formulas 2 and 3 for the photoketone. However, the consideration of possible reaction paths for the dienone 1 leads us to believe that a rearrangement *via* the intermediate 6 to the dienone 2 is conceivable (Scheme II). The postulation of the intermediate 6 in the conversion 1 \rightarrow 2 is in agreement with the proposals of a structurally equivalent zwitterion (*cf.* 8a; Scheme III) or its protonated form (*cf.* 8b, c) as a key intermediate⁷⁻⁹ in the photochemical transformations of 1-dehydrotestosterone acetate (7) in dioxane to the primary photoisomer 9¹¹ and in aqueous acetic acid to the hydroxy ketones, 10^{8,10,12} and 11.¹⁰ The reaction step 6 \rightarrow 2 is the first



hydrogenation products and with either of the structures 2 or 3 for the photoketone. Additional evidence is provided by the nuclear magnetic resonance spectra: the presence of an olefinic methyl group (CH_3 -19), a methylene group bisallylic to the carbonyl group



and to the double bond, and one vinyl proton in the photoketone is indicated by three singlet peaks at δ 1.86 (3H), 2.94 (2H), and 5.92 (1H),⁶ respectively. The dihydro product 4 shows a slightly broadened singlet (half-width $<4\text{ c.p.s.}$) at δ 5.90 (1H) for the vinyl proton at C-4, and the tetrahydro product, 5 (17-OAc), shows no absorption in the vinyl region

(6) N.m.r. data were obtained in deuteriochloroform at 60 Mc.; shifts are expressed as δ -values (p.p.m.) from tetramethylsilane as internal standard.

example for the nonhydrolytic cyclopropane fission

(7) *Cf.* H. E. Zimmerman and I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961); **84**, 4527 (1962).

(8) C. Ganter, E. C. Utzinger, K. Schaffner, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **45**, 2403 (1962).

(9) For a different view on the sequence of the hypothetical intermediates see ref. 10.

(10) P. J. Kropp and W. F. Erman, *J. Am. Chem. Soc.*, **85**, 2456 (1963).

(11) H. Dutler, C. Ganter, H. Ryl, E. C. Utzinger, K. Weinberg, K. Schaffner, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **45**, 2346 (1962).

(12) *Cf.* also C. Ganter, R. Warszawski, H. Wehrli, K. Schaffner, and O. Jeger, *ibid.*, **46**, 320 (1963).

between C-5 and C-10 in a (hypothetical) type 8 intermediate. In view of the *exclusive* conversion $7 \rightarrow 9$ under identical irradiation conditions,^{11,13} the choice between the reaction paths $6 \rightarrow 2$ and $8a \rightarrow 9$ is evidently controlled by the size of ring B in the dienones 1 and 7, respectively.

Acknowledgment.—We thank Dr. J. Seibl for the measurement of the mass spectra. Financial support of this work from the Schweiz. Nationalfond zur Förderung der wissenschaftlichen Forschung (Project No. 2839) is gratefully acknowledged.

(13) Unpublished results by R. Wenger.

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The Importance of Steric Factors in Substitution Reactions of Metal Complexes. A Pseudo-octahedral Complex

Sir:

With the rebirth of the crystal field theory¹ and its application to metal complexes, the importance of the electronic structures in these systems in explaining their properties is well documented. We wish to report here an example where steric factors, not electronic structure, are responsible for the substitution reaction of a metal complex.

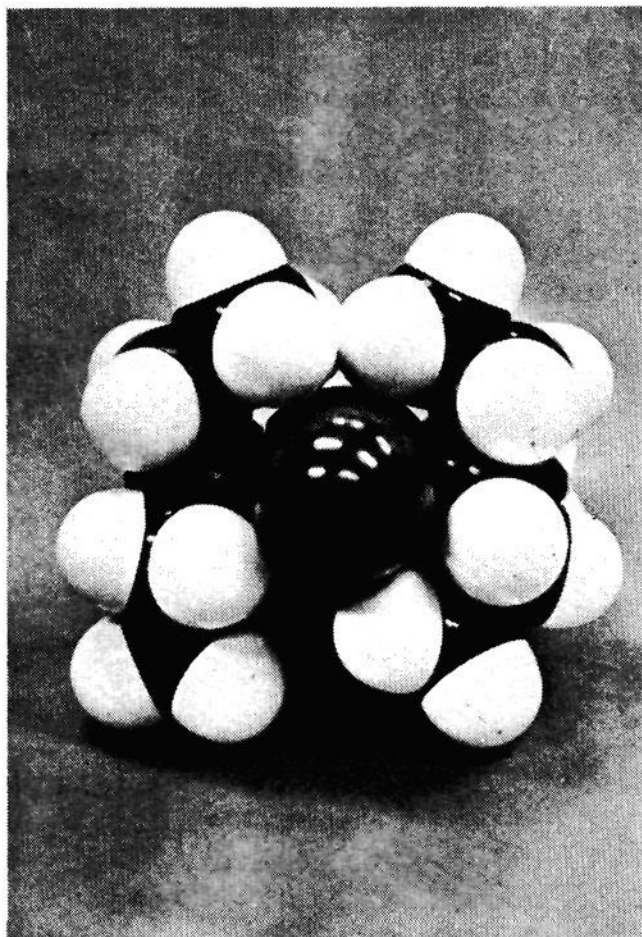


Fig. 1.—Molecular model of the pseudo-octahedral complex $[\text{Pd}(\text{Et}_4\text{dien})\text{Cl}]^+$.

The rates of substitution reactions of octahedral metal complexes do not generally depend on the reagent.² For square-planar complexes, the rates of reaction do depend on the reagent.³ The question arises as

(1) H. Bethe, *Ann. Physik*, [5] **3**, 133 (1929).

(2) (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, Chapter 3; (b) M. Eigen, *Pure Appl. Chem.*, **6**, No. 1, 97 (1962).

(3) F. Basolo and R. G. Pearson, "Progress in Inorganic Chemistry," Vol. 4, F. A. Cotton, Ed., Interscience Publishers, Inc., New York, N. Y., 1962.

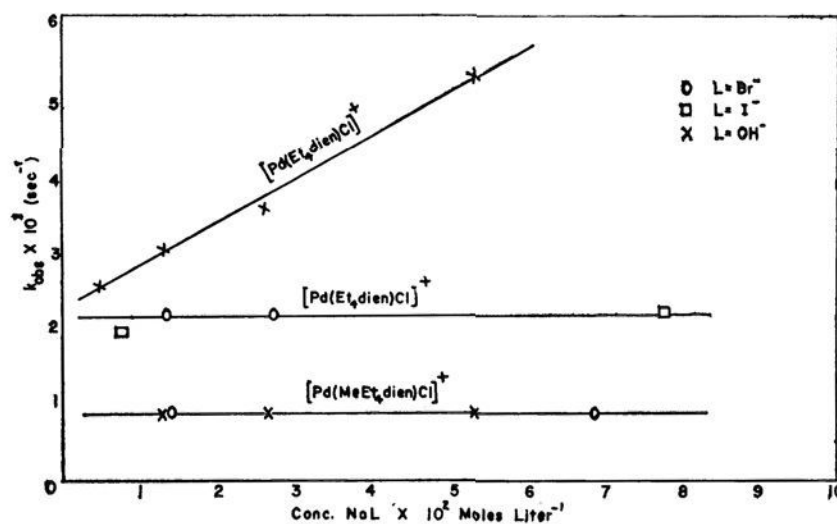


Fig. 2.—Rates of reaction of pseudo-octahedral Pd(II) substrates with various reagents at 25° in water.

to whether this difference in behavior between octahedral and square-planar substrates is due to a difference in electronic structure or in molecular (steric) structure. It would appear that the reactions differ in type because of steric factors. For example the low-spin d^8 complex⁴ $[\text{Pd}(\text{Et}_4\text{dien})\text{Cl}]^+$ looks like and reacts like an octahedral complex (Fig. 1). Because of this we call it a *pseudo-octahedral* complex.

The reaction of $[\text{Pd}(\text{dien})\text{Cl}]^+$ with OH^- and Br^- at 10^{-3} M concentration of reactants is too fast to study at room temperature by the stopped flow method which means it has a $t_{1/2} < 10^{-3}$ sec. However $[\text{Pd}(\text{Et}_4\text{dien})\text{Cl}]^+$ reacts with various reagents at 25° with $t_{1/2} = 6$ min. Except for OH^- , the rate of reaction 1 does



not depend on L^- (Fig. 2.). This most striking result is reminiscent of reactions of chloroamminecobalt(III) complexes.^{2a} The unique behavior of OH^- is due to a rapid acid-base pre-equilibrium forming the more reactive amido species $[\text{Pd}(\text{Et}_4\text{dien-H})\text{Cl}]$, an $\text{S}_{\text{N}}1\text{CB}$ mechanism. That this is correct is supported by the fact that OH^- has no effect on the rate of reaction of $[\text{Pd}(\text{MeEt}_4\text{dien})\text{Cl}]^+$ which contains no N-H hydrogen.

Therefore, these pseudo-octahedral substrates behave unlike their low-spin d^8 relatives, but like octahedral complexes. This provides striking evidence of the importance of steric factors in these systems.

The complexes $[\text{Pd}(\text{Et}_4\text{dien})\text{X}]$, where $\text{X} = \text{Cl}^-$, Br^- , were prepared quite simply by mixing H_2PdCl_4 with an excess of the amine and warming the solution for a few minutes on a steam bath. Addition of excess LiX to the resulting clear orange solution caused the complex to separate as yellow crystals. The solid was separated by filtration and recrystallized from aqueous ethanol. *Anal.* Calcd. for $[\text{Pd}(\text{Et}_4\text{dien})\text{Cl}]\text{Cl}$: Pd, 27.1. Found: Pd, 27.4. Conductivity measurements show the complex to be a 1:1 electrolyte in water. *Anal.* Calcd. for $[\text{Pd}(\text{Et}_4\text{dien})\text{Br}]\text{Br}$: Pd, 22.1; C, 29.9; H, 6.1. Found; Pd, 22.4; C, 30.1; H, 6.4. The cation $[\text{Pd}(\text{MeEt}_4\text{dien})\text{Cl}]^+$ could not be isolated as the chloride, since a sticky, oily material always resulted. It was therefore isolated as the hexafluorophosphate. *Anal.* Calcd. for $[\text{Pd}(\text{MeEt}_4\text{dien})\text{Cl}]\text{PF}_6$: C, 30.2; H, 6.0. Found: C, 30.6; H, 6.0. Conductivity measurements show this complex to be a 1:1 electrolyte in both water and nitrobenzene.

(4) dien = $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$, $\text{Et}_4\text{dien} = (\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$, $\text{MeEt}_4\text{dien} = (\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$.