

that the σ bonded complex does not form. The hydrogenation of some short chain monoenes is illustrated in Table II (19b).

With short chain dienes, rearrangement to the conjugated isomer accompanies hydrogenation and in some cases is much more rapid. Once the conjugated hydrocarbon is formed, it does not hydrogenate to any marked extent (19b). This is seemingly because it forms such a stable complex with the platinum that no further reaction can take place. Evidence for this is found in the fact that the addition of a little butadiene to soybean oil methyl ester completely inhibits the hydrogenation of the latter. Table III illustrates the behaviour of the hexadienes (19b). It reveals a great tendency to form conjugated systems, and that migration of terminal double bonds to interior positions takes place easily. Even when double bonds are terminal, the formation of hexane is overshadowed by the formation of a molecule with internal double bonds (preferably conjugated).

Studies on this system are continuing in attempts to develop more active catalysts as well as heterogeneous catalysts which will show a high degree of specificity.

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Further Advances in Catalytic Hydrogenation

NEW REACTIONS WITH PALLADIUM AND RHODIUM CATALYSTS

Workers from Hoffman-La Roche reported to a recent symposium held by the New York Academy of Sciences that acid chlorides can be converted to aldehydes by a modified Rosenmund reaction using palladium on charcoal catalyst poisoned with quinoline-sulphur inhibitor. The development of this reaction at 50 lb/in² has reduced catalyst requirements and it opens the way to manufacture of pharmaceutical chemicals from cheaper aldehyde intermediates by using cheap hydrogen instead of expensive hydrides for hydrogenation of pure acid chlorides. The end point of the reaction was determined by seeing how much hydrogen had been used. The conventional Rosenmund reaction

barium sulphate moderator was not needed.

A group from Monsanto showed that optically active phosphine complexes of rhodium(III) can catalyse hydrogenation of olefins to optically active products. For example, 28 per cent optical purity, i.e., 64 per cent of one optical isomer and 36 per cent of the other, was obtained during hydrogenation of α -phenylacrylic acid to α -phenylpropionic acid at 300 to 400 lb/in². The group has not yet finalised the reaction mechanism. The catalyst was formed in situ by reacting the 1,5-hexadiene complex of rhodium(III) with an optically active phosphine-based ligand such as methylphenyl-*N*-propylphosphine.