References and Notes

(1) Dimyristoyllecithin (DMPC) is the common name for 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine

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Received October 2, 1978

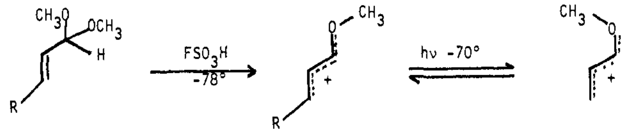
Photochemical and Thermal Isomerizations of 1-Methoxyallyl Cations. A Further Photoisomerization Pathway of Protonated Enones

Sir:

There have been several investigations into the photoisomerizations of protonated unsaturated carbonyl compounds in strong acid solutions and a variety of molecular rearrangements of these systems have been described.[1,2] We report here that a further, fundamental type of reaction can occur, namely photoisomerism about the carbon-oxygen partial double bond.

Such reactions have previously remained undetected, presumably as a result of competing exchange reactions between the proton on oxygen and the acid solvent pool.[3,4] To avoid this complication, we chose to work with the corresponding *O*-methyl derivatives of some of these cations and describe here the preparation, photoisomerism and thermal rearrangements of some 1-methoxyallyl cations.

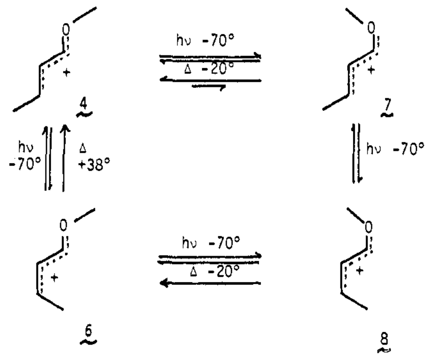
Extraction of the acetals **1** and **2** from Freon 11 into FSO_3H at −78 °C gave solutions of the cations **3** and **4**, respectively.



1, R=H
2, R=CH_3
3, R=H λ_{max} 234 nm, log ε 3.97
4, R=CH_3 λ_{max} 256 nm, log ε 4.28
5

The overall identity of the cations was clearly shown by their ^1H NMR spectra, (Table I) which are similar to those of protonated acrolein[5] and protonated (2*E*)-crotonaldehyde.[2] In each case, one of the two possible C-O bond stereoisomers predominates to a very large extent and, on the basis of the known steric preferences of protonated enals,[4] these have been assigned the C_1O, *E* configuration.

Scheme I



Irradiation of a FSO_3H solution of **3** at −70 °C, using light of 254-nm wavelength, caused it to partially isomerize to a new cation. While this new cation could not be isolated, it was clear from ^1H NMR spectra of the mixture that it had the structure indicated by **5** (Table I).[6] A photostationary state was established between **3** and **5** consisting of 73% **3** and 27% **5**. When the acid solution was warmed to −20 °C, **5** isomerized back to **3** with a first-order rate constant of $1.1 \times 10^{-4}\ s^{-1}$. A careful examination of the NMR spectra of solutions of **3** showed that **5** was in thermal equilibrium with **3** (96% **3**; 4% **5** at −40 °C).

The cation **4** behaved similarly to **3** with the additional possibility of isomerism about the C_2-C_3 bond. Thus, irradiation of **4** (−70 °C, λ 254 nm) led to the establishment of a photostationary state consisting of a mixture of four cations, Scheme I. At −20 °C, two of these ions were thermally labile and reverted to the other two ($k \sim 6 \times 10^{-4}\ s^{-1}$ at −20 °C). The two remaining ions were identified as **4** and **6** on the basis of a comparison of their ^1H NMR spectra with those of the corresponding protonated crotonaldehydes.[2] The NMR spectra of the two less stable ions were consistent with the structures of **7** and **8**. At +38 °C, **6** isomerized to **4** ($k = 4.4 \times 10^{-4}\ s^{-1}$). A thermodynamic equilibrium between **7** and **4** were eventually set up consisting of **7** (13%) and **4** (87%) at +40 °C.

Comparable photoisomerizations of **3** and **4** occurred in FSO_3H/SbF_5 media. Minor changes were seen in the rates of the thermal stereomutations about the C_1-O bonds in this more strongly acidic medium (**5** → **4**, $k = 2.8 \times 10^{-5}\ s^{-1}$ at −20 °C; **7** and **8** to **4** and **6**, $k \sim 4 \times 10^{-4}\ s^{-1}$ at −20 °C). As was found with the protonated crotonaldehydes,[2] the barrier to isomerization about the C_2-C_3 bond was greatly affected by the addition of SbF_5 to FSO_3H (**6** → **4**, $k = 4.0 \times 10^{-6}\ s^{-1}$ at +50 °C in 3:1 FSO_3H/SbF_5).

Several points emerge from these results, two of which will be commented on here. Firstly, it is quite clear that a photoinduced stereomutation can occur about the carbon-oxygen bond in these systems. It would seem very probable that comparable photoisomerizations can also occur with protonated carbonyl compounds and, while such processes might remain undetected because of proton exchange reactions, they could represent an important way in which the excited states of

Table I. ^1H Chemical Shifts of Cations

cation	chemical shifts, ppm[a]					coupling constants, Hz		
	H_1	H_2	H_3	H_4	OCH_3	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$
3	9.21 (d)	7.16 (m)	7.83 (d), 7.76 (d)		5.01 (s)	9	10, 16.5	
5	9.30 (d)	7.43 (m)	8.06 (d), 7.96 (d)		4.87 (s)	10	10, 16	
4	8.96 (d)	6.99 (dd)	8.54 (dq)	2.55 (d)	4.84 (s)	9	15	7
6	9.50 (d)	6.91 (t)	8.45 (dq)	2.60 (d)	4.89 (s)	10	10.5	7
7	9.06 (d)	7.40	(8.7)[b]	2.65	4.68 (s)	8		
8	9.56 (d)	(7.4)[b]	(8.7)[b]	(2.7)[b]	4.70 (s)	10.5		

[a] All shifts are relative to $(CH_3)_4N^+BF_4^-$ taken as δ 3.1; d = doublet, m = multiplet, q = quartet, s = singlet. [b] Peak is obscured by resonances of the cations and exact chemical shift uncertain.

0002-7863/79/1501-1052$01.00/0

protonated carbonyl compounds can relax to their ground states. In this context, the photoreactions of **3** and **4** described here can perhaps be better compared to those of 1,3-dienes rather than conjugated enones.[7]

Secondly, it is of interest to consider the mechanism of the thermal isomerization about the C–O bonds. Several possibilities can be eliminated from consideration. Thus, the minimal effect of introducing a methyl group at C_3 on the rate of isomerization about the C–O bond renders a direct rotation process unlikely as this involves a large change in the charge distribution in the system. The absence of any appreciable medium effect eliminates any base addition route, while the substantially different activation energies for isomerism about the C–O and C_2–C_3 bonds rules out the intervention of a common *O*-methyloxetium ion in these two rearrangements. Rather, it appears that the most likely process occurring is an inversion or "lateral shift" mechanism[8] as has also been found with the isoelectronic aldimines and ketimines.[9]

Acknowledgment. This work was supported by the National Research Council of Canada.

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(6) It is formally possible to get stereoisomerism about the C_1–C_2 bond in these cations. However, the barrier to the thermal stereomutation about this bond is expected to be too low to permit the separate observation of these stereoisomers under the conditions used here.[2,4] Despite repeated attempts, we have been unable to detect such isomerism in related protonated enones.

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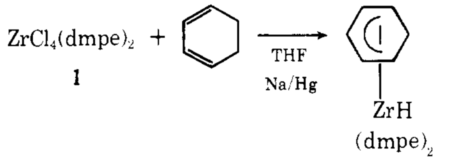
Received September 27, 1978

Tertiary Phosphine Complexes of Low-Valent Zirconium and Their Properties

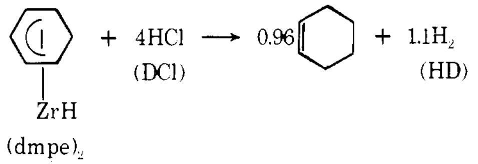
Sir:

The low-valent chemistry of the group 4 transition elements has been restricted to derivatives with carbocyclic ligands. Thus, Ti(II), Zr(II), and Ti(0) compounds containing ligated benzene,[1] cyclooctatetraene,[2] cyclopentadienyl,[3] and substituted cyclopentadienyl[4] ions and tropylium ion[5] are known. No stable derivatives of Zr(0) or Hf(0) have been reported. We report the preparation of Zr(0) and Zr(II) complexes of the chelating, bidentate phosphine 1,2-bis(dimethylphosphino)ethane and their activity as hydrogenation and hydrogen-transfer catalysts.

Treatment of $ZrCl_4$ with dmpe affords $ZrCl_4(dmpe)_2$[6] (**1**), analogous to dodecahedral $MCl_4(diars)_2$ (M = Ti,[7] Zr;[8] diars = 1,2-bis(dimethylarsino)benzene). Direct reduction of **1** (Cs in benzene, Na/Hg in THF) gives intractable products which are thermally unstable, reverting to **1** and a black deposit, presumed to be zirconium metal. However, reduction of **1** in the presence of excess 1,3-cyclohexadiene gives, after recrystallization from hexane, a red-brown crystalline solid, formulated as $Zr(H)(\eta^5\text{-}C_6H_7)(dmpe)_2$ (**2**) (eq 1) on the basis of spectroscopic and chemical data.[9] The ZrH unit in **2** was not located spectroscopically (IR, NMR);[10] its presence is inferred from the formation of 1 equiv of HD/1 equiv of Zr on treatment of **2** with DCl (eq 2).

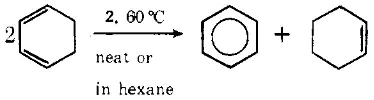


2 (40%) (1)



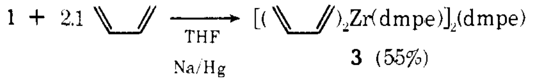
(2)

Although **2** is thermally stable at moderate temperatures, on photolysis, or at elevated temperatures (*T* > 130 °C), decomposition occurs with the deposition of black solids and the stoichiometric formation of 1 equiv each of hydrogen and benzene/1 equiv of Zr. At temperatures below its decomposition point, **2** is an efficient catalyst for the disproportionation of cyclohexadiene, as indicated in eq 3.[11,12] Less efficient rhodium- and iridium-based catalysts are known for this reaction.[13] Indeed, intermediates related to **2,** i.e., derived by insertion of the metal ion into a methylene C–H bond of cyclohexadiene, have been proposed in the disproportionation catalyzed by $(\eta\text{-}C_5Me_5)Rh(\eta^4\text{-}C_6H_8)$[13b] and $[Rh(norbornadiene)(\eta^4\text{-}C_6H_8)]BF_4$.[13c]

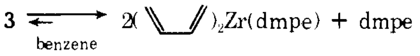


(3)

Presumably, **2** is formed by trapping of a Zr^0P_4 fragment, produced on reduction of **1**, with cyclohexadiene and insertion into the C–H bond of an allylic methylene group. Dienes lacking allylic C–H bonds should, therefore, lead to Zr(0) complexes. Accordingly, reduction of **1** in the presence of 2 equiv of butadiene proceeds as shown in eq 4. **3** may be isolated as purple crystals by recrystallization from hexane. The dmpe-bridged, dimeric formulation is suggested by analytic and ^1H NMR data;[14] the latter shows only coordinated butadiene and dmpe in the ratio 2.0/1.5. A parent ion is not present in the mass spectrum of **3;** however, an intense feature corresponding to $(C_4H_6)_2Zr(dmpe)^+$ is observed (calcd for $^{12}C_{14}{}^1H_{28}{}^{31}P_2{}^{90}Zr$, 348.0709; found, 348.0699), as well as features at lower mass corresponding to loss of dmpe and butadiene. No phosphorus couplings to the butadiene protons are observed in the ^1H NMR at 30 °C, suggesting rapid, reversible dissociation of dmpe as shown in eq 5. This proposal is consistent with molecular weight measurements (cryoscopic in benzene) (calculated for the three-particle system on the



3 (55%) (4)



(5)