

## Stereochemistry of a Friedel–Crafts Intermediate: Crystal Structure of Benzoyl Chloride–Aluminium Chloride

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FRIEDEL–CRAFTS and related reactions have recently been extensively reviewed.<sup>1</sup> Many intermediates have been suggested in various reactions and several have been isolated.

Acyl halides react with anhydrous aluminium chlorides in many organic solvents, forming stable addition compounds. The benzoyl chloride–aluminium chloride complex was prepared from carefully purified reagents, using carbon disulphide as the reaction medium. Pure white crystals were obtained. They are monoclinic, with space group

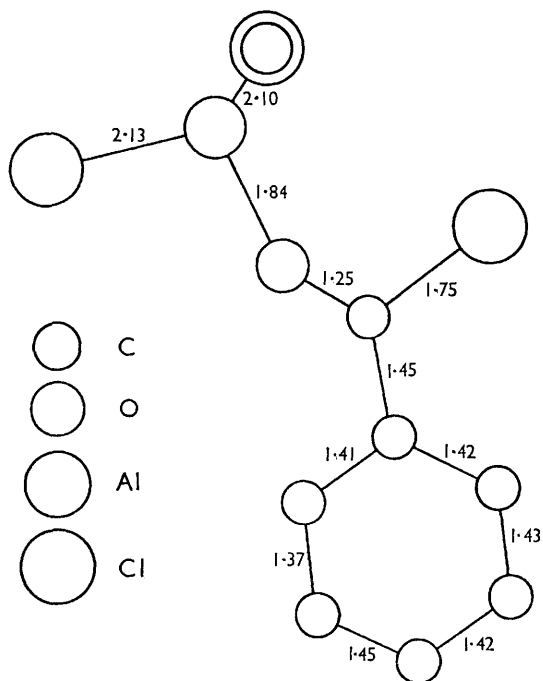
$P2_1/m$ , and  $a = 8.80$ ,  $b = 7.82$ ,  $c = 9.49$  Å,  $\beta = 104^\circ.3$ ,  $z = 2$ .

Intensities were measured by using an automatic diffractometer of the Arndt–Phillips design.<sup>2</sup>

A three-dimensional X-ray structural analysis of the complex has been carried out using conventional Patterson techniques. Five cycles of diagonal matrix least-squares refinement of positional and isotropic thermal parameters and four cycles of refinement using anisotropic thermal parameters and a block diagonal matrix programme

<sup>1</sup> G. Olah, "Friedel–Crafts and Related Reactions," Interscience, 1963.

<sup>2</sup> U. W. Arndt and D. C. Phillips, *Acta Cryst.*, 1961, **14**, 807.



have led to a discrepancy index,  $R$ , of 8.6% for 950 non-zero reflexions. A difference Fourier synthesis revealed the positions of the hydrogen atoms.

The crystal contains molecules of composition  $C_6H_5COCl, AlCl_3$ . The molecule has symmetry  $m$  with sixteen atoms in the symmetry plane and one chlorine atom above and one below the molecular plane. The figure shows the molecule projected on the symmetry plane. The benzoyl chloride molecule is co-ordinated with an  $AlCl_3$  group *via* the oxygen atom. The Al-Cl distances are close to the short Al-Cl distances in  $Al_2Cl_6$ .<sup>3</sup> The Al-O bond is remarkably short: 1.84 Å.

The co-ordination around aluminium is essentially tetrahedral. The bond lengths and angles of the benzoyl chloride group are close to the expected values for the free molecule.

A large number of carbonyl compounds react with aluminium chloride. We suggest that, in general, acyl halides and ketones form aluminium-co-ordination compounds with structures which are closely related to the structure reported here.

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<sup>3</sup>K. J. Palmer and N. Elliott, *J. Amer. Chem. Soc.*, 1938, **60**, 1852.