

THE HYDROGEN-CARBON DIOXIDE REACTION

Sir:

Smith and Hirst [*Ind. Eng. Chem.*, **22**, 1037 (1930)] observed that hydrogen and carbon dioxide formed carbon monoxide and water over methanol catalysts at atmospheric pressure.

We have been able to confirm this reaction and in addition obtain the regular methanol formation simultaneously using an unsupported zinc-copper-aluminum catalyst under pressure at high temperatures. This catalyst was not particularly active but served as an indication of the course of the reaction. For example, with an initial gas mixture of 27% CO₂, 71% H₂ and 2% N₂ at 325° and 1700 lb. pressure, the effluent gas contained 4% CO and calculations showed an exact agreement with the water found in the condensate compared with the amount produced in the formation of the methanol by the regular reaction.

This suggests that the primary step in the synthesis of methanol from carbon dioxide and hydrogen involves the reduction of carbon dioxide, and the nature of the catalyst determines the extent to which the resultant carbon monoxide will be hydrogenated. Experimental results indicate that as the activity of the catalyst decreases the methanol reaction is most affected, as illustrated by an increase in the carbon monoxide percentage and a decrease in methanol as the catalyst aged. Experiments with this same catalyst using water gas gave appreciable amounts of carbon dioxide in the exit gas.

This observation coupled with the apparent formation of a copper carbonyl during the same reaction suggests a new mechanism for the synthesis of methanol which will be discussed later.

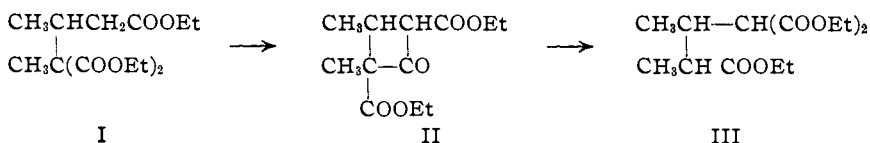
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ALBERTA
EDMONTON, ALBERTA, CANADA
RECEIVED DECEMBER 23, 1931
PUBLISHED JANUARY 7, 1932

E. H. BOOMER
H. E. MORRIS

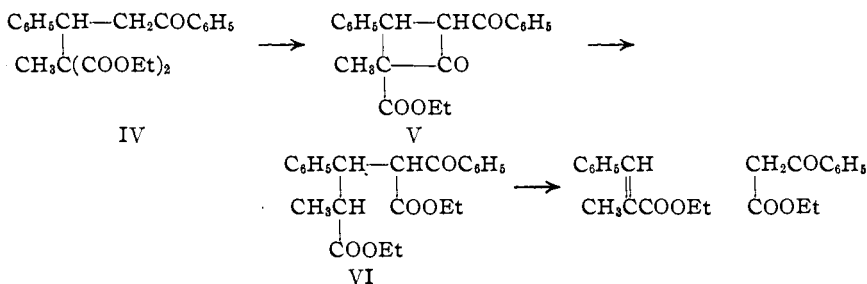
THE ADDITION OF SODIUM ENOL ALKYL MALONIC ESTER TO BENZAL-
ACETOPHENONE

Sir:

In a recent communication [Michael and Ross, *THIS JOURNAL*, **52**, 4598 (1930)] it was shown that addition of sodium enol methylmalonic ester to crotonic ester resulted in a 60% yield of α,β -dimethyl- γ -carbethoxyglutaric ester and it was concluded that the methyl group migrated directly in the addition process. Holden and Lapworth [*J. Chem. Soc.*, 2368 (1931)] have suggested that the primary addition compound may be converted into the final product through the intermediate formation and decomposition of the cyclobutanone structure II

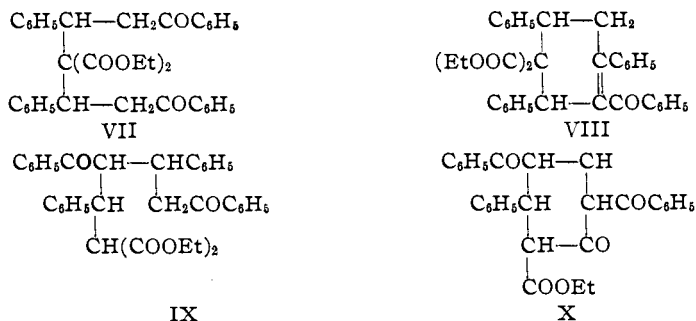


This interpretation involving the formation of a cyclobutanone derivative under these conditions is open to theoretical objections. Holden and Lapworth have based their argument upon their demonstration that treatment of benzalacetophenone (chalcone) with a suspension of sodium enol methylmalonic ester in benzene gives benzoylacetic and α -methylcinnamic esters with some high boiling products. By analogy with the above scheme the benzoylacetic and α -methylcinnamic esters were considered to be produced by retrogression of the structure VI derived from the tetracyclic ketonic compound V

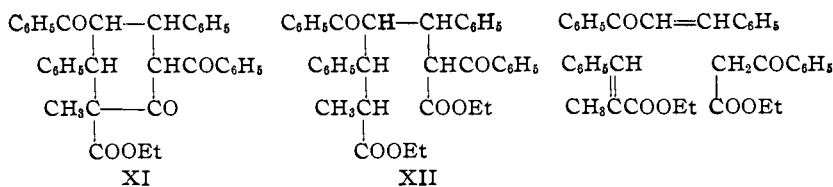


These authors have overlooked the fact that a close parallel does not exist in the addition reactions of crotonic ester and chalcone. The latter compound forms addition products with extraordinary facility [compare Kostanecki and Tambor, *Ber.*, **29**, 1495 (1896)]. Dieckmann and Kron [*Ber.*, **41**, 1277 (1908)] showed that with sodium enol malonic ester a hexacyclic compound IX is produced.

In a reëxamination of the last reaction we have found that two types of compounds are formed which are illustrated by structures VII, VIII, IX and X, respectively



With methylmalonic ester only addition products of the type IX and X can be formed



The ester XI upon treatment with sodium ethoxide in ether solution readily undergoes fission to give benzoylactic and α -methylcinnamic esters and benzalacetophenone, which is in agreement with the results of Dieckmann on the decomposition of open chain and cyclic keto-esters.

Since under the conditions of Holden and Lapworth's experiment, the hexacyclic compound XI could be formed, it is probably the intermediate in the series of reactions which produce α -methylcinnamic and benzoyl-acetic esters. Consequently the obtaining of the latter products cannot be considered as support for their view of the mechanism of this addition reaction.

Corresponding reactions involving one molecule of methylmalonic ester and two molecules of crotonic ester cannot explain the production of α,β -dimethyl- γ -carbethoxyglutaric ester in the addition of sodium enol methylmalonic and crotonic esters.

CONVERSE MEMORIAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS
RECEIVED DECEMBER 24, 1931
PUBLISHED JANUARY 7, 1932

ARTHUR MICHAEL
JOHN ROSS

NEW BOOKS

André Job. *Formes Chimiques de Transition. Oeuvres recueillies par J. Perrin et G. Urbain.* (Chemical Forms of Transition. Collected Works by J. Perrin and G. Urbain.) Hermann et Cie, 6 Rue de la Sorbonne, Paris, France, 1931. xvii + 340 pp. Portrait. Price, fr. 95.

This impressive memorial volume contains a collection of the more important works of André Job. In the first section are the memoirs dealing with problems in theoretical chemistry, and in particular with the mechanism of chemical reaction; in the second section are the memoirs describing experimental investigations. A thoughtful and moving Discourse by Jean Perrin and a Notice on the Life and Works of André Job by Georges Urbain serve as an appropriate introduction.

As is pointed out in the Preface, Job in his diction and style conforms to the French tradition of elegance and brevity. Like the masters of our science whom he admired, Job strove to retain only those results which