

prolyl-L-leucyl-L-valine methyl ester (XIII, oil). Upon removal of benzyl groups from XIII by hydrogenation at 55° over palladium-charcoal, there was obtained the terminal-blocked octapeptide I, N-formylglycyl- α -L-aspartyl-L-serylglycylglycyl-L-prolyl-L-leucyl-L-valine methyl ester, m.p. 192–193°, $[\alpha]_D -84^\circ$; amino acid ratios in acid hydrolysate gly_{3.12}asp_{1.03}ser_{0.94}pro_{0.97}leu_{0.98}val_{0.94}.

The optical purity of certain of the peptides synthesized was determined using appropriate enzyme systems. The dipeptide V was completely hydrolyzed by leucine aminopeptidase¹⁴; under similar conditions the corresponding DL-peptide, m.p. 95–97°, was only partially hydrolyzed. The tetrapeptide XII, m.p. 219° dec. (prepared by hydrogenation of XI), was converted completely to its component amino acids by a mixture of leucine aminopeptidase and prolidase.^{14,15} Finally, the tetrapeptide VIII was completely hydrolyzed by carboxypeptidase-A.

The octapeptide I and various intermediate compounds are being investigated for possible esterase and peptidase activity. In addition, compound I serves as an intermediate for more extensive syntheses, including its incorporation into macromolecular polypeptide systems containing other amino acids involved in proteolytic enzyme action.

Acknowledgment.—We are pleased to acknowledge the support of this work by U. S. Public Health Service Grant No. AM-07300 and by the Office of the Surgeon General, Department of the Army. Mr. Richard Maine provided competent technical assistance. We thank Dr. Elizabeth R. Simons for participation in the enzymic work.

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RECEIVED AUGUST 24, 1964

σ -Bonded Alkyl Compounds of Niobium and Tantalum. Trimethyldichloroniobium and Trimethyldichlorotantalum¹

Sir:

Recent developments in the organometallic chemistry of the elements of group V-A have been confined mainly to arene complexes. To this date, there have been no reports of σ -bonded alkyl compounds of these metals, although many attempts to prepare them have been described.² Accordingly, we wish to report the first successful syntheses of alkyl derivatives of niobium and tantalum. Trimethyldichloroniobium, $(\text{CH}_3)_3\text{NbCl}_2$, and trimethyldichlorotantalum, $(\text{CH}_3)_3\text{TaCl}_2$, have been prepared by the low temperature exchange of methyl groups and chlorine between dimethylzinc and the pentachlorides of niobium and tantalum, respectively.

In a typical experiment, 7.45 mmoles of NbCl_5 was sublimed *in vacuo* and treated with 18.26 mmoles of

$(\text{CH}_3)_2\text{Zn}$ in 15 ml. of pentane. The vessel containing the NbCl_5 and pentane was cooled to -78° , and the $(\text{CH}_3)_2\text{Zn}$ was admitted in small portions because of the exothermic character of the reaction. A precipitate (probably ZnCl_2) was observed immediately following addition of the first portion of $(\text{CH}_3)_2\text{Zn}$. After each addition the reaction mixture was warmed nearly to room temperature and agitated. After the final addition of $(\text{CH}_3)_2\text{Zn}$, all volatiles were removed at room temperature; the $(\text{CH}_3)_3\text{NbCl}_2$ was trapped at -36° . The yield was 12.7% based on NbCl_5 . Trimethyldichlorotantalum was prepared in an identical manner. All manipulations were carried out in a high vacuum system.

Trimethyldichloroniobium forms golden yellow crystals which sublime readily under vacuum at room temperature. However, the compound will darken and release methane when left at room temperature for several hours. It appears to be indefinitely stable at -78° .

Trimethyldichlorotantalum forms pale yellow crystals of similar volatility. This compound, however, appears to be much more thermally unstable than the niobium analog. The thermal stability of both compounds was found to be adversely affected by small quantities of impurities. Both compounds are highly reactive toward water and air.

The formulas of the new compounds were established by hydrolyzing freshly prepared samples *in vacuo* with aqueous KOH, measuring the resultant CH_4 directly by means of a Sprengel pump, and determining niobium and tantalum gravimetrically as the pentoxides. The chloride was also determined gravimetrically. The CH_4 was subsequently shown to be quantitatively pure by means of infrared and mass spectroscopy. For each compound, all analytical data were determined independently on the same weighed sample.

Anal. Calcd. for $(\text{CH}_3)_3\text{NbCl}_2$: CH_3 , 21.59; Nb, 44.47; Cl, 33.94. Found: CH_3 , 21.6; Nb, 44.6; Cl, 34.0.

Anal. Calcd. for $(\text{CH}_3)_3\text{TaCl}_2$: CH_3 , 15.19; Ta, 60.93; Cl, 23.88. Found: CH_3 , 14.8; Ta, 63.0; Cl, 23.6.

In addition, samples of the new compounds were subjected to slow hydrolysis by exposure to the air, and the residues were analyzed spectrographically. No significant quantities of zinc or other extraneous metals were found to be present.

Attempts to obtain the molecular weights by gas density and vapor pressure depression measurements have not been successful because of the instability of these compounds under the experimental conditions used.

The mass spectrum of the niobium compound is indicative of $(\text{CH}_3)_3\text{NbCl}_2$ monomer, although parent peaks (mass 208, 210, 212) were not observable at an ionizing voltage of 70 e.v. Major fragments are the $[(\text{CH}_3)_2\text{NbCl}_2]^+$ ions at masses 193, 195, and 197 (relative abundances of 57, 37, and 6%, respectively).

Proton nuclear magnetic resonance spectra were obtained for $(\text{CH}_3)_3\text{NbCl}_2$ at -10° in CCl_4 containing a trace of $(\text{CH}_3)_4\text{Si}$. All spectra were obtained with a Varian A-60 spectrometer. Trimethyldichloroniobium exhibits a peak (line width 0.6 c.p.s.) 29.8 c.p.s. upfield from $(\text{CH}_3)_4\text{Si}$ which is characteristic for protons on a

(1) This paper presents results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS7-100, sponsored by the National Aeronautics and Space Administration.

(2) F. A. Cotton, *Chem. Rev.*, **55**, 551 (1955).

carbon atom directly bonded to a metal atom. For purposes of comparison, $(\text{CH}_3)_2\text{Zn}$ gives a peak (line width 0.6 c.p.s.) 28.6 c.p.s. upfield from $(\text{CH}_3)_4\text{Si}$. A sample containing both $(\text{CH}_3)_3\text{NbCl}_2$ and $(\text{CH}_3)_2\text{Zn}$ and $(\text{CH}_3)_4\text{Si}$ in CCl_4 was also examined. Only one peak (line width 0.9 c.p.s.) 29.6 c.p.s. upfield from the internal standard was observed. The merging of the two peaks and the slight broadening are suggestive of methyl group exchange between $(\text{CH}_3)_2\text{Zn}$ and $(\text{CH}_3)_3\text{NbCl}_2$. No n.m.r. spectra were obtained for $(\text{CH}_3)_3\text{TaCl}_2$ because of the rapid decomposition of this material in CCl_4 at -10° .

Samples of $(\text{CH}_3)_3\text{NbCl}_2$ and $(\text{CH}_3)_3\text{TaCl}_2$ were pyrolyzed by passage at pressures < 1 mm. through a quartz tube at 700° . In both cases metallic films were formed. At present, only the niobium film has been found to be a superconductor. The volatile products from the pyrolysis were methane and a halogenated hydrocarbon unidentified at present.

Studies of the chemistry of these new compounds are continuing.

Acknowledgment.—The author wishes to thank Dr. Stanley L. Manatt for helpful discussions and for the n.m.r. spectra, and Mr. Daniel Kuwada for the mass spectra.

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RECEIVED AUGUST 13, 1964

Electron Spin Resonance of Triplets from Benzene 1,4-Diazo oxides

Sir:

We wish to report the electron spin resonance (e.s.r.) spectra, including hydrogen hyperfine structure, of the ground state triplets (Ia–d) produced by photolysis of some benzene 1,4-diazo oxides (IIa–d). Such triplets have been suggested as intermediates in the reactions of IIa and its derivatives.¹ The interaction between the unpaired electrons in Ia indicates that the π -system approximates that of a phenoxyl radical. The σ -system should be similar to that of a phenyl radical, and the hyperfine interaction observed is of the order of magnitude expected for such a σ -radical. Ia may be also regarded as a triplet phenyl cation substituted by an oxygen anion. Such a triplet state of the phenyl cation with one π - and one σ -unpaired electron has been suggested by Taft.²

IIa–d were produced by diazotization of the corresponding *p*-aminophenols. Finely powdered samples at 77 or 4°K . were irradiated with a mercury lamp for 1 min. or less. IIa was in "solid solution" in *p*-dichlorobenzene and IIc in 1,2,3-trichlorobenzene; IIb and II d were neat. The spectra were determined with a Varian V-4500 spectrometer equipped with 100-kc. modulation. The spectrum for Ia is given in Fig. 1. The zero-field parameters obtained from these observations were³: for Ia, $D = 0.3179$, $E = 0.0055$ cm.⁻¹;

(1) For a recent review of the structure and reactivity of Ia and some derivatives see M. J. S. Dewar and K. Narayanaswami, *J. Am. Chem. Soc.*, **86**, 2422 (1964), and references cited therein.

(2) R. W. Taft, *ibid.*, **83**, 3350 (1961).

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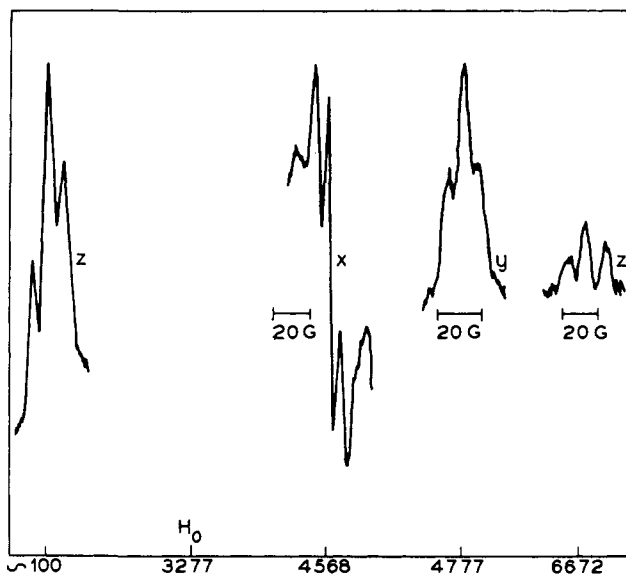
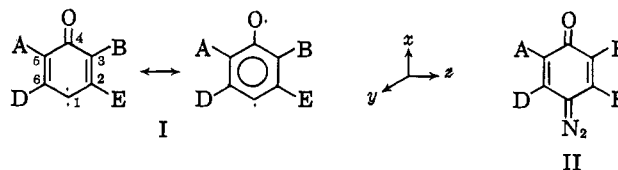


Fig. 1.—E.s.r. spectrum of Ia in *p*-dichlorobenzene. H_0 is the field for resonance of a free electron. Field measurements were not possible for the line near 100 gauss.

Ib, $D = 0.3284$, $E = 0.0086$ cm.⁻¹; Ic, $D = 0.3470$, $E = 0.0010$ cm.⁻¹; and Id,⁴ $D = 0.3333$, $E = 0.0112$ cm.⁻¹.



- a, A, B, D, E = H
b, A, B = Cl; D, E = H
c, A, B = H; D, E = Cl
d, A + D = $-\text{C}_6\text{H}_4^-$; B, E = H

By arguments analogous to those employed with cyclopentadienylidene (III) and indenylidene (IV)⁵ we can show that Ia–d each have one unpaired electron largely localized in a σ -orbital at C-1, the "divalent" carbon atom, and another delocalized in a π -orbital. For such a distribution of the unpaired electrons, D is largely determined by ρ_1 , the π -spin density at C-1. By comparison with III and IV⁵ we expect $\rho_1 \sim 0.4$. This value is compatible with the π -system being similar to that of a phenoxyl radical. The hydrogen hyperfine splitting at the *para* position of the phenoxyl radical is 10.4 gauss⁶ and indicates a $\rho_{\text{para}} \sim 0.42$ – 0.45 .⁷

The small values of E with Ia–d may be rationalized by assuming "bent bonds" at C-1^{5,8} and by including the interaction of the unpaired σ -electron at C-1 and the π -spin density at other atoms.⁵ The one-center and two-center terms occur with opposite sign and largely cancel.

The hyperfine splittings between the components of the triplets in Ia are 8.7, 6.6, and 10.6 gauss, along the

(4) A second set of lines corresponding to $D = 0.323$ and $E = 0.010$ cm.⁻¹ were also observed with Id. Presumably, these were due to a second site in the crystal with a slightly different environment.

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