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METHODS FOR THE DETERMINATION OF CARBOXYL GROUPS*†

By C. O. Willits and E. E. Stinson

INTRODUCTION

A wide variety of organic compounds show acid properties and might be classed as acids if salt formation and the neutralization of alkalies were the sole criteria [52]. The functional group that most consistently displays all the phenomena of acidity is the carboxyl or —COOH group, and it is to substances containing this characteristic group that this subsection is confined [30, 60].

The degree of dissociation of a carboxylic compound and the pH of its solution depend largely upon the nature of R in R—COOH. The acidities of simple aliphatic acids decrease with increasing length of R. The acidity is increased by the presence of a triple bond. Salt formation is characteristic of most acids, with the sodium salts being more soluble in water than the corresponding acids. The hydroxyl group of the carboxyl can be replaced by a halogen atom, giving an acid halide; and acid anhydrides can be formed by the loss of a molecule of water from two molecules of acid.

Aliphatic monobasic acids are found in plant and animal materials, both free and as glycerides (fats). In this group of straight-chain acids, those having an odd number of carbon atoms have melting points lower than their neighbors with even numbers of carbon atoms, and similar differences are observed in their surface tensions and molecular volumes.

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METHODS FOR THE DETERMINATION OF HYDROXYL GROUPS

By Virgil C. Mehlenbacher

Table 12-21. Scope and Limitations of Procedures Employed for the Determination of Hydroxyl Groups

Procedure	Scope	Interferences
1. Acetylation (Ac ₂ O).....	Alcohols, essential oils, fats, glycols, hydroxy acids, phenols, sugars, waxes	Acetylated compds. not hydrolyzed with H ₂ O, low-molecular-weight aldehydes, primary and secondary amines, sulfhydryl groups
2. Bromination (KBrO ₃ + KBr) ..	Phenols (→ replacement of H by Br at <i>o</i> - and <i>p</i> -positions)	Aliphatic hydrazines, unsatd. compds.
3. Coupling.....	Phenolic compds.	Amines, active methylene groups
4. Esterification (HOAc + BF ₃)...	Aliphatic and alicyclic alcohols, aromatic alcohols with OH in aliphatic side chain, hydroxy acids	Acetals, aldehydes, amines, ketals, ketones
5. Formylation (HOAc-HCOOH) ..	Citronellol, essential oils, linalool, easily dehydrated terpene alcohols, terpineol
6. Grignard rxn. (CH ₃ MgI).....	Tertiary OH groups	Other compds. or groups contg. active H atoms