INFLUENCE OF LIGAND ENVIRONMENT ON STABILITY OF CARBENIUM ION STABILIZED WITH MANGANESE OR RHENIUM

A. G. Ginzburg, Sh. G. Kasumov,

V. N. Setkina, and D. N. Kursanov

The stability of metallocenyl carbenium ions $M - C^+RR'$, where M is a metallocenyl radical, depends on the nature and donor properties of the M, R, and R' groupings. In the example of the previously investigated [1-4] cymantrenyl carbenium ions (CO)LL'MnC₅H₄C⁺RR', we have carried out the first study of metallocenyl carbenium ions dealing with the influence of the nature of the ligand environment of the metal atom on the stability of these cations

 $(I) \overset{OH}{\underset{H_{2}0}{\overset{H^{+}}{\underset{H_{2}0}}}} (I) \overset{H^{+}}{\underset{H_{2}0}{\overset{H^{+}}{\underset{H_{2}0}}}} (I) \overset{H^{+}}{\underset{H_{2}0}{\overset{M_{n}}{\underset{L'}{L'}{\underset{L'}{\atopL}{\underset{L'}{\underset{L'{L'}{\atopL}{\underset{L'}{\underset{L'}{L'}{\underset{L'$

 $LL' = (CO)_2$, (CO)(PPh₃) or $Ph_2PCH_2CH_2PPh_2$.

The replacement of one or two CO groups in the $(CO)_{3}MnC_{5}H_{4}$ group by donor phosphine ligands leads to a sharp increase in the thermodynamic and kinetic stability of the α cymantrenyl carbenium ions. The monophosphine and particularly the diphosphine cations are formed at considerably lower acidities of the medium than are the cations with the $(CO)_{3}Mn$ group.

The value of $p_{K_{R+}}$ for the (CO)₃MnC₅H₄C⁺Ph₂ cation, -6.5 [5], very nearly coincides with $p_{K_{R+}}$ for Ph₃C⁺, -6.63 [6]. From this it follows that the unsubstituted cymantrene group stabilizes the cationic center to approximately the same degree as does Ph, but to a far less degree than does ferrocenyl. For (CO)₂(L)MnC₅H₄C⁺Ph₂ ions in aqueous CF₃COOH [7], the following values have been found for $p_{K_{R+}}$ with the following ligands L: CO -6.7 (this is close to the value in H₂SO₄), PPh₃ -4.0 ± 0.5, and PEt₃ -1.5 ± 0.5. The replacement of two CO groups by the chelate diphosphine ligand leads to a still greater increase in stability. Even though we were not able to measure $p_{K_{R+}}$ for the diphosphine carbenium ions in aqueous H₂SO₄ or CF₃COOH, we did obtain the following evidence of their high stability.

Solutions of the diphosphine cations (II), where R = R' = Alk or R = Ph and R' = Alkare decomposed instantaneously by water, forming the original carbinols (I) or their mixtures with the corresponding olefins (identified on the basis of 'H and ''C NMR spectra). However, the cation (II), where R = R' = Ph and LL' = $Ph_2PCH_2CH_2PPh_2$, is so stable that its solution in CF₃COOH/CH₂Cl₂ is decomposed only very slowly by water (8-12 h). This indicates that the value of pK_{R+} for this cation must be no less than 1-3 (some carbenium ions exist in water with pK_{R+} no less than 4.5, for example the tropylium cation $C_7H^+_7$, pK_{R+} 4.6 [8].

In the primary carbinol with the diphosphine ligand (CO) $(Ph_2PCH_2CH_2PPh_2)$ MnC₅H₄CH₂OH, nucleophilic substitution of OH by OMe or OEt proceeds very readily. By merely recrystallizing this carbinol from MeOH or EtOH, it is converted completely to the corresponding ether with the fragment CH₂OMe or CH₂OEt, which coincides completely with the properties of phenyl ferrocenyl carbinol C₅H₅FeC₅H₄CH(OH)(Ph) [9] (pK_{R+} 0.4 [10]).

In order to evaluate the kinetic stability of cations containing Mn or Re, we selected the solvolysis of acetates as a model reaction and measured the rate of hydrolysis in aqueous acetone and the rate of methanolysis of acetates with residues containing Mn or Re (Table 1).

664

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 884-887, April, 1981. Original article submitted June 16, 1980.

TABLE 1				
		Solvolysis rate c	constant, 1	0 ⁵ • sec -1
Acetate	Formula	hydroly	sis	methanolysis,
		80% acetone	60% ace - tone	МеОН
(111)	(CO) ^a MnC ₅ H ₄ C(H) (Ph)OAc	75°C, no reaction	75°, 3,3	75°, 2,4
	$\left[\left(\mathrm{CO}\right)_{3}$ HeC ₅ H ₄ C(H) $\left(\mathrm{Ph}\right)_{0}$ Ac	Same	75', 3,7	7.57, 2,9
$\hat{\Sigma}$	(CU) 2PPh3MnC3H4C(H) (Ph)UAc	40', 3,4	1	I
(VI)	(CO) PEt3MDC5H4C(H) (PD) OAc	40°, 30,0	1	
(IIA)	$ (CO)(P-P)MnC_{s}H_{4}C(H) (Ph)OAc $	0°C, very]	0 C, very
(IIII)	(CO) (P-P) MnC+H ⁴ C(H) (Me) OAc	fast _	ł	$0^{\circ}, >500 *$
(XI)	Ċ,H,FeC,H,C(H)(Me)OAc	1	ł	0°, 1,7
X	(CO) $(P-P)$ MnC ₅ H ₄ CH ₂ OAc	1		0, 300
(IXI)	C.H.FeC.H.CH2OAc	I	1	0°, 0,1

*As a rough estimate of the lower limit of the rate constant, $k > 5 \times 10^{-3} \text{ sec}^{-1}$, (P-P) = $Ph_2PCH_2CH_2PPh_2$.

TABLE 2

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			H	Found/calculated,	ofo		Peak with greatest
Compound	mp, °C	Empirical formula	υ	H	metal (Mn, Re, Fe)	Ъ	Inass in mass spectrum
(IV)	63-65	C ₁₇ H ₁₃ O ₅ Re	41,70/42,10	2,60/2,29	38,15/38,52	1	482 and 484 (M ⁺)
(A)	114-116	C ₃₄ H ₂₈ MnPO4	70,00/69,62	4,71/4,77	9,09/9,38	5,61/5,52	586 (M+)
(IV)	Oil	C ₂₂ H ₂₈ MnPO4	1	ł	I	1	442 (M+)
(VIII)	117-120	$\mathrm{C}_{36}\mathrm{H}_{35}\mathrm{MnP}_{2}\mathrm{O}_{3}$	68,20/68,35	5,85/5,53	8,75/8,70	9,86/9,81	544 (M-CH _s COOH-CO)
(X)	160-165	$\mathrm{C}_{35}\mathrm{H}_{33}\mathrm{MnP}_{2}\mathrm{O}_{3}$	68,40/67,96	5,50/5,34	8,75/8,90	10,40/10,03	560 (M-OC 2H ₂)
(IX)	61-69	$C_{13}H_{12}O_2Fe$	60, 13/60, 46	5,20/5,43	21,50/21,70	I	258 (M ⁺)
(IIIX)	149-152	$\mathrm{C}_{33}\mathrm{H}_{34}\mathrm{MnO}_{2}\mathrm{P}_{2}$	68,40/68,74	5,54/5,40	9,25/9,50	10,38/10,70	576 (M+)
(IIIX)	167 - 169	C ₃₅ H ₃₅ MnO ₂ P ₂	69,43/69,53	6,02/5,79	8,70/9,10	10,09/10,26	604 (M+)

The hydrolysis of the acetates (III) and (IV) in 80% aqueous acetone does not go forward even at 75° C; in 60% aqueous acetone or in methanolysis, the rates for the two compounds are very close to each other; i.e., Mn and Re stabilize the carbonium center almost identically. In the series Fe-Ru-Os, the rates of solvolysis of the acetates C₅H₅MC₅H₄CH(Me)OAc are in the ratio 1/1.2/5 [11].

When one of the CO groups is replaced by PPh₃ or PEt₃, the acetate hydrolysis rate is higher. The hydrolysis of the acetates (V) and (VI) proceeds under milder conditions (at 40°C in 80% acetone) than for the acetates (III) and (IV) (at 75°C in 60% acetone). When the change is made from PPh₃ to the stronger donor ligand PEt₃, the hydrolysis rate increases appreciably; i.e., the corresponding secondary carbenium ion becomes more stable.

Methanolysis of the secondary acetates (VII) and (VIII) with the chelate diphosphine ligand $Ph_2PCH_2CH_2PPh_2$ proceeds so rapidly that even at 0°C the reaction rate is very high; the methanolysis of the acetate (VII) goes to completion in only 5-10 min; for the acetate (VIII), k > 5×10⁻³ sec⁻¹. Under these same conditions, ferrocenylmethyl acetate (IX) reacts at a far slower rate, k = 1.7×10^{-5} sec⁻¹. These data indicate that the carbenium ions stabilized by the cymantrene residue with a chelate diphosphine ligand are extremely high in stability, comparable to ferrocenyl carbenium ions.

When the change is made from secondary to primary acetates, the methanolysis rate decreases, so that we can compare the rates for the acetates (X) and (XI). The methanolysis of the acetate (X) with the residue (CO)(P-P)MnC₅H₄ goes forward at a rate three orders of magnitude greater than the methanolysis of the acetate (XI) with the ferrocene residue. The high rate of the S_N reaction of the acetates (VII), (VIII), and (X) indicates the strong electron donor capability of the (CO)(P-P)MnC₅H₄ residue. Apparently its donor properties and its capability for stabilizing the α -carbonium center are equal to or greater than the donor capability of the ferrocene residue.

EXPERIMENTAL

The carbinols of the cymantrene series with one [2, 3] and two [4] phosphine ligands $(CO)_{3}MnC_{5}H_{4}CH(OH)Ph$ [12], the carbinols with the ferrocene residue [11, 13], and the acetates (III) and (IX) [11, 12] were obtained as described previously. The carbinol $(CO)_{3}ReC_{5}H_{4}CH(OH)Ph$ (XIV) was obtained by reaction of $(CO)_{3}ReC_{5}H_{4}Li$ with PhCHO in accordance with [14]. The acetates (IV)-(XI) were obtained by reactions of the carbinols with acetic anhydride in pyridine [15]. The elementary analyses and properties of these compounds are shown in Table 2. The structures of the products from hydrolysis and methanolysis were established by comparison with known preparations, IR spectroscopic data, and measurements of molecular weight (mass spectra).

 $(CO) (P-P)MnC_5H_4CH_2OH (XII). The carbinol (CO)_3MnC_5H_4CH_2OH (3 mmoles) [16] and Ph_2PCH_2CH_2PPh_2 (3 mmoles) were irradiated with UV for 8-12 h while refluxing in benzene (100 ml); the course of the reaction was monitored on the basis of the IR spectra. After filtration and removal of the solvent, the residue was recrystallized from a heptane/CH_2Cl_2 mixture (25/1). Obtained (XII), orange crystals, yield 0.9 g (40%), mp 149-152°C, v(CO) 1835 cm⁻¹ (in CHCl_2).$

 $(CO) (P-P) MnC_5H_5 CH_2OCH_2 CH_3 (XIII). The carbinol (XII) was recrystallized from EtOH, obtaining orange crystals with mp 167-169°C. IR spectrum (<math>\nu$, cm⁻¹) 1832 (CO) mass spectrum M⁺604. ¹H NMR spectrum (in CS₂, δ , ppm): 1.0 t (CH₃), ν 2 m (CH₂P), 3.1 q (CH₂), 3.7, narrow singlet (CH₂ with C₅H₄), 3.3 and 4.1 sh (α and β positions of C₅H₄), ν 7 m (C₆H₅). Ratio of intensities is close to theoretical 3:4:2:2:2:2:20.

 $(CO)_{3}ReC_{5}H_{4}CH(OH)Ph$ (XIV). A solution of $(CO)_{3}ReC_{5}H_{4}Li$ was obtained from 4.5 mmoles of $(CO)_{3}ReC_{5}H_{5}$ in a mixture of THF and hexane and 5 mmoles of 1 M butyllithium in hexane at -60°C. At this temperature, a solution of PhCHO (4.5 mmoles) in hexane was added. The mixture was stirred for 1 h at -60°C, then slowly warmed to 20°C and decomposed with water. After treatment, recovered 1.66 g (83%) of the carbinol (XIV), white crystals, mp 85-86°C. In the mass spectrum there were two intense peaks M⁺ with m/z 442 and 440 (¹⁸⁷Re, ¹⁸⁵Re).

The kinetic experiments were performed with a concentration of 5×10^{-3} mole/liter under conditions of pseudofirst order. The reaction kinetics were followed by means of IR spectra on the basis of the decrease in intensity of the v(C=0) band of the acetate group at 1720-1740 cm⁻¹. The reaction was terminated by removing the solvent and volatile reaction products (CH₃COOH) under vacuum, down to 10^{-2} mm (1.3 Pa). The IR spectra were taken in CS₂ in CaF₂ cuvettes (lightpath 1.0 or 2.6 mm) in the NaCl prism region, in a UR-20 spectrophotometer.

The values of pK_{R+} for the carbinols (CO)₂(L)MnC₅H₄C(OH)Ph₂ were determined by the procedure of [6] in aqueous CF₃COOH [7] (wavelength λ for ligand CO 390, PPh₃ 370, PEt₃ 355 nm). In the region of high concentrations of CF₃COOH, where mainly carbenium ions are present, the course of the change in optical density was normal (the same as for Ph_3C^+). For the cations with PPh₃ and PEt₃, upon going into the region of CF₃COOH concentrations where the carbinol form predominates, the solutions become cloudy, since the carbinols that are formed are almost insoluble in the aqueous CF_3COOH (analogously in aqueous H_2SO_4). Therefore, the values shown for pK_{R+} are approximate. For the diphosphine carbonium ions with the indicated chelate ligand, we were not able to measure pKR+ by means of the UV spectra.

SUMMARY

1. Substitution of one and two CO groups by donor phosphine ligands PPh3 and PEt3 leads to an increased stability of the α -cymantrenyl carbonium ions, with diphosphine ligands manifesting a greater stabilizing effect than the monophosphines.

2. Manganese and rhenium stabilize the α -carbonium center to an almost identical degree.

3. The residue (CO) (Ph₂PCH₂CH₂PPh₂)MnC₅H₄ is a strong electron donor, at least as strong as the ferrocene residue.

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