

Straightforward Formation of Carbocations from Tertiary Carboxylic Acids via CO Release at Room Temperature

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Receipt/Acceptance Data [DO NOT ALTER/DELETE THIS TEXT]

5 Publication data [DO NOT ALTER/DELETE THIS TEXT]

DOI: 10.1039/b000000x [DO NOT ALTER/DELETE THIS TEXT]

Abstract. We report an unprecedented mode of reactivity of carboxylic acids. A series of tertiary carboxylic acids, containing at least one phenyl α -substituent, undergo loss of carbon monoxide at room temperature (295 K), by one pot reaction with 0.5-1 molar equivalents of WCl_6 in dichloromethane. A plausible mechanism for the $\text{Ph}_3\text{CCO}_2\text{H}/\text{WCl}_6$ reaction, leading to $[\text{CPh}_3][\text{WOCl}_5]$ and Ph_3CCl , is proposed on the basis on DFT calculations. The analogous reactions involving $\text{CEt}(\text{Ph})_2\text{CO}_2\text{H}$, $\text{CMe}(\text{Ph})_2\text{CO}_2\text{H}$ and $\text{CMe}_2(\text{Ph})\text{CO}_2\text{H}$ selectively afforded stable hydrocarbons (alkene or indene, depending on the case), apparently resulting from the rearrangement of elusive tertiary carbocations.

Carboxylic acids are key functional groups in organic chemistry, being involved in a wide variety of synthetic routes.¹ In a number of useful transformations, the carboxylic acid unit may act as a leaving one, with elimination of either carbon dioxide^{2,3} or, less frequently, carbon monoxide.^{4,5} Concerning the decarbonylation reactions, leading to valuable alkenes or C-C coupling products, these are usually promoted by low valent transition metal compounds and require harsh conditions (typically, temperatures in the range 150-300 °C). In the absence of sacrificial anhydride as additive, the process is believed to proceed with the intermediate formation of carboxylato ligands.⁶ Remarkably, the decarbonylation of a palladium-acetate complex was recently detected upon thermal decomposition in the gas phase by means of a mass spectrometry experiment.⁷ Also carboxylic acid chlorides may be susceptible to metal mediated CO release under thermal treatment,⁸ proceeding with an oxidative addition mechanism.⁹

Herein, we present the unique chemistry recognized for a series of tertiary carboxylic acids, containing a variable number of

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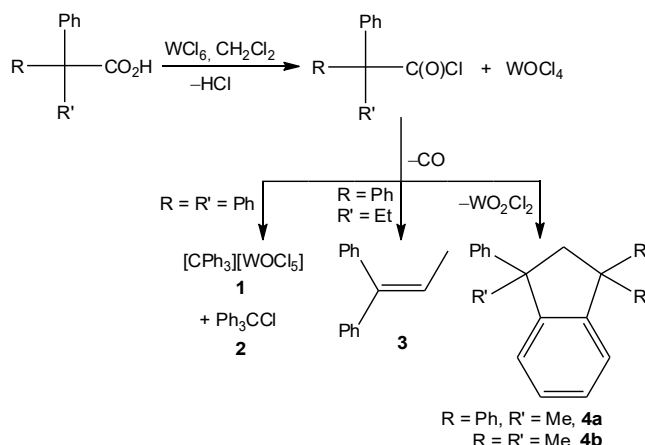
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† Supporting Information include experimental details, characterization of the products, X-ray crystallography, DFT structures, NMR spectra. CCDC 1869885 (1) and 1869886 (4a) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data centre via www.ccdc.cam.ac.uk/data_request/cif.

phenyl α -substituents, when allowed to interact with a high valent metal chloride at room temperature. Thus, the 1:1 molar reaction of WCl_6 with triphenylacetic acid in dichloromethane afforded $[\text{CPh}_3][\text{WOCl}_5]$, **1**, and Ph_3CCl , **2**, in ca. 1:2 molar ratio (NMR), see Scheme 1. Abundant formation of carbon monoxide was detected by gas chromatography.



Scheme 1. Reactions of WCl_6 with tertiary α -phenyl carboxylic acids at room temperature.

The salt **1** was isolated in 32% yield after work-up, and then characterized by X-ray diffraction, analytical and spectroscopic methods (see Supporting Information for details). The crystal structure of **1** (Figure 1) consists of an ionic packing of $[\text{CPh}_3]^+$ cations¹⁰ and $[\text{WOCl}_5]^-$ anions,¹¹ both displaying the expected bonding parameters.

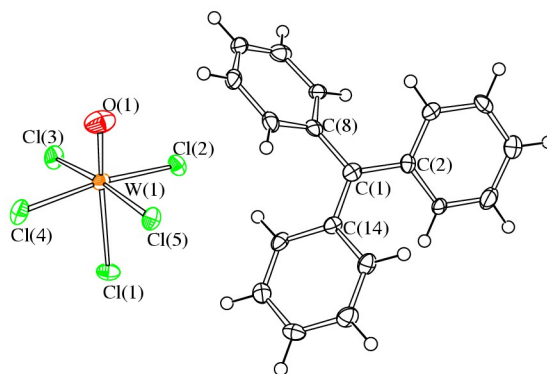


Figure 1. Molecular structure of $[\text{CPh}_3][\text{WOCl}_5]$, **1**, with key atoms labelled. Thermal ellipsoids are at the 50% probability level. Selected bond distances (Å) and angles (°): W(1)–O(1) 1.650(4), W(1)–Cl(1) 2.4898(16), W(1)–Cl(2) 2.3171(16), W(1)–Cl(3) 2.3401(15), W(1)–Cl(4) 2.3154(18), W(1)–Cl(5) 2.3280(15), C(1)–C(2) 1.445(9), C(1)–C(8) 1.449(9), C(1)–C(14) 1.443(9), O(1)–W(1)–Cl(1) 173.91(17), Cl(3)–W(1)–Cl(5) 172.86(6), Cl(2)–W(1)–Cl(4) 170.21(6), C(2)–C(1)–C(14) 121.1(6), C(8)–C(1)–C(14) 118.8(6), C(2)–C(1)–C(8) 120.0(6).

It is a common feature of coordination chemistry that the addition of carboxylic acids (including triphenylacetic acid¹²) to metal chlorides proceeds with HCl release and affords the corresponding, stable metal-carboxylates.¹³ However, the generation of acid chlorides by Cl/O interchange may be viable when oxophilic metal species are involved.¹⁴ With reference to tungsten hexachloride, it was previously found that the reactions with a number of aliphatic and aromatic carboxylic acids are non-selective, leading to mixtures of metal carboxylates and acid chlorides.¹⁵

To the best of our knowledge and to a general extent, the one pot formation of carbocations from tertiary carboxylic acids (through CO elimination) is unprecedented.

Based on the experimental facts, a plausible pathway for the $\text{WCl}_6/\text{Ph}_3\text{CCO}_2\text{H}$ reaction was traced by DFT calculations (Scheme 2).

The first interaction between the reactants is likely to occur via coordination of the carbonyl oxygen to the metal centre, reinforced by H---Cl hydrogen bond (intermediate **a** in Scheme 2). Subsequent chloride migration should lead to $[\text{WCl}_5\{\text{OCCl}(\text{OH})\text{CPh}_3\}]$ (**b**). The formal elimination of one HCl molecule from **b** affords a mixture of $[\text{WOCl}_4]$ and $\text{Ph}_3\text{CC}(\text{O})\text{Cl}$ as stationary point (**c**), with a strong lowering of the Gibbs free energy.

In accordance with this DFT outcome, monitoring the $\text{WCl}_6/\text{Ph}_3\text{CCO}_2\text{H}$ reaction by IR and NMR spectroscopy revealed the intermediate formation of $\text{Ph}_3\text{CC}(\text{O})\text{Cl}$. Accordingly, the reaction of WOCl_4 with $\text{Ph}_3\text{CC}(\text{O})\text{Cl}$, freshly prepared from $\text{Ph}_3\text{CCO}_2\text{H}$ and PCl_5 , finally yielded a mixture of **1** and **2**. It has to be remarked that CO extrusion from $\text{Ph}_3\text{CC}(\text{O})\text{Cl}$ cannot involve here the classical oxidative addition pathway, on considering that WCl_6 and WOCl_4 contain the metal atom in its highest oxidation state.

The coordination of acyl chloride to $[\text{WOCl}_4]$ (**d**) is only slightly favourable from a thermodynamic point of view. More importantly, all the computational attempts to find a transition state for the decarbonylation of $\text{Ph}_3\text{CC}(\text{O})\text{Cl}$ indicated that the coordination adduct **d** is not on the route. Instead, the salt $[\text{Ph}_3\text{CCO}][\text{WOCl}_5]$ (**e**) is more probably implicated in the formation of **2**, being originated from chloride interchange between $\text{Ph}_3\text{CC}(\text{O})\text{Cl}$ and $[\text{WOCl}_4]$. Compound **e** is about 16.7 kcal mol⁻¹ less stable than **c**, and the related transition state (**ts1**) is energetically close to **e**. It has to be mentioned that the possible existence of “oxocarbenium” species analogous to the cation in **e**, and their tendency to lose CO, was previously demonstrated by Olah.¹⁶ The driving force of the entire process appears to be the decomposition of $[\text{Ph}_3\text{CCO}]^+$ into $[\text{CPh}_3]^+$ and CO (**f**), and the related activation energy is only about 13.7 kcal mol⁻¹ (**ts2**). The resulting salt, **1**, can undergo chloride migration to give **2** and $[\text{WOCl}_4]$ (**g**). Although the Gibbs energy difference between **f** and

g does not consider the reticular energy of $[\text{CPh}_3][\text{WOCl}_5]$ and the aggregation of $[\text{WOCl}_4]$ units,¹⁷ the DFT data agree with the experimental observation of a mixture of **1** and **2** as final products.

Scheme 2 about here

Scheme 2. DFT-calculated reaction pathway for the conversion of WCl_6 and $\text{Ph}_3\text{CCO}_2\text{H}$ to $[\text{CPh}_3][\text{WOCl}_5]$ (**1**), Ph_3CCl , **2**, and $[\text{WOCl}_4]$. Relative Gibbs free energies in kcal mol⁻¹. Transition states in red. C-PCM/ ω B97X calculations, dichloromethane as continuous medium.

The present investigation was extended to a selection of phenylacetic acids, whose reactions with WCl_6 were checked by GC and NMR analyses. Significant amounts of CO were found to be released from $\text{CMe}_2(\text{Ph})\text{CO}_2\text{H}$, $\text{CPh}_2(\text{Me})\text{CO}_2\text{H}$, $\text{CPh}_2(\text{Et})\text{CO}_2\text{H}$, $\text{CPh}_2(\text{Pr})\text{CO}_2\text{H}$, $\text{CPh}_2(\text{CH}_2\text{CH}_2\text{Br})\text{CO}_2\text{H}$, and $\text{CPh}(\text{C}_5\text{H}_{10})\text{CO}_2\text{H}$ (1-phenyl-1-cyclohexanecarboxylic acid).¹⁸ Organic products could be cleanly isolated in a limited number of cases, and in particular the alkene $\text{Ph}_2\text{C}=\text{CH}(\text{Me})$, **3**, was obtained from $\text{WCl}_6/\text{CPh}_2\text{EtCO}_2\text{H}$. The reactions of WCl_6 with $\text{CMe}_2(\text{Ph})\text{CO}_2\text{H}$ and $\text{CPh}_2(\text{Me})\text{CO}_2\text{H}$ were conveniently performed using 1:2 stoichiometry, and afforded the indenenes **4a-b** over a precipitate of gray WO_2Cl_2 ¹⁹ (IR, elemental analysis), as the by-product (Scheme 1).

Compounds **3** and **4a-b** were efficiently isolated in 62-88% yields after hydrolysis of the respective reaction mixtures and subsequent purification of the organic phase by chromatography on alumina, and then characterized by elemental analysis, IR and NMR spectroscopy. Furthermore, the molecular structure of **4a** was elucidated by a single crystal X-ray diffraction study (a view of the structure is supplied in the SI, Figure S34).

Analogously to the formation of **1-2** from $\text{WCl}_6/\text{Ph}_3\text{CCO}_2\text{H}$, the synthesis of **3-4** takes place through the preliminary formation of the carboxylic acid chlorides (detected by NMR). These should reasonably convert into the elusive carbocations $[\text{PhC}(\text{Me})(\text{R})]^+$ (R = Me, 1-methyl-1-phenylethyl; Et, 1,1-diphenylpropyl; Ph, 1,1-diphenylethyl), to finally afford **3-4**. Evidence was collected for the generation of $[\text{CPh}_2(\text{Me})]^+$ along the route to **4a** (¹H NMR resonances at 7.8 and 3.9 ppm, see SI for details). On the other hand, $[\text{PhC}(\text{Me})(\text{Et})]^+$ was previously found in equilibrium with its deprotonated form **3**,²⁰ while **4b** was observed from the degradation of $[\text{PhC}(\text{Me})_2]^+$ at $T > -40$ °C.²¹ Up to now, carbocations $[\text{PhC}(\text{Me})(\text{R})]^+$ (R = Me, Et, Ph) have been generated using various strategies, i.e. by protonation of alkenes or alcohols in strongly acidic media,²² photolysis of alkene,²³ oxygen²⁴ or dimeric precursors,²⁵ hydrogen/chloride abstraction from quaternary hydrocarbons,²⁶ and photochemical N_2 extrusion from indazoles.²⁷

In summary, we have described for the first time the one pot CO elimination reaction from the carboxylic acid function occurring at room temperature, as favoured by phenyl α -substituent(s) and promoted by stoichiometric amounts of W(VI) hexachloride. Thus, tertiary carboxylic acids undergo conversion into the corresponding acid chlorides, presumably followed by formation of oxocarbenium cations and then carbocations (also Ph_3CCl was obtained from triphenylacetic acid). The latter are relatively

stabilized by the α -phenyl substituents, and evolve to stable hydrocarbons according to their characteristic nature and chemistry. The viability of this unusual reactivity seems related to the multitasking role played by WCl_6 ,²⁸ being a strong Lewis acid, effective chlorinating agent and precursor of the stabilizing $WOCl_5^-$ counteranion. It is noteworthy that, in contrast, the typical decarbonylation of carboxylic acid chlorides requires high temperatures and intermediate oxidative addition to redox active metal centres.

Acknowledgments

We are grateful to Mr. Francesco Del Cima and Dr. Debora Preti for executing GC analyses, to Ms. Gioia Marrazzini for assistance with the experimental work and to the University of Pisa for financial support (*Fondi di Ateneo 2017*).

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190 Scheme 2.

