Lewis Acid Complexes of Diphenylcyclopropenone

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Condensation reactions of diphenylcyclopropenone (**1**) with active methylene compounds are known to be catalysed by boron trifluoride etherate.[1] Cyclopropenone-Lewis acid complexes could be intermediates, in view of the well known tendency of forming Lewis acid complexes of ketones[2] and the activation of (**1**) by hydrogen chloride[3] or triethyloxonium tetrafluoroborate.[4] In the latter the corresponding intermediates are obviously cyclopropenium cation derivatives.

We wish to report the isolation and the spectral features of 1:1 diphenylcyclopropenone-Lewis acid complexes[5] such as BF_3-complex (**2**), mp 166—167°C and $SbCl_5$-complex (**3**), 216—217°C prepared quantitatively by adding $BF_3 \cdot OEt^2$ to **1** in acetic acid and $SbCl_5$ to **1** in dry methylene dichloride both at room temperature. Both complexes were stable and non-hygroscopic. The structures were determined by analytical (satisfactory for C and H) and spectroscopic (pmr and IR) data and chemical reactions. Hydrolysis of both **2** and **3** liberated diphenylcyclopropenone water complex (**4**) quantitatively. **2** was also obtained from diphenylethoxycyclopropenium tetrafluoroborate after standing for a long time.

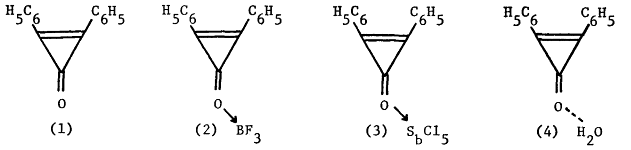
Table 1. Phenyl proton chemical shifts (τ in ppm) in $AsCl_3$[a]

Species	ortho[b]	para+meta[b]	(para+meta) − ortho
1	1.83	2.22	0.39
	2.00[c]	2.39[c]	0.39
2	1.70	2.18	0.48
3	1.80	2.14	0.34
4[d]	1.83	2.22	0.39
	2.00[c]	2.39[c]	0.39

a) Taken with a Jeolco C-60-H at room temperature in the concentration range 1.25—5% in $AsCl_3$, except otherwise stated.
b) The center of the corresponding multiplets of AB_2C_2-systems.[7]
c) In $CDCl_3$
d) Water complex prepared according to literature.[8]

Neither concentration effect nor appreciable dissociation of the complexes were observed on the NMR for several hours.

To ascertain the structures of complexes **2** and **3**, the spectra were compared with those of the related species **1** and **4** (Table 1). By complexation with water the IR spectrum changes but not the pmr spectrum (phenyl protons) of **1**. Appreciable lower shifts of 1850 (broad) and 1640 cm^{-1} bands in **1** to 1840 (broad) and 1600 (broad) cm^{-1} bands were observed. It seems likely[9] that 1885 (broad) and 1528 cm^{-1} bands in **2** as well as 1860 (sharp) and 1502 cm^{-1} bands in **3** correspond to 1850 and 1640 cm^{-1} bands in **1**, respectively. This shift may be explained by the order of acidity of Lewis acids ($SbCl_5 > BF_3$).[2] The O–B and O–Sb bonds in the complexes (**2**,**3**) are presumably the electron pair (σ) bond, because even water complex **4** should be formed by energy greater than 8.1 kcal/mol.[11] This is supported by the existence of the strong ν(B–F) 1100 cm^{-1} band[12] due to non-planar BF_3 in **2** and the strong ν(Sb–Cl) 360 cm^{-1} band[13] in **3**. The downfield shifts of (para+meta) protons of the complexes **2** and **3** from those of **1** are 2.4 Hz and 4.8 Hz, respectively, which are comparable with the change between those of 1-phenylcyclohexyl and 1-phenylcyclopentyl cation.[7] The corresponding values for ortho protons of **2** and **3** are 6.0 Hz and 1.8 Hz, respectively. From a comparison of both data it is suggested that an anomalous shielding-effect acts on the ortho-protons in $SbCl_5$ complex. The greater shifts of ortho proton in BF_3 complex than that of (para+meta) might be characteristic influence of strained carbonium ions[7] on phenyl-proton chemical shift. These spectral features might be interpreted in terms of the structure as shown in Fig. 1.



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