Atti Accademia Nazionale dei Lincei

Classe Scienze Fisiche Matematiche Naturali

Rendiconti

Annamaria Drusiani, Angelo G. Giumanini

Hydrogen transfer from aliphatic hydrocarbons to unsaturated carboxylic acids promoted by aluminum trichloride

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Serie 8, Vol. **54** (1973), n.5, p. 761–762.

Accademia Nazionale dei Lincei

<http://www.bdim.eu/item?id=RLINA_1973_8_54_5_761_0>

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Accademia Nazionale dei Lincei, 1973.

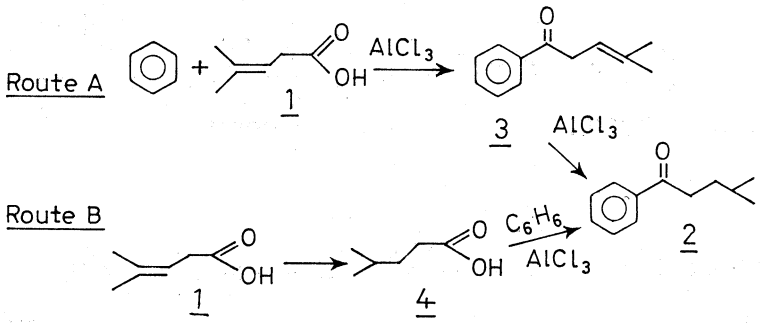
SEZIONE II

(Fisica, chimica, geologia, paleontologia e mineralogia)

Chimica. — *Hydrogen transfer from aliphatic hydrocarbons to unsaturated carboxylic acids promoted by aluminum trichloride* (*). Nota di ANNAMARIA DRUSIANI e ANGELO G. GIUMANINI, presentata (**) dal Socio G. SEMERANO.

RIASSUNTO. — Alcuni acidi carbossilici insaturi possono venire ridotti ai corrispondenti composti saturi mediante reazione con idrocarburi paraffinici in presenza di cloruro di alluminio anidro.

A minor component of the mixture from the reaction of 4-methyl-3-pentenoic acid (*1*) with benzene in presence of aluminum trichloride was 1-phenyl-4-methyl-pentan-1-one (*2*) (1). Two distinct pathways may be proposed to rationalize the formation of *2*: route A envisages the acylation of benzene by *1* to the unsaturated ketone *3*, which is eventually reduced to 2; route B assumes the preliminary reduction of the unsaturated acid *1* to 4-methylpentanoic acid (*4*), which in turn reacts with benzene to yield the observed product *2*.



In tests performed to check the possibility of route B, we observed the reduction of *1* by one of the components of the complex Friedel-Crafts mixture.

We have now extended our initial observation and wish to report that some unsaturated carboxylic acids could be reduced to the corresponding

(*) Lavoro eseguito presso l'Istituto Chimico G. Ciamician e Centro di Gascromatografia–Spettrometria di Massa, Università di Bologna (Italia).

(**) Nella seduta del 12 maggio 1973.

(1) A. DRUSIANI, A. G. GIUMANINI and L. PLESSI, in course of publication.

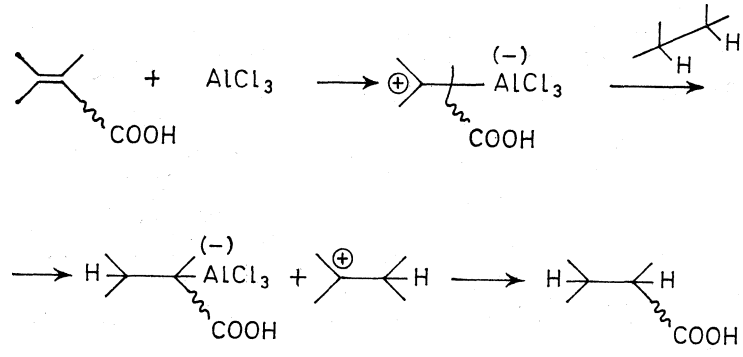
saturated compounds by reaction with *n*-hexane or a mixture of hydrocarbons (ligroin) at room (slower reaction) or reflux temperature in presence of aluminum trichloride. The reaction is both of theoretical and practical interest.

Typically, 4-methyl-3-pentenoic acid (*1*, 2.0 g), *n*-hexane (25 ml) and 2 equiv. $AlCl_3$ were stirred during 46 h at room temperature. Acid base separation gave a liquid, which did not react with bromine, did not exhibit carbon carbon double bond ir absorption and distilled at 61° (1 Torr). Its gaschromatographic trace revealed that no starting material was left and a new single peak had originated [2], whose retention time (enhancing technique) and mass spectrum were identical with those of an authentic specimen of 4-methylpentanoic acid (*4*). A quantitative reduction was also obtained refluxing *1* (2.28 g), *n*-hexane (25 ml) and $AlCl_3$ (5.32 g).

We have similarly reduced 4-methyl-2-pentenoic acid to *4*, cynnamic acid to 3-phenylpropanoic acid and crotonic acid to butirric acid in reactions which were not quantitative. 3-Methylcrotonic acid (ligroin, reflux, 4 h) gave 3-methyl-butanoic acid quantitatively.

High molecular weight fatty acids (e.g.: oleic acid) behaved in a different fashion, yielding complex mixtures which are under study.

It may be inferred mechanistically that the olefin bond of the acid coordinated with $AlCl_3$ to yield a carbenium ion species able to abstract a hydride ion from the hydrocarbon solvent. The intermediate thus formed would then pick up a proton to complete the material transfer of a molecule of hydrogen. This mechanism is well known to be operative in petroleum chemistry.



(2) All glc analyses were performed on the free acid(s), whenever feasible, and the corresponding methyl esters using phases and conditions under which the unsaturated and the saturated compounds were neatly separated.