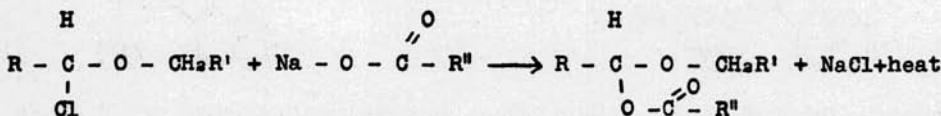


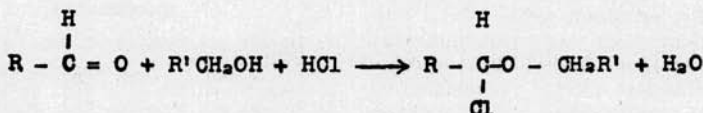
ACYLALS¹FRANK O. GREEN, *Greenville, Illinois*

Hurd and Cantor² have suggested the name 'Acylal' for the product formed when the hydroxyls in the aldehydrol form of an aldehyde are replaced by ester groups. Therefore when one hydroxyl is replaced by an ester group and one by an alcohol group, the product may be called a mixed acetal-acylal.

When a sodium salt of an organic acid is shaken with a hemiacetal chloride, an exothermic reaction takes place whereby the acetal-acylal and sodium chloride are produced.³ It is necessary to use an excess of the salt or rapid decomposition sets in, with the resultant production of a red tar-like material. The reaction appears to be general.



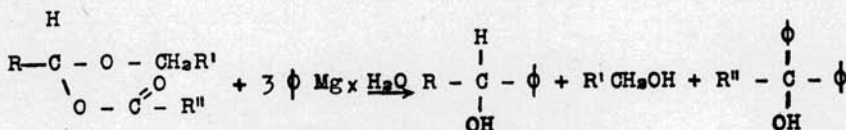
The hemiacetal chloride may be produced by the action of dry HCl gas on a cold, equimolecular mixture of alcohol and aldehyde. The procedure is a modification, similar to that due to Shoemaker and Boord,⁴ of the Henry method.



The yields of acetal-acylal based upon crude hemiacetal chloride vary from forty to sixty percent of the theoretical, with an indication of better yields as based upon pure chloride. The densities of the compounds prepared vary from ninety-seven hundredths to eighty-nine hundredths, with increasing molecular weight. The molecular refractivities agree with theory. At twenty-five millimeters pressure the boiling points increase approximately ten degrees for each CH₂ unit added, regardless of its relative position in the molecule. If, pure, dry, and free from acid, the compounds are stable for some months.

The $\begin{array}{c} \text{O} \\ \diagup \\ \text{R} - \text{C} \\ \diagdown \\ \text{O} \end{array}$ linkage in the compounds is apparently more of the acetal than the ester type. The compounds are somewhat resistant to alkali hydrolysis and are very responsive to acid hydrolysis.

At the present it seems quite likely that Grignard's reagent reacts with the compounds just as would be predicted, to produce a primary, a secondary, and a tertiary alcohol.



The compounds appear to produce the titanium chloride complexes analogous to those prepared by Pacsu⁵ from similar structures in glycosides. The reaction takes place with great ease at room temperature, becoming violent unless a diluent is used. Approximately twenty new compounds have been prepared this year.

¹ This work is a continuation of work begun at Northwestern University. The author is indebted to the Illinois Academy of Science for a Research Grant; and to Dr. Lauder of the Pet Milk Laboratories for the use of a Carbon-Hydrogen Combustion Apparatus.

² Hurd and Cantor, *J. Am. Chem. Soc.*, **60**, 2678, footnote 8 (1938).

³ Shoemaker and Boord, *J. Am. Chem. Soc.*, **53**, 1505 (1931).

⁴ A similar procedure was used by Farren, Fife, Clark and Garland, *J. Am. Chem. Soc.*, **47**; 2421 (1925) for the preparation of formylals.

⁵ Pacsu, *Ber.*, **61**, 1508 (1928).