

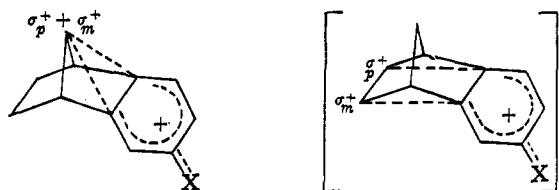
TABLE I
ACETOLYSIS RATES OF THE BROSYLATES

Compound	Temp., °C.	$k\psi$, sec. ⁻¹	Calculated $k\psi^b$ (77.60°) sec. ⁻¹	Rel. rate ^b (77.60°)
XI	77.65 ± 0.03	8.265 × 10 ⁻⁴	7.943 × 10 ⁻⁴	53.3
	77.65 ± 0.03	7.996 × 10 ⁻⁴		
	64.41 ± 0.03	1.556 × 10 ⁻⁴		
	59.85 ± 0.03	6.871 × 10 ⁻⁵		
XII	97.75 ± 0.03	1.235 × 10 ⁻⁴	1.488 × 10 ⁻⁵	1
	95.75 ± 0.05	1.058 × 10 ^{-4a}		
	77.65 ± 0.03	1.495 × 10 ⁻⁵		
	74.79 ± 0.05	1.022 × 10 ^{-5a}		
XIII	120.55 ± 0.07	1.134 × 10 ⁻⁴	7.412 × 10 ⁻⁷	0.050
	103.55 ± 0.04	2.105 × 10 ⁻⁵		
	77.65 ± 0.03	7.367 × 10 ⁻⁷		

^a Cited from ref. 1. ^b Calculated from the least square slopes of the Arrhenius plots.

evidence of *syn*-isomers. The solvolysis rates are summarized in Table I. For comparison, the rate constants at 77.60° were calculated using least square slopes, derived from Arrhenius plots. The relative rates of CH₃O, H and Cl were 53.3:1:0.050.

The large substituent effect and the formation of only *anti*-products strongly suggests a large electron demand from the aromatic ring in the transition state. Although we have insufficient data to establish which kind of σ -value best fits in this homobenzylic system, a plot of $\log k$ vs. ($\sigma_p^+ + \sigma_m^+$) resulted in a good straight line with a ρ of -2.42. A plot of $\log k$ vs. σ_p also gave a straight line with a ρ of -6.15. However, the latter treatment may be dubious because strongly electron-demanding reactions usually follow σ^+ better than σ ; also, the ρ -value is extraordinarily high. All other substituent treatments considered by us did not give a linear relation. It seems reasonable that the aromatic carbons participating in solvolyses at the 7-position will be those which are *para* and *meta* to the 4'-substituent. We tentatively suggest a homoconjugated carbonium ion intermediate, which may be pictured as



If our suggestions are correct, the correlations of homoconjugation on the 3-carbon with σ_p^+ and on the 2-carbon with σ_m^+ would be expected. Further studies in this field are in progress and will be reported later.

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MECHANISMS OF α -ELIMINATION. REACTIONS OF NITROBENZYL ONIUM IONS WITH AQUEOUS SODIUM HYDROXIDE

Sir:

It has been found that *p*-nitrobenzyltrimethylsulfonium *p*-toluenesulfonate forms *p,p'*-dinitrostilbene (99%) when allowed to react with aqueous sodium hydroxide.¹ An α -elimination mechanism was postulated. An alternative mechanism could be the displacement of dimethyl sulfide by a carbanion (ylide) attack on a

second sulfonium ion. The second-order kinetics [(salt)(HO⁻)] would eliminate the carbanion displacement mechanism if the removal of the methylene protons were rapidly reversible. The sulfonium salt isolated after partial reaction in D₂O showed infrared absorptions characteristic of C-D bonds.¹ Although the methylene protons would be most likely to be replaced, the infrared evidence does not prove this. By means of n.m.r. it is possible to determine which protons have been replaced. We carried out a deuterium exchange study as described before.¹ The n.m.r. spectrum of the recovered sulfonium salt showed that at least 97% of the methylene protons were exchanged and about 50% of the methyl protons were exchanged. This eliminates the carbanion displacement mechanism.

The nature of the substituent on the phenyl ring is critical. It has been found that unsubstituted, *m*-chloro- and *p*-methylbenzyltrimethylsulfonium ions when treated with base do not yield the corresponding stilbenes but give high yields of alcohol.²

An aqueous solution 0.1 *M* in *m*-nitrobenzyltrimethylsulfonium bromide³ and an aqueous solution 0.1 *M* in *p*-nitrobenzyltrimethylammonium bromide³ and 0.2 *M* in sodium hydroxide, after heating on a steam bath for 20 hr., gave a brown amorphous precipitate (I) which was isolated by filtration. The filtrate was extracted with ether and the ether dried with magnesium sulfate. After evaporation of ether and purification on an alumina column, a 5% yield of *m*-nitrobenzyl alcohol was obtained. The brown solid I gave a white crystalline solid which melted at 154–155° and a brown tar after chromatography on alumina. The white solid was homogeneous by thin layer chromatography and was shown to be *m,m'*-dinitrostilbene oxide, in 41% yield. (Anal. Calcd. for C₁₄H₁₀N₂O₅: C, 58.74; H, 3.52; N, 9.79. Found: C, 58.50; H, 3.62; N, 9.33, mol. wt. (osmom.), 276). An infrared spectrum showed peaks at 1260, 920 and 860 cm.⁻¹ (epoxide) and at 1520 and 1340 cm.⁻¹ (nitro group).⁴ The n.m.r. spectrum showed absorption in the aromatic region at 7.9 δ^5 and a single sharp peak at 4.0 δ with areas in the ratio 4:1. Ethylene protons of stilbene oxide are known to absorb at 3.9 δ and the phenyl protons at 7.4 δ .⁶ A nitro group should shift the absorption of the phenyl protons downfield. The tar is being investigated further. Under nitrogen, with heating for 5 hr., 43% of the stilbene oxide and 5% of *m*-nitrobenzyl alcohol were obtained.

Carbene formation from ammonium salts has been reported.⁷ We allowed an aqueous solution 0.1 *M* in *p*-nitrobenzyltrimethylammonium bromide³ and 0.2 *M* in sodium hydroxide to react on a steam bath for 72 hr. After this period of time a quantitative recovery of ammonium salt was made. Under the same conditions the *p*-nitrobenzyltrimethylsulfonium salt gave a quantitative yield of *p,p'*-dinitrostilbene within 1 hr. The relative inertness of the ammonium salt could be due to the fact that trimethylamine is a poorer leaving group than dimethyl sulfide.⁸ Also, sulfur has d-orbitals which may help to stabilize the transition state, but

(2) C. G. Swain and E. R. Thornton, *J. Org. Chem.*, **26**, 4808 (1961).

(3) This compound gave a satisfactory microanalysis.

(4) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 118, 298.

(5) Obtained with a Varian HR-60 spectrometer in CDCl₃; chemical shifts in parts per million downfield from tetramethylsilane.

(6) R. Ketcham and V. P. Shah, *J. Org. Chem.*, **28**, 229 (1963).

(7) V. Franzen, *Chem. Ber.*, **93**, 557 (1960); V. Franzen and G. Wittig, *Angew. Chem.*, **72**, 417 (1960); C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 2357 (1929).

(8) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 184; K. Lohmann, Ph.D. Thesis in Organic Chemistry, M.I.T., 1959.

(1) C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **83**, 4033 (1961).

nitrogen does not. Stabilization of transition states by d-orbitals has been suggested before.⁹

Phosphorus has d-orbitals which seem to lower the energy of transition states where a negative charge is developed on an atom next to the phosphorus atom.^{9a} We investigated the reaction of *p*-nitrobenzyltriphenylphosphonium bromide³ with sodium hydroxide. This salt has been prepared previously and allowed to react with sodium hydroxide in 50% alcohol.¹⁰ Triphenylphosphine oxide and *p*-nitrotoluene were reported as products but no yields were given. An aqueous solution 0.05 *M* in phosphonium salt and 0.1 *M* in sodium hydroxide was allowed to reflux on a steam bath 72 hr. A yield of 97% of crude triphenylphosphine oxide was removed by filtration and after purification through an alumina column gave 88% of analytically pure material. A 56% yield of *p*-nitrotoluene was scraped from the reflux condenser. No *p,p'*-dinitrostilbene or *p*-nitrobenzyl alcohol could be found by thin layer chromatography. Phosphorus has low-lying d-orbitals but phosphonium salts react rapidly with hydroxide ion by a mechanism other than carbene formation.¹¹ Also, although there is a scarcity of data, there is an indication that triphenylphosphine may be a rather poor leaving group relative to dimethyl sulfide.¹²

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(9) (a) W. E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **77**, 521 (1955); (b) W. E. Doering and K. C. Schreiber, *ibid.*, **77**, 514 (1955); C. W. Crane and H. N. Rydon, *J. Chem. Soc.*, 766 (1947); P. Mamalis and H. N. Rydon, *Nature*, **166**, 404 (1950); *Chem. Ind. (London)*, 93 (1951).

(10) F. Krohnke, *Chem. Ber.*, **83**, 291 (1950).

(11) M. Zanger, C. A. VanderWerf and W. E. McEwen, *J. Am. Chem. Soc.*, **81**, 3806 (1959).

(12) A. W. Johnson and R. B. LaCount, *ibid.*, **83**, 417 (1961).

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FORMATION OF GASEOUS TITANIUM(IV) HYDRIDE AND CHLOROHYDRIDES OF TITANIUM

Sir:

Titanium compounds in which Ti is in the II, III and IV oxidation states are known but the highest known hydride of titanium is crystalline TiH₂; actually, the latter is non-stoichiometric and approaches TiH₂ as a limiting composition.¹ Titanium(II) compounds are generally ionic while those of Ti(IV) are usually covalent. There has long been speculation upon the possible existence of a TiH₄ hydride but this compound has never been prepared. In a recent review of hydride formation by atomic hydrogen reactions, it was pointed out that many hitherto unknown hydrides might be observed if atomic hydrogen reactions with volatile compounds containing metal atoms were studied with a time of flight mass spectrometer.² Using this technique we have now observed the formation of TiH₄ and also previously unknown chlorohydrides of Ti(IV). This has been accomplished by following the reaction products of the mercury-photosensitized decomposition of TiCl₄-H₂ mixtures at low pressures.

In applying the time of flight mass spectrometer technique, it is particularly desirable to place the reactor directly adjacent to the spectrometer leak which is situated in the wall of the ionization chamber.

(1) D. Hurd, "Chemistry of the Hydrides," John Wiley and Sons, Inc., New York, N. Y., 1952.

(2) B. Siegel, *J. Chem. Educ.*, **38**, 496 (1961).

One can use the Bendix fast reaction inlet system for this purpose. In this way the mass spectrometer analyzes the reaction gas composition directly adjacent to the leak since this composition is essentially frozen upon crossing the leak; once within the ionization chamber very few molecular collisions can occur. Mixtures of H₂-TiCl₄ (9H₂:1TiCl₄) saturated with mercury were irradiated with light of 2537 Å. in a reaction cell situated as described above. Mass spectra of the product mixtures were taken at reactant pressures of 30, 8 and 4 mm. using an ionizing potential of 70 electron volts. Since the reactor was continually being pumped out through the mass spectrometer leak, constant pressure of reactants was maintained by continuous introduction of pre-mixed TiCl₄-H₂ from a large reservoir.

The reaction is very much pressure-dependent. Using the relative intensities of the mass peak 188, which corresponds principally to the major fragment ion (Ti⁴⁸Cl₄³⁵⁺), as a measure of the extent of reaction, it was observed that this reference mass peak decreased only slightly at 30 mm. after the ultraviolet source was activated, but decreased 70-74% at the lower pressures. Clearly the extent of reaction is greater at lower pressures where the hydrogen atom concentrations are larger. The gaseous products of the reaction were identified by the appearance of new or intensified mass peaks after irradiation. At 30 mm. it was not possible to detect the formation of halohydrides of Ti. However, at 8 mm. we observed an increase in the ratio of mass peaks 120/118, corresponding mainly to Ti⁴⁸Cl₂³⁵H₂⁺/Ti⁴⁸Cl₂³⁵⁺, and a striking increase in the ratio of mass peaks 86/83, corresponding mainly to Ti⁴⁸Cl³⁵H₃⁺/Ti⁴⁸Cl³⁵⁺; whereas the latter ratio is 0.04 to 0.05 prior to irradiation, it increases to 0.45 after the source is activated. At 8 mm., TiClH₃ is a major component of the gas phase, and some TiCl₂H₂ is also present.

At 4 mm. one again observes an increase in the mass peak ratio 86/83, rising from 0.05 to 0.47, indicating the presence of TiClH₃. However, in contrast to the runs at 8 mm. where there was little increase in intensity at mass numbers 49 through 52, at 4 mm. one observes the appearance of new peaks at 52 and 51, indicating the presence of Ti⁴⁸H₄⁺ and Ti⁴⁸H₃⁺; one also observes substantial increases in the mass ratios 50/48 and 49/48, mainly attributable to Ti⁴⁸H₂⁺ and Ti⁴⁸H⁺. This certainly demonstrates that TiH₄ was formed, but the lower hydride peaks may be fragmentation patterns of TiH₄ rather than indicative of TiH₃, TiH₂ and TiH.

It is known that TiCl₄ can be reduced with H₂ at higher pressures³ and temperatures, and also by electric discharge,⁴ to form TiCl₃(s) and TiCl₂(s), as well as HCl. Since little change in the gas composition was noted at 30 mm. in our experiments, several experiments were performed in another apparatus to verify the extent of the mercury-photosensitized reaction at higher pressures. In particular, it was intriguing to determine whether crystalline subhalides of titanium could be prepared by this technique from TiCl₄ alone or TiCl₄ and H₂ at room temperature. However, no appreciable reactions were noted for short reaction times with TiCl₄ vapor alone or a 9:1 mixture of H₂-TiCl₄ at 90 mm. These experiments were carried out in an infrared cell with NaCl windows in a plane perpendicular to one containing a quartz window. If reaction did proceed, then HCl would have been

(3) K. Funaki and K. Uchimura, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **59**, 14 (1956); N. C. Baenzinger and R. E. Rundle, *Acta Cryst.*, **1**, 274 (1948); W. E. Reid, Jr., et al., *J. Electrochem. Soc.*, **104**, 21 (1957).

(4) V. Gutmann, H. Nowotny and G. Ofner, *Z. anorg. allgem. Chem.*, **278**, 78 (1955).