

shows clearly the effects of the lanthanide contraction. The volatility of the complexes appears to decrease⁶ as the size of the metal ion (as indicated by the empirical ionic radii of the trivalent ions⁷) increases. This can be explained if it is assumed that in going from the lighter, larger, less volatile lanthanides to the smaller members local dipoles that act to decrease volatility either become smaller or else are more effectively shielded from near neighbors as the outer ligand shell becomes more compact. It should be noted that the retention times cannot be correlated with mass. The yttrium complex has about the same retention time as that of erbium even though the atomic weight of yttrium is only about one-half that of erbium.

Work in this laboratory now in progress is directed to the synthesis of derivatives of H(thd), particularly of the type in which fluorocarbon moieties are incorporated, in hopes of obtaining complexes that are even more volatile. Spectral, magnetic susceptibility, and single crystal X-ray data are also being studied⁸ to further characterize these unusually volatile complexes.

Acknowledgment. This research was supported in part by the ARL In-House Independent Laboratory Research Funds, Office of Aerospace Research, U. S. Air Force.

(6) That the increase in retention times reflects decreasing volatility is inferred from the fractional sublimation data.

(7) V. M. Goldschmidt, *Geochemische Verteilungsgesetze der Elemente*, 8, 69 (1926); *Ber.*, 60, 1263 (1927).

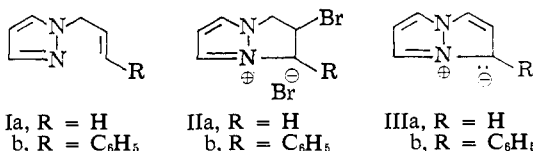
(8) E. A. Boudreaux and L. M. Trefonas, private communication, Aug. 1965.

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4,8-Diazapentalene¹

Sir:

In two earlier publications² we reported the synthesis of stable 1-benzoyl-2-phenyl derivatives of the 4,8-diazapentalene³ system (IIIa). We now report p.m.r.



evidence for the existence of the parent 4,8-diazapentalene (IIIa) and its 1-phenyl derivative (IIIb).

1-Allylpyrazole⁴ was treated with bromine in 48% hydrobromic acid. The crude dibromide that formed underwent cyclization in boiling acetone to IIa, m.p. 156.5–159° (p.m.r.: doublet, τ 1.33; triplet, 2.98; multiplet, 4.38; multiplet, 4.96; areas 2:1:1:4).⁵ The bromo compound, IIa, was then dissolved in deuteriodimethyl sulfoxide in a p.m.r. tube and treated with an excess of lithium hydride. A nitrogen atmosphere was provided and the tube was sealed. The

(1) Presented at the Heterocyclic Chemistry Conference, Bozeman, Mont., Aug. 12, 1965.

(2) (a) T. W. G. Solomons and F. W. Fowler, *Chem. Ind. (London)*, 1462 (1963); (b) T. W. G. Solomons, F. W. Fowler, and J. Calderazzo, *J. Am. Chem. Soc.*, 87, 528 (1965).

(3) Pyrazolo[1,2-*a*]pyrazole.

(4) I. L. Finar and K. Utting, *J. Chem. Soc.*, 5272 (1960).

(5) Satisfactory analytical and p.m.r. data have been obtained for all new compounds reported. Wherever possible picrates and tetraphenylboron derivatives were also prepared and analyzed.

p.m.r. spectrum showed the characteristic A₂X spectrum expected for the 4,8-diazapentalene. The spectrum consisted of a doublet at τ 2.95 and a triplet at τ 3.52 with $J = 2.5$ c.p.s. The ratio of intensities was 2:1.⁶ The aliphatic protons present in IIa were all absent, and the only other peaks present were assigned to LiOH⁷ and the solvent. It is interesting to note the shift in positions of the A₂X protons of the pyrazolium ring in IIa as it is transformed to IIIa. The 1 and 3 protons of the pyrazolium compound are shifted upfield by 96 c.p.s., while the 2 proton is shifted upfield by only 32 c.p.s. This is consistent with the change from a ring bearing a positive charge (IIa) to a neutral system (IIIa) in which resonance structures place a negative charge on the 1 and 3 positions.

Cinnamylpyrazole (Ib),⁵ b.p. 101° (0.025 mm.), was converted to the salt IIb,⁵ m.p. 164–166°, by bromination and cyclization. Dehydrobromination of IIb with lithium hydride in deuteriodimethyl sulfoxide produced what we believe to be 1-phenyl-4,8-diazapentalene (IIIb). The p.m.r. spectrum showed a complex multiplet in the region τ 2.33–3.36. All of the peaks due to the aliphatic protons in IIb disappeared during the conversion.

When exposed to air, a solution of the 4,8-diazapentalene rapidly oxidized to a dark insoluble substance. This oxidation seems to be much slower in dimethyl sulfoxide than in other solvents which were tried.

4,8-Diazapentalene formed an orange crystalline picrate,⁵ m.p. 140–141°. Attempts to form an adduct with methyl propiolate or dimethyl acetylenedicarboxylate have so far been unsuccessful. Benzoylation has also been attempted and resulted in a very dark solid which melts above 360°.

The visible-ultraviolet spectra of IIIa and IIIb were measured in 95% ethanol.⁸ Maxima were found at 257 m μ (log ϵ 3.7) and 465 m μ (log ϵ 3.5) for IIIa and 254 m μ (log ϵ 4.1) and 480 m μ (log ϵ 3.5) for IIIb.

Acknowledgment. The authors are grateful to the donors of the Petroleum Research Fund administered by the American Chemical Society and to the National Science Foundation for support of this work.

(6) It should be noted that the 4,8-diazapentalene absorbs at lower fields than the pentalene dianion, and the relative positions of the doublet and triplet are reversed. Cf. T. J. Katz, M. Rosenberger, and R. K. O'Hara, *J. Am. Chem. Soc.*, 86, 249 (1964).

(7) The salt IIa was partially hydrated.

(8) Weighed amounts of IIa and IIb were placed in nitrogen-flushed volumetric flasks. Excess lithium hydride and a small amount of dimethyl sulfoxide were added. When the reaction was completed the mixture was diluted with 95% ethanol and the spectra were determined.

(9) American Chemical Society Petroleum Research Fund Undergraduate Scholar, 1964–1965; National Science Foundation Undergraduate Research Participant, 1965.

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On the Inertia of Aqueous Phosphite Ion to Oxidation

Sir:

Recent work on the oxidation of arsenite¹ and of sulfite² by HCrO₄⁻ in aqueous solution containing

(1) J. G. Mason and A. D. Kowalik, *Inorg. Chem.*, 3, 1248 (1964).

(2) G. P. Haight, Jr., E. Perchonock, P. Emmenegger, and G. Gordon, *J. Am. Chem. Soc.*, 87, 3835 (1965).

Table I. Oxidation of $H_nXO_3^{n-3}$ Species by $HCrO_4^-$

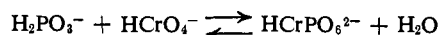
Reductant	Oxidation products	Rate	k	$K_f[H_{n-1}CrXO_6]$	Ref.
$H_2AsO_3^-$	$H_2AsO_4^-$	$\frac{K_f k [Cr(VI)] [H_2AsO_3^-]}{1 + K_f [H_2AsO_3^{2-}]}$	3.5×10^{-4}	22.4	a
$H_2PO_3^-$	$H_2PO_4^-$	No reaction at 25°	...	7.0	b
H_3PO_3	H_3PO_4	$\frac{K_f k [Cr(VI)] (H_3PO_3) [H^+]}{1 + K_f [H_3PO_3]}$	3×10^{-5}	26.0	b
HSO_3^-	$S_2O_6^{2-} + SO_4^{2-}$	$\frac{k K_f [Cr(VI)] [HSO_3^-]^2 [H^+]}{1 + K_f [HSO_3^-]}$	4×10^6	36	c

^a See ref. 1. ^b This work. ^c See ref. 2.

acetate buffer showed striking differences in rates and stoichiometry. HSO_3^- is oxidized half to $S_2O_6^{2-}$ and half to SO_4^{2-} , while $H_2AsO_3^-$ is oxidized exclusively to $H_2AsO_4^-$. The rate constant (not strictly comparable) for oxidation of HSO_3^- is about 10^6 vs. 10^{-4} for oxidation of $H_2AsO_3^-$. Since the structure of arsenite in solution is not certain while that for $H_2PO_3^-$ is known to contain an H-P bond, it seemed interesting to obtain the kinetics and stoichiometry for the reaction of $H_2PO_3^-$ with $HCrO_4^-$ in an acetate buffer for comparison.

The reaction of H_3PO_3 with $HCrO_4^-$ has been studied previously in rather concentrated solutions of $HClO_4$, H_2SO_4 , and HCl containing enough Cr(VI) that $Cr_2O_7^{2-}$ was probably the principle species present.³ No formal rate law was determined.

In acetate buffer no reaction between $HCrO_4^-$ and $H_2PO_3^-$ is observed over a period of several days. At 100° very slow reaction occurs with apparently all the $H_2PO_3^-$ being converted to $H_2PO_4^-$, similar to the oxidation of arsenite. Thus, $S_2O_6^{2-}$ but neither $As_2O_6^{4-}$ nor $P_2O_6^{4-}$ can be produced by acid chromate oxidation of HSO_3^- , $H_2AsO_3^-$, and $H_2PO_3^-$, respectively. The equilibrium



was studied directly by spectrophotometric techniques previously reported.⁴ The results on the three systems are compared in Table I. Apparently the H-P bond in $H_2PO_3^-$ inhibits oxidation of phosphite and limits the product to phosphate using $HCrO_4^-$ as an oxidant.

Oxidation of H_3PO_3 by $HCrO_4^-$ in 1 M H^+ is reasonably fast for study. Preliminary results indicate the rate law is

$$\text{rate} = \frac{(H_3PO_3)(Cr(VI))(H^+)(k_1 + k_2[H_3PO_3])}{(1 + K(H_3PO_3))}$$

where k_1 and k_2 are $\sim 10^{-4}$ and $K = [H_2CrPO_6^{2-}]/[H_3PO_3][HCrO_4^-] = 26$. Units are moles per liter and seconds. Chloride ion forms CrO_3Cl^- and inhibits the reaction.

Table I gives the preliminary results of our study showing the striking differences in behavior of HSO_3^- , $H_2PO_3^-$, and As(III) as reducing agents for $HCrO_4^-$ in aqueous solution.

(3) B. Kirson, *Bull. soc. chim. France*, 52 (1948).

(4) G. P. Haight, Jr., D. Richardson, and N. Coburn, *Inorg. Chem.*, 3, 1777 (1964).

Acknowledgment. This work was supported by the Swarthmore College Faculty Research Funds.

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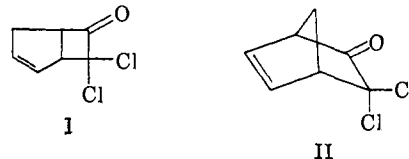
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A New Tropolone Synthesis via Dichloroketene

Sir:

Since Staudinger's unsuccessful attempt to prepare dichloroketene in 1913 by the thermal decomposition of mixed dichloromalonic anhydrides¹ the literature has been void of further references. In connection with a study of reactive chlorine compounds obtainable from basic chlorocarbon materials we investigated an alternate synthesis based on the dehydrochlorination of dichloroacetyl chloride. Although products from the low-temperature reaction were generally polymeric, we were successful in obtaining simple cycloadducts when generating dichloroketene *in situ* in the presence of reactive olefins. Of particular interest to this report is the 1:1 adduct readily obtained with cyclopentadiene which proved to be an immediate precursor of tropolone.²

In a typical cycloaddition experiment, a tenfold excess of cyclopentadiene over dichloroacetyl chloride in dry *n*-hexane was treated with a hexane solution of triethylamine at 0-5°. Removal of the solid hydrochloride and distillation at reduced pressure afforded an adduct $C_7H_6OCl_2$ in 70-75% yield. The liquid product (b.p. 38° (0.25 mm.), n_D^{20} 1.5163, g.l.p.c. purity 99+%) showed a single carbonyl band at 1806 cm^{-1} and olefinic unsaturation at 1609 cm^{-1} . Its proton resonance spectrum exhibited a complex multiplet centered at τ 4.1 relative to tetramethylsilane.



(1) H. Staudinger, E. Anthes, and H. Schneider, *Ber.*, 46, 3541 (1913).

(2) An ingenious three-step tropolone synthesis reported by J. J. Drysdale, W. W. Gilbert, and K. K. Schneider (*J. Am. Chem. Soc.*, 80, 3672 (1958)) involves cycloadducts of tetrafluoroethylene and cyclopentadiene. A cumbersome pyrolytic step at 700-750° and 5 mm. is required to convert the adducts to an isomeric mixture of tetrafluoroheptadienes prior to hydrolysis to tropolone.

(3) Elemental analyses of all compounds reported were satisfactory.