A similar calculation using the data in Table I yields 30.32, which is in closer agreement with the calculated value.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF TEXAS
AUSTIN, TEXAS
RECEIVED AUGUST 31, 1931
PUBLISHED JANUARY 7, 1932

CHARLES M. BLAIR[5]
HENRY R. HENZE

COMMUNICATIONS TO THE EDITOR

THE 4-*n*-ALKYL-GUAIACOLS

Sir:

In a recent paper by Coulthard, Marshall and Pyman [*J. Chem. Soc.,* 280 (1931)] on the variation of phenol coefficients, a number of *n*-alkyl guaiacols were prepared and studied. In view of the fact that the latter compounds were under investigation in the authors' laboratory at a much earlier date [Master of Science Thesis submitted by Norine Hower Howells at the Oklahoma A. and M. College, 1929] and since the methods of synthesis were somewhat different, it appears worth while to report briefly the results of this earlier work.

The 4-*n*-alkyl guaiacols were prepared here by the reduction of the corresponding acyl guaiacols, which were obtained after the method of Howells, Little and Andersen [THIS JOURNAL, **52,** 4077 (1930)] by the oxidation of the carbinols resulting through the reaction of the benzoate of vanillin with *n*-alkylmagnesium halides. Unlike the work of Coulthard, Marshall and Pyman, the readily formed solid benzoate ester and diphenyl urethan were selected as derivatives for characterizing the new phenols.

The 4-*n*-pentyl guaiacol (b. p. 156–158° at 20 mm.) which resulted in good yields when 4-*n*-valeryl guaiacol was reduced by the Clemmensen method, was found also to have the maximum phenol coefficient for the series, comparable to the findings of the above authors.

DEPARTMENT OF CHEMISTRY
OKLAHOMA A. AND M. COLLEGE
STILLWATER, OKLAHOMA
RECEIVED NOVEMBER 18, 1931
PUBLISHED JANUARY 7, 1932

NORINE HOWER HOWELLS
HENRY P. HOWELLS

INTERMEDIATE PRODUCTS IN THE THERMAL DECOMPOSITION OF AMMONIA

Sir:

An attempt has been made to identify the molecule NH as an intermediate product in the thermal decomposition of ammonia, through a study of the absorption spectrum of the decomposing gas. The emission band at $\lambda\lambda$ 3360–70, long known from photographs of the ammonia–oxygen

[5] This note is taken from a portion of a thesis submitted by Charles M. Blair in partial fulfilment of the requirements for the degree of Master of Arts.

flame, has been ascribed to the NH molecule by Hulthen and Nakamura [*Nature*, 119, 235 (1927)]. Gaviola and Wood [*Phil. Mag.*, [7] 6, 1191 (1928)] obtained the band in fluorescence, by the action of excited mercury atoms on a mixture of nitrogen and hydrogen. Recently Bates and Lavin [*Proc. Nat. Acad. Sci.*, 16, 804 (1930)] were unsuccessful in obtaining this band in absorption from the active products issuing from a discharge in ammonia. They concluded, however, from a chemical study that the gas contained either NH or NH_2.

Since it is possible that NH molecules formed on a surface may be unable to leave as free radicals, the attempt was made to obtain light absorption by the molecules on the surface in the following way: continuous ultraviolet radiation from a hydrogen discharge was focused, at a slight angle, at the end of a highly polished platinum tube whose ends were sealed into soft glass tubes furnished with plane quartz windows. The light suffered multiple reflections within the tube, and that coming out was focused on the slit of a Hilger quartz spectrograph. Ammonia was passed at a slow rate through the tube at atmospheric pressure in some experiments; in others the tube was filled with ammonia at various pressures and the rate measured simultaneously in a static system. The temperatures used were from 800 to 1125°.

Absorption in the region 3360 Å. could not be found on any of the plates. The absorption bands of ammonia from 2260 Å. to about 1900 Å. appeared very strong in all photographs taken at temperatures below 800° even at 20 mm. pressure. Above 800° these gradually disappeared, until at 1125° no trace remained. A few new weak bands, not previously reported, appeared in the region 2300–2450 Å. but were not sufficiently intense for wave length determinations. These may be due, perhaps, to absorption by ammonia in some higher vibrational state. We infer from the weak intensity of ammonia bands and from reaction velocity measurements that almost complete decomposition must have resulted at the higher temperatures. The duration of the absorption measurements was usually one-half hour.

Failure to detect the NH band can be due neither to insufficient decomposition of NH_3 nor to a too short life of the NH molecule. In the gas phase it is reported to have a lifetime of 10^{-3} seconds, which is longer than the usual lives of adsorbed molecules. Either the surface decomposition does not proceed according to the mechanism $NH_3 = NH + H_2$, or due to a possibly low absorption coefficient our effective absorbing layer was too short.

DEPARTMENT OF CHEMISTRY   A. B. F. DUNCAN
THE JOHNS HOPKINS UNIVERSITY   DONALD A. WILSON
BALTIMORE, MARYLAND

THE CONVERSION OF PARA HYDROGEN TO ORTHO HYDROGEN OVER IRON SYNTHETIC AMMONIA CATALYSTS

Sir:

From studies carried out by various authors [Bonhoeffer and Harteck, *Z. physik. Chem.*, **4B**, 113 (1929); A. Farkas, *ibid.*, **10B**, 419 (1930); **14B**, 371 (1931); Bonhoeffer and Farkas, *ibid.*, **12B**, 231 (1931); Taylor and Sherman, THIS JOURNAL, **53**, 1614 (1931)] it has generally been concluded that hydrogen becomes "activated" during its conversion on metallic surfaces from the para to the ortho form. This "activation" on tungsten and platinum in particular has been interpreted as a surface dissociation into adsorbed hydrogen atoms [Bonhoeffer and Farkas, and Farkas, *loc. cit.*]. In continuing the study that this Laboratory has been making of the mechanism of the catalytic synthesis of ammonia, it has seemed worth while to determine the conditions under which hydrogen molecules on iron synthetic ammonia catalysts become sufficiently activated to bring about the para–ortho conversion and to compare the rates of this conversion to the known rates of ammonia synthesis on the same catalysts.

The only references heretofore made to the activity of iron for the para–ortho conversion were by Bonhoeffer and Harteck (*loc. cit.*), who reported coarse iron to be inactive and pyrophoric iron to be capable of effecting only a relatively slow transformation at room temperature, the times of contact of the hydrogen and iron in neither case·being specified. The present experiments have been carried out by a flow method, a stream of 49:51 para–ortho hydrogen being passed over 5 cc. of an ammonia catalyst at various temperatures at a rate of flow of 50 cc. per minute. A pure iron catalyst prepared by the reduction in hydrogen at 450–550° of fused Fe_3O_4 has been used. It is much less active as an ammonia catalyst than some of the promoted varieties. Nevertheless, at a temperature of 40° it converts a 49:51 para–ortho mixture to a 27.6:72.4 mixture in the very short time of contact accompanying the above-mentioned flow. At −20, 0, 20 and 40°, the percentage conversions from the entering 49:51 to the equilibrium 25:75 mixture are 19, 42, 69 and 89%, respectively.

The extent to which hydrogen must be activated by the catalyst in the catalytic synthesis of ammonia from hydrogen–nitrogen mixtures is not at present known [see Frankenberger's article in Ullman's "Enzyklopädie der Technischen Chemie, 1928]. It is well established, however, that on the catalyst used in the present experiments appreciable rates of ammonia synthesis are not obtained below 300–400°. Accordingly, from the present experiments if one assumes that the activation of hydrogen during its conversion by an iron catalyst from the para to the ortho form is a type that puts it in an active form so far as catalytic hydrogenations in

general are concerned, then one may conclude that the limiting factor in the synthesis of ammonia is not the rate of activation of the hydrogen but the rate at which the nitrogen molecule can be brought into a reactive form by the catalyst.

Benton and White [THIS JOURNAL, **53**, 3301 (1931)] have pointed out that activated adsorption of hydrogen on a sample of this same iron catalyst begins between $-78°$ and about $0°$. The results obtained in the present research seem entirely consistent with their conclusion. The study of the kinetics and temperature coefficient of the para–ortho hydrogen conversion on various synthetic ammonia catalysts is being continued.

BUREAU OF CHEMISTRY AND SOILS   P. H. EMMETT
U. S. DEPARTMENT OF AGRICULTURE   R. W. HARKNESS
WASHINGTON, D. C.
RECEIVED DECEMBER, 15, 1931
PUBLISHED JANUARY 7, 1932

THE ALLYLIC REARRANGEMENT OF CROTYL BROMIDE AND CROTYL-MAGNESIUM BROMIDE

Sir:

In view of the recent appearance of an article by Gilman and Harris[1] on the allylic rearrangement of cinnamylmagnesium chloride, it seems advisable to present a preliminary report on the allylic rearrangement of crotylmagnesium bromide.

Using the method of Dillon, Young and Lucas[2] we have analyzed butenes obtained from the following steps: *trans*-crotonaldehyde $\longrightarrow$ crotyl alcohol $\longrightarrow$ crotyl bromide $\longrightarrow$ 2-butene. The 2-butenes obtained by the action of (a) zinc and aqueous alcohol on crotyl bromide and (b) dilute acid on crotylmagnesium bromide, both contained approximately 10% 1-butene. This was contrary to our expectations since crotyl bromide, according to the work of Prévost[3] and Bouis[4] should be free from α-methylallyl bromide and thus give pure *trans*-2-butene. The presence of 1-butene in these mixtures must be attributed to an allylic rearrangement of the crotyl bromide or of the Gringard reagent and the corresponding zinc compound. Recent work in this Laboratory on crotyl alcohol and work on 2-pentene-1-ol by Meisenheimer and Link[5] indicates that an allylic transformation probably does occur during the preparation of the bromide. For example, the boiling ranges of different crotyl bromide preparations vary from $1–12°$ depending on the procedure used.

[1] Gilman and Harris, THIS JOURNAL, **53**, 3541 (1931).
[2] Dillon, Young and Lucas, *ibid.*, **52**, 1953 (1930).
[3] Prévost, *Ann. chim.*, [10] **10**, 147–181 (1928).
[4] Bouis, *Bull. soc. chim.*, [4] **41**, 1160 (1927).
[5] Meisenheimer and Link, *Ann.*, **479**, 260 (1930).

In order to determine whether or not an allylic transformation also results during the formation of the Grignard reagent, we have converted all of these bromide preparations containing variable quantities of α-methylallyl bromide, into the magnesium compound under identical conditions. The resulting butene mixtures should be of constant composition regardless of the composition of the bromides if an allylic equilibrium is involved; if not, the butene mixtures should have compositions corresponding to those of the bromide preparations. The results of these experiments will be available in the near future.

DEPARTMENT OF CHEMISTRY   WILLIAM G. YOUNG
UNIVERSITY OF CALIFORNIA AT LOS ANGELES   ARTHUR N. PRATER
LOS ANGELES, CALIFORNIA
RECEIVED DECEMBER 2, 1931
PUBLISHED JANUARY 7, 1932

TESTS FOR ELEMENT 87 (VIRGINIUM) BY THE USE OF ALLISON'S MAGNETO-OPTIC APPARATUS

Sir:

In December, 1930, one of us (McGhee) handed out by number to Professor Allison twelve (to him) "unknowns" which were tested by him and checked by two assistants 100% correctly in three hours. The improved model of his machine which was later installed in our laboratory under Dr. Allison's direction has been proved to be reliable by numerous tests on known solutions of pure substances. No two, different, metallic salts of the same acid produce minima that coincide. Hence we read with interest the footnote to an article by Papish and Wainer [THIS JOURNAL, **53**, 3818 (1931)] in which it was suggested that "solutions of $SnCl_4$ and $ReCl_2$ gave minima which were coincident with those obtained for element 87," possibly due to the formation of the complex ions, $SnCl_3^+$ and $ReCl^+$.

To test this question, hydrochloric acid solutions of the minerals samarskite, pollucite and lepidolite, and of crude cesium chloride were made up. Element 87 (Virginium) had been reported in all of them. When observations were made on these solutions within the scale limits between which ViCl would fall, twelve minima were found. Similar observations on the sulfates of the minerals yielded only six minima. Since the same number of minima are always found for any one metal, no matter to which acid radical it might belong, it was thought that six of the minima appearing in the chloride region might indeed be due to $ReCl^+$ and $SnCl_3^+$. With this in view, a solution of pure $SnCl_4$ was made up and examined for minima. In addition to the minima of $SnCl_4$ previously determined, four minima at 44.20, 44.40, 44.98, 46.06 were found. Likewise a solution of $ReCl_2$ (obtained by adding hydrochloric acid to pure potassium perrhenate) was examined for minima. Beside those previously attributed

to ReCl₂, minima at 45.93 and 47.54 were observed. The four minima of SnCl₄ and the two of ReCl₂ which occur at the scale readings given above, coincide with six of those observed in hydrochloric acid solutions of the minerals tested. The other six, which belong to Virginium, occur at 44.01, 44.62, 45.11, 46.22, 46.42, 47.80. *There are no corresponding minima for rhenium and tin in sulfate solutions of these minerals. None of the minima attributed to ViCl was found in the solutions of stannic chloride or rhenium chloride.*

A careful observer need not confuse the minima of Virginium with those of rhenium and tin since the minima of Virginium are in no case nearer than 2.5 cm. to the minima of these elements. In this work each of us has made ninety independent observations, sixty-three of which agree within 1 mm. each with the other; and twenty within 2 mm., while no other variation exceeds 3 mm.

DEPARTMENT OF BIOCHEMISTRY   J. L. McGHEE
    OF EMORY UNIVERSITY   MARGARET LAWRENZ
EMORY UNIVERSITY, GEORGIA
RECEIVED DECEMBER 2, 1931
PUBLISHED JANUARY 7, 1932

DRY DISTILLATION OF COPPER PHTHALATE DOES NOT YIELD FLUORANE

Sir:

In THIS JOURNAL, **52**, 3003 (1930), Ekeley and Mattison published a paper entitled "Fluorane from the Dry Distillation of Copper Phthalate." In a recent letter to me (the senior author), L. P. Kyrides of the Monsanto Chemical Works stated that the results as described in the above paper could not be duplicated in his laboratory. I regret to say that I also am unable to duplicate them, the distillate evidently being an impure phthalic anhydride. In 1923 at my suggestion the junior author of the paper performed the experimental work. It never occurred to me to doubt the accuracy of the melting point determinations and the two sets of combustion data as reported by her, since the product she presented dissolved in concentrated sulfuric acid with yellow-green fluorescence. Publication of the results was withheld until similar experiments could be performed on copper tetrachlorophthalate which seemed to point to the formation of dodekachlorofluorane, though analyses by another experimenter no nearer than within 1% of the theoretical were ever obtained. The final responsibility for the publication of the 1923 results on copper phthalate rests upon me, since I should have verified the junior author's data before publication and thus have avoided the erroneous statement appearing in the literature.

DEPARTMENT OF CHEMISTRY   JOHN B. EKELEY
UNIVERSITY OF COLORADO
BOULDER, COLORADO
RECEIVED DECEMBER 22, 1931
PUBLISHED JANUARY 7, 1932

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% CO_2, 71% H_2 and 2% N_2 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   E. H. BOOMER
UNIVERSITY OF ALBERTA   H. E. MORRIS
EDMONTON, ALBERTA, CANADA
RECEIVED DECEMBER 23, 1931
PUBLISHED JANUARY 7, 1932

THE ADDITION OF SODIUM ENOL ALKYLMALONIC 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-carbethoxy-glutaric 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

$$
\begin{array}{ccc}
\underset{|}{\text{CH}_3\text{CHCH}_2\text{COOEt}} & \underset{|}{\text{CH}_3\text{CHCHCOOEt}} & \text{CH}_3\text{CH}-\text{CH(COOEt)}_2 \\
\text{CH}_3\text{C(COOEt)}_2 & \text{CH}_3\text{C}-\text{CO} & \text{CH}_3\text{CH COOEt} \\
& \text{COOEt} & \\
\text{I} & \text{II} & \text{III}
\end{array}
$$
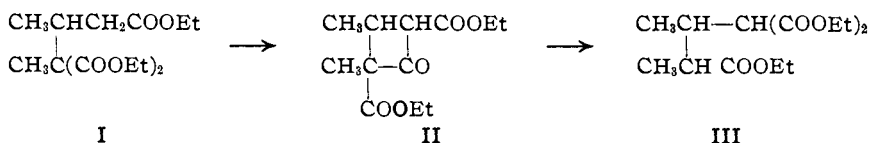
This interpretation involving the formation of a cyclobutanone derivative under these conditions is open to theoretical objections. Holden and Lapworth have based their argument upon their demonstr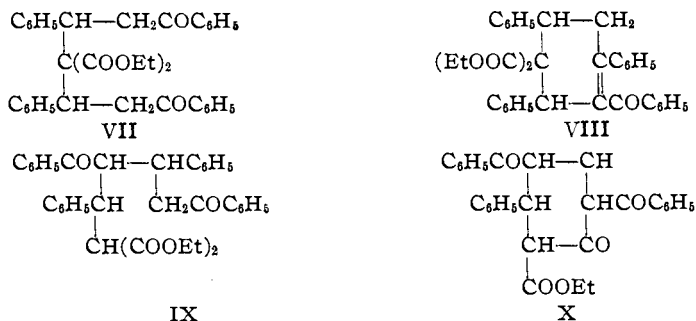ation that treatment of benzalacetophenone (chalcone) with a suspension of sodium enol methylmalonic ester in benzene gives benzoylacetic and α-methylcinnamic esters with some high boiling products. By analogy with the above scheme the benzoylacetic and α-methylcinnamic esters were considered to be produced by retrogression of the structure VI derived from the tetracyclic ketonic compound V

$$
\begin{array}{cc}
\underset{|}{\text{C}_6\text{H}_5\text{CH}-\text{CH}_2\text{COC}_6\text{H}_5} & \underset{|}{\text{C}_6\text{H}_5\text{CH}-\text{CHCOC}_6\text{H}_5} \\
\text{CH}_3\text{C(COOEt)}_2 & \text{CH}_3\text{C}-\text{CO} \\
& \text{COOEt} \\
\text{IV} & \text{V}
\end{array}
$$

$$
\begin{array}{ccc}
\underset{|}{\text{C}_6\text{H}_5\text{CH}-\text{CHCOC}_6\text{H}_5} & \text{C}_6\text{H}_5\text{CH} & \text{CH}_2\text{COC}_6\text{H}_5 \\
\text{CH}_3\text{CH COOEt} & \text{CH}_3\text{CCOOEt} & \text{COOEt} \\
\text{COOEt} & & \\
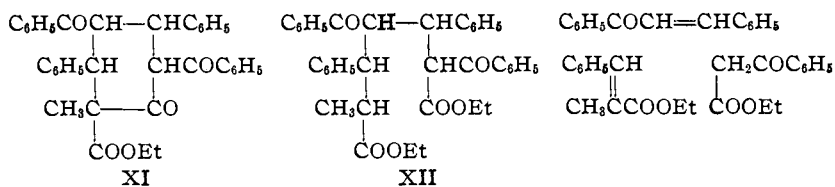\text{VI} & &
\end{array}
$$
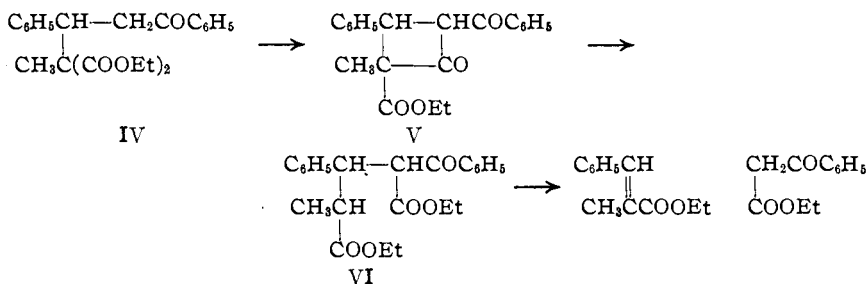
These authors have overlooked the fact that a close parallel does not exist in the addition reactions of crotonic ester and chalcone. The latter compound forms addition products with extraordinary facility [compare Kostanecki and Tambor, *Ber.*, **29**, 1495 (1896)]. Dieckmann and Kron [*Ber.*, **41**, 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

$$
\begin{array}{cc}
\underset{|}{\text{C}_6\text{H}_5\text{CH}-\text{CH}_2\text{COC}_6\text{H}_5} & \underset{|}{\text{C}_6\text{H}_5\text{CH}-\text{CH}_2} \\
\text{C(COOEt)}_2 & \text{(EtOOC)}_2\text{C}\quad\text{CC}_6\text{H}_5 \\
\text{C}_6\text{H}_5\text{CH}-\text{CH}_2\text{COC}_6\text{H}_5 & \text{C}_6\text{H}_5\text{CH}-\text{CCOC}_6\text{H}_5 \\
\text{VII} & \text{VIII}
\end{array}
$$

$$
\begin{array}{cc}
\underset{|}{\text{C}_6\text{H}_5\text{COCH}-\text{CHC}_6\text{H}_5} & \underset{|}{\text{C}_6\text{H}_5\text{COCH}-\text{CH}} \\
\text{C}_6\text{H}_5\text{CH}\quad\text{CH}_2\text{COC}_6\text{H}_5 & \text{C}_6\text{H}_5\text{CH}\quad\text{CHCOC}_6\text{H}_5 \\
\text{CH(COOEt)}_2 & \text{CH}-\text{CO} \\
& \text{COOEt} \\
\text{IX} & \text{X}
\end{array}
$$

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

C$_6$H$_5$COCH—CHC$_6$H$_5$ C$_6$H$_5$COCH—CHC$_6$H$_5$ C$_6$H$_5$COCH=CHC$_6$H$_5$
C$_6$H$_5$CH   CHCOC$_6$H$_5$ C$_6$H$_5$CH   CHCOC$_6$H$_5$ C$_6$H$_5$CH   CH$_2$COC$_6$H$_5$
CH$_3$C——CO   CH$_3$CH   COOEt   CH$_3$CCOOEt COOEt
COOEt   COOEt
XI   XII

The ester XI upon treatment with sodium ethoxide in ether solution readily undergoes fission to give benzoylacetic 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   ARTHUR MICHAEL
HARVARD UNIVERSITY   JOHN ROSS
CAMBRIDGE, MASSACHUSETTS
RECEIVED DECEMBER 24, 1931
PUBLISHED JANUARY 7, 1932

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