[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

The Conductivity, Dielectric Constants, and E.m.f.'s of Some Ethylmagnesium Compounds

RAYMOND E. DESSY AND RICHARD M. JONES

Received May 26, 1959

The conductivity of ethereal solutions of "ethylmagnesium bromide,"[1] diethylmagnesium, magnesium bromide, and mixtures of diethylmagnesium and magnesium bromide have been measured. Some discrepancies existing in the literature have been rectified. Some data on the dielectric constants of these solutions are presented. An observed linear relationship between the ln (molar conductance) of "ethylmagnesium bromide" solutions and the e.m.f.'s of such solutions is discussed.

The first report of the electrical conductivity of ethereal solutions of "ethylmagnesium bromide" was by Jolibois,[2] and this report was confirmed in a preliminary paper by Nelson and Evans.[3] A study by Kondyrew[4] indicated that the equivalent conductance decreased with increasing concentration while a study of "ethylmagnesium iodide"[5] showed a maximum. The results of a study of "ethylmagnesium bromide" by Evans and Lee[6] indicated that the molar conductance increased with decreasing concentration. This apparent discrepancy was explained by Evans in analogy with the "ethylmagnesium iodide" work as being due to a difference in the concentration ranges used for the two studies. Evans felt that the "ethylmagnesium bromide" should also show a maximum. A critical evaluation of Kondyrew's work shows, however, that both investigations were carried out in the same range of concentration. The original misinterpretation by Evans arose because of the frequency with which Kondyrew changed his definition of formula and equivalent weight.

Since the electrical properties of such solutions may in time lead to a better understanding of the structure of the Grignard reagent, it was evident that a careful reinvestigation of the conductivity of "ethylmagnesium bromide" was necessary.

It has recently been found[7] that the presence of tertiary amines markedly increases the rate of reaction of Grignard reagents with certain substrates. While this effect has been studied in other ways[8,9] no conductance data has been reported.

The purpose of this paper is therefore fourfold: (1) to resolve the difference in the values of conductance reported for "ethylmagnesium bromide," (2) to provide some data on the conductance of a Grignard reagent in the presence of a tertiary amine, (3) to shed some light on the constitution of "ethylmagnesium bromide" solutions by a study of the conductances of some diethylmagnesium–magnesium bromide systems, and (4) to present some data concerning the dielectric constants of some of these solutions.

In addition some correlations with observed e.m.f. values will be presented, and some tentative explanations for these correlations offered.

EXPERIMENTAL

Ether. Merck Anhydrous Analytical Reagent freshly distilled from "ethylmagnesium bromide."

Ethylmagnesium bromide. The "ethylmagnesium bromide" was prepared in the usual manner from ethyl bromide and magnesium turnings in ethyl ether.[10]

The magnesium used was Mallinckrodt magnesium metal turnings. The ethyl bromide was freshly distilled. The bromine/basic Mg ratio was 1.09.

Diethylmagnesium. Prepared as previously described.[11]

Magnesium bromide in ether. Prepared as previously described.[12]

Since it was felt that the vigorous reaction conditions indicated by this method (direct bromination of magnesium in ether) might lead to erroneous results the magnesium bromide was prepared from the hexahydrate by fusion with ammonium bromide followed by dissolution in ether. The two solutions showed no difference with respect to conductivity. Magnesium bromide in ether forms a two phase system—the heavy lower layer showing a concentration of $MgBr_2$ of 2.63M, the light upper layer a concentration of 0.138M. Depending upon the final concentration desired both layers were used.

---

[1] Since evidence seems to indicate that no such species as C_2H_5-Mg-Br exists in ethereal solution, quotation marks will be used around the name ethylmagnesium bromide to indicate a reagent prepared from ethyl bromide and magnesium. No actual structure is meant to be implied. *Cf.* R. E. Dessy and G. S. Handler, *J. Am. Chem. Soc.*, **80**, 5824 (1958).

[2] P. Jolibois, *Compt. rend.*, **155**, 353 (1912).

[3] J. M. Nelson and W. V. Evans, *J. Am. Chem. Soc.*, **39**, 82 (1917).

[4] N. W. Kondyrew and D. P. Manogew, *Ber.*, **58B**, 464 (1925).

[5] N. W. Kondyrew and A. K. Ssusi, *Ber.*, **62B**, 1856 (1929).

[6] W. V. Evans and F. H. Lee, *J. Am. Chem. Soc.*, **55**, 1974 (1933).

[7] J. H. Wotiz, C. A. Hollingsworth, and R. E. Dessy, *J. Org. Chem.*, **20**, 1949.

[8] J. H. Wotiz, C. A. Hollingsworth, R. E. Dessy, and Lang Ching Lin, *J. Org. Chem.*, **23**, 228 (1958).

[9] J. H. Wotiz and A. W. Simon, 133rd Meeting, ACS, San Francisco, Calif., April 13–18, 1958, Division of Organic Chemistry, p. 7N.

[10] *Cf.* J. H. Wotiz, C. A. Hollingsworth, and R. E. Dessy, *J. Org. Chem.*, **20**, 1545 (1955).

[11] R. E. Dessy and G. F. Handler, *J. Am. Chem. Soc.*, **80**, 5824 (1958).

[12] J. H. Wotiz, C. A. Hollingsworth, and R. E. Dessy, *J. Org. Chem.*, **21**, 1063 (1956).

Triethylamine. The triethylamine was purified by distillation from "ethylmagnesium bromide" followed by storage in sealed ampoules.

Handling of reagents. All reagents were handled with hypodermic syringes in dry boxes, polyethylene bags filled with an inert atmosphere, etc. All glass ware was suitably dried at 110°. The reagents were stored in serum-capped bottles in desiccators. Care was taken to prevent oxygen contamination at all steps.

Conductivity measurements. The conductivity measurements were made using the following bridge: The source unit was an audio frequency generator giving variable frequencies from 10–100,000 c.p.s. at a level of from 0–10 v. The bridge itself was a Heath Model 1B-2A Impedance Bridge modified to accept compensating capacitors. The detector was a VTVM feeding an amplified signal to an oscilloscope which was used as a final balance indicator in the manner described by Fuoss.[13]

The cell was a spherical glass container possessing 2 bright platinum electrodes 3 cm. in diameter placed 5 mm. apart. The cell constant was 0.04. The reagents were added through a capillary side arm protected by a stopcock.

Dielectric measurements. The dielectric measurements were made in a Sargent Model V Chemical Oscillometer at 5 megacycles using a cell with external electrodes.

DISCUSSION AND RESULTS[14]

Fig. 1 shows plots of molar conductance *vs.* concentration for "ethylmagnesium bromide" and diethylmagnesium. The data for "ethylmagnesium bromide" agree well with those of Evans[6] and indicate that the work of Kondyrew[4] is in error. On the chance that the two workers may have been working at different frequencies, an experimental condition not reported, the effect of frequency on conductance was examined.

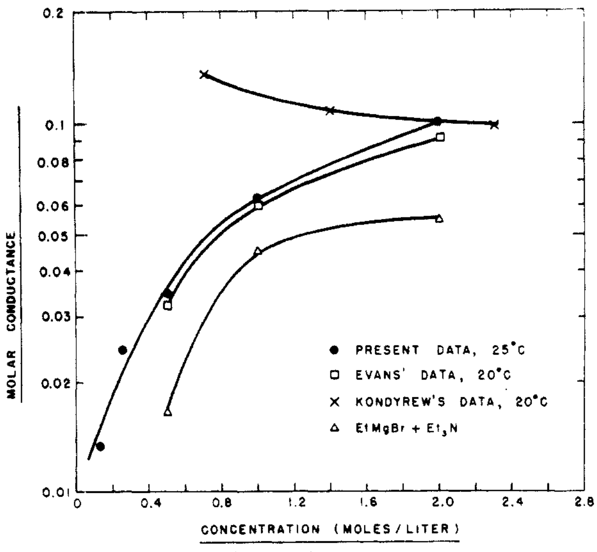
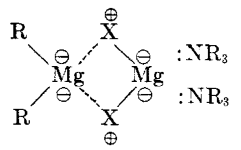


Fig. 1. Plots of molar conductance *versus* concentration for "ethylmagnesium bromide" as reported by various workers

From 300–100,000 c.p.s. no appreciable change in conductance values was noted. There appears to be no logical explanation for the erroneous data reported by Kondyrew. In any event, all of the data for other Grignard reagents reported by him are open to question.

Fig. 1 also shows the results of the addition of equimolar amounts of triethylamine to solutions of "ethylmagnesium bromide." By varying the amount of amine at a fixed concentration of "ethylmagnesium bromide" it was found that the conductance varied approximately inversely with the amount of amine present.

Examination of reaction rate data of "ethylmagnesium bromide" with hexyne-1 would lead to the tentative conclusion that the ionization is enhanced by the addition of amine.[8] The mechanism of such an effect would be through the coordination of the amine with the magnesium-bearing Lewis acid species in solution. This coordination would be a replacement of the previously coordinated ether by the more basic amine. The greater electron donor ability of the amine would then facilitate the release of a carbanion from such a structure as



Since it has been found[8] that the relative reactivity of diethylmagnesium with hexyne-1 is unaffected by the presence of triethylamine there appears to be good justification for associating the amine with the magnesium bromide.

Unfortunately the conductance data belies the foregoing proposals and any others which would give enhanced ionization or dissociation as the reason for greater reactivity. Further investigation seems to be indicated in order to resolve the effect of amines on the reactivity of Grignard reagents.

Table I shows the results of conductance measurements on various mixtures of diethylmagnesium and magnesium bromide.

It is interesting to note that over the concentration ranges employed that the log (specific conductivity) *versus* molar concentration for diethylmagnesium is linear. It is hoped that this will prove valuable in future kinetic investigations. It is also apparent from the data that diethylmagnesium and magnesium bromide interact when mixed to form a system which is more conducting than would be predicted from the conductivity of the two components.

This appears to be quite logical since diethylmagnesium may act as a Lewis acid and magnesium

---

[13] R. M. Fuoss and D. Edelson, *J. Chem. Ed.*, **27**, 610 (1950).

[14] Because of the difficulty in assigning a definite structure to "ethylmagnesium bromide" it is necessary to define clearly what a mole is in presenting conductivity data. In all of the data which follows a mole of "ethylmagnesium bromide" will be taken as the formula weight of the unit C_2H_5MgBr, and there will be, by definition, one equivalent weight per mole. For diethylmagnesium one mole will be, as usual, taken as the formula weight of the unit $(C_2H_5)_2Mg$, with *two* equivalents per mole.

TABLE I

THE CONDUCTANCE OF VARIOUS MIXTURES OF DIETHYLMAGNESIUM AND MAGNESIUM BROMIDE AT 25° IN ETHER

Molar Et_2Mg	Concentration $MgBr_2$	Specific Conductance ohm^{-1} cm.$^{-1}$ ($\times 10^4$)
0.139	...	0.013
0.250	...	0.032
0.500	...	0.092
1.000	...	0.328
...	0.069	0.079
...	0.139	0.056
0.139	...	0.013
0.139	0.139	0.460
0.125	0.500	Two Phase System
0.250	0.500	1.15
0.500	0.500	2.26
0.750	0.500	2.57
0.500	0.125	0.370
0.500	0.250	6.89
0.500	0.500	2.26
0.500	0.750	2.30

bromide as a Lewis base. Together they would then form a complex which would have a greater ability to ionize than either one as an individual. The data thus support a structure for "ethylmagnesium bromide" of the type $Et_2Mg \cdot MgBr_2$.

It is somewhat disconcerting to compare the values for solution 0.5*M* in magnesium bromide and 0.5*M* in diethylmagnesium with solutions 1.0*M* in "ethylmagnesium bromide." Work indicates that the same species is (are) present in both solutions.[15] In spite of this the values of specific conductance of the two systems are at variance with each other ($2.26 \cdot 10^{-4}$ ohm^{-1} cm.$^{-1}$ for Et_2Mg, $MgBr_2$; $0.61 \cdot 10^{-4}$ ohm^{-1} cm.$^{-1}$ for "EtMgBr"). Two different lots of ethylmagnesium bromide were made and run to check this discrepancy and it was found in both cases. The method of preparing the magnesium bromide was also varied but no change in conductivity was noted. Considering the crude synthetic methods involved in the preparation of the reagents and the inability to purify it is not difficult to foresee side reactions which could create this difference. However, it is still a most unfortunate circumstance.

Two other points should be noted (1) that as the diethylmagnesium concentration is increased in a solution containing a fixed amount of magnesium bromide, the specific conductivity increases, as would be expected, but that (2) as the magnesium bromide concentration is increased in a solution containing a fixed amount of diethylmagnesium the specific conductivity goes through a distinct maximum, and then falls to a constant level.

Table II presents the dielectric constants *versus* concentration for various ethylmagnesium systems. The measurements were made on a Sargent Model V Oscillometer at 5 megacycles. Above specific conductances of 10^{-4} the conductivity of the solutions will effect the apparent capacity of the cell by introducing a conductive path having a resistance. Therefore above 1 molar concentrations values could not be measured.

TABLE II

THE DIELECTRIC CONSTANTS (*K*) OF VARIOUS ETHYLMAGNESIUM SYSTEMS AT 25° IN ETHER

System	Molar Concentrations	*K*
"EtMgBr"	0.125	5.1
	0.250	6.5
	0.500	11
	0.750	20
	1.000	35
Et_2Mg	0.125	4.6
	0.250	5.3
	0.500	6.6
	0.750	9.0
	1.000	11
"EtMgBr" + Et_3N	1.00	30
Et_2Mg + Et_3N	0.500	6.2

The dielectric constant of ethereal solutions of diethylmagnesium is a linear function of the concentration, indicating that no serious association is occurring; the data for "ethylmagnesium bromide" indicate increasing association.

In both cases the addition of triethylamine reduces the dielectric constant, thus confirming the results of the conductivity measurements.

One very interesting detail should be pointed out. It is often assumed in many discussions of reactions of organometallic compounds in nonpolar solvents that the medium cannot support ionic mechanisms in the ordinary sense of the word because of its low dielectric. The present data indicates that a one molar solution of Grignard reagent in ether does indeed present a highly polar environment.

It is interesting to speculate, rather freely it is admitted, on the relationship between the present data and that reported by Gay[16] on the e.m.f.'s of various concentrations of ethylmagnesium bromide in ether using a Pt-calomel electrode system (Table III). Gay showed that the observed potential, E_c, could be expressed as follows

$$E_c = E_c^0 + \frac{RT}{F} \ln (c)^2 \qquad (1)$$

where E_c^0 is the potential of a solution of unit activity, taken as 1 molar, *n* is the number of

---

(15) R. E. Dessy and G. S. Handler, *J. Am. Chem. Soc.*, **79**, 3476 (1957).

(16) Unpublished results by F. R. Gay, Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Del. Abstracts of Papers, 131st Meeting, American Chemical Society, Miami, Fla., 1957, p. 50-O.

TABLE III

RELATIVE POTENTIALS[a] OF "ETHYLMAGNESIUM BROMIDE" SOLUTIONS

M	E.m.f.
1.28	1.255
0.65	1.227
0.59	1.221
0.29	1.195
0.185	1.181
0.099	1.150

[a] Uncorrected for Pt-saturated calomel electrode potentials.

Faraday's per mole involved, R is the gas constant, T the absolute temperature, F the Faraday, and (c) the concentration of Grignard.

The present conductivity data for ethylmagnesium bromide can be represented in the form

$$\ln(\Lambda) = k \ln(c) + k' \qquad (2)$$

where Λ is the molar conductance and k and k' are constants having the values 0.7 and 1.22 respectively.

If one assumed that in solvents of sufficiently low dielectric constant triple ions of the type $(+ - +)$ or $(- + -)$ are stable, and that they arise from equilibria of the following nature

$$\begin{aligned} AB &\rightleftharpoons A^{+} + B^{\ominus} \\ AB_2^{\ominus} &\rightleftharpoons AB + B^{\ominus} \\ A_2B^{\oplus} &\rightleftharpoons AB + A^{\ominus} \end{aligned} \qquad (3)$$

it is easy to show[17] that

$$\Lambda = K_1 c^{-1/2} + K_2 c^{1/2} \qquad (4)$$

if one assumes that c_{AB}, the concentration of AB, is equal to the stoichiometrical concentration c—in other words, that little ionization and/or dissociation occurs. As c increases the molar conductance will pass through a minimum, and eventually yield a curve in which the molar conductance is direction proportional to $c^{1/2}$, or $\ln \Lambda = 0.5 \ln (c) + k'$. The observed slope 0.7, therefore seems to indicate that the conductivity measurements support triple ion formation in Grignard reagents in ether, and that these are the current carriers. Previous rough measurements of transport numbers[15] have also indicated that the ions are large aggregates, probably involving 2 or 3 molecules, since the amount of material transported during an electrolysis of ethylmagnesium bromide is approximately 4 times that discharging at the electrodes.

It is obvious that we may relate E_c and V as follows

$$E_c = K \ln \Lambda + K' \qquad (5)$$

where K and K' are again constants. The physical significance of this relationship is not difficult to conceive if one assumes that the species responsible for the conductivity of the solution are those responsible for the e.m.f. It has recently been shown[18] by tracer techniques that the Grignard reagent is best written as a complex $Et_2Mg \cdot MgBr_2$, and that in the electrolysis of ethyl Grignard the ionization appears to involve

$$Et_2Mg \cdot MgBr_2 \rightleftharpoons EtMg^{\oplus} + EtMgBr_2^{\ominus} \qquad (6)$$

These species, involved in discharge, might reasonably also be involved in the conductivity and e.m.f. processes, although, one realizes that the species that discharges is not necessarily the main current carrier.

This speculation receives support from the fact that the relative e.m.f.'s of various Grignard reagents, such as ethyl, *i*-propyl, *t*-butyl, *n*-propyl, and *i*-butyl, at 1 molar concentrations, as determined by Gay, are approximately inversely related to the decomposition potentials, E_d, of these same Grignard reagents as determined by Evans.[19] Although the electrode processes are not necessarily the same, the relationship seems reasonable. If these three processes (1) conductivity (2) e.m.f. and (3) decomposition potential do have a species concentration in common it is perhaps worth while to carry the extrapolation a little bit farther. It has been pointed out[20] that there is a linear relationship between E_d, and the ln (relative rate) as determined by the reaction

$$R{-}C{\equiv}C{-}H + R'MgX \longrightarrow R'H + R{-}C{\equiv}C{-}MgX \qquad (7)$$

for the Grignards mentioned above. The decomposition potential can be expressed as

$$E_d = E^\circ - \frac{RT}{aF} \ln q \qquad (8)$$

where a is a constant and q is the activity quotient given by

$$q = \frac{a\,(\text{product})}{a\,(\text{Grignard reagent})} \qquad (9)$$

If E° is assumed constant throughout the series together with the activity of the products, then E_d will be a function of a(Grignard reagent). The linear relationship suggests that the rate of equation (7) could be given by

$$d\,\frac{(\text{RH})}{dt} = c(1/q)^n a(\text{R—C}{\equiv}\text{C—H})^m \qquad (10)$$

where c, m, and n are constants. This would imply that the activation energy is constant throughout the series and that variations in E_d and relative reactivity are reflections of changes in the activity

---

[17] M. Dole, *Principles of Experimental and Theoretical Electrochemistry*, p. 78, McGraw-Hill Book Co., Inc., New York, 1935.

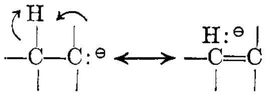
[18] R. E. Dessy, G. S. Handler, *J. Am. Chem. Soc.*, **80**, 5824 (1958).

[19] W. V. Evans, F. H. Lee, and C. H. Lee, *J. Am. Chem. Soc.* **57**, 489 (1935).

[20] R. E. Dessy, C. A. Hollingsworth, and J. H. Wotiz, *J. Am. Chem. Soc.*, **77**, 4410 (1955).

of the reactive species in both reactions, regardless of its form.

The resonance stabilization of carbanions (free or incipient) that has been proposed by Polanyi[21] could explain the order of the reaction rates and decomposition voltages if the results obtained by assuming $E°$ a constant are used.



It thus appears that all four sets of data can be tied together in a common ground—the concentration, or availability of, a common ion.

TABLE IV

RELATIVE POTENTIALS[a] OF ALKYLMAGNESIUM BROMIDES AT $1M$ CONCENTRATIONS

R	E.m.f.[16]	E_{D}^{19}
Et	1.24[b]	1.28[b]
i-Pr	1.27[b]	1.07[b]
t-Bu	1.41[c]	0.87[b]
n-Pr	1.23[c]	1.42[b]
i-Bu	1.21[c]	1.29[b]

[a] Uncorrected for Pt-saturated calomel electrode potentials. [b] Values for 1 molar solution. [c] Extrapolated from range 0.05–0.2M solutions.

Work is presently being carried out using both conductivity measurements and dielectric constant measurements as a method of following the rates of reaction of Grignard reagents with various substrates.

Acknowledgment. The authors would like to thank E. H. Sargent and Company for the loan of a Sargent Model V Chemical Oscillometer.

CINCINNATI 21, OHIO

---

(21) E. C. Bangham, M. G. Evans, and M. Polanyi, *Trans. Faraday Society*, **37**, 377 (1947).

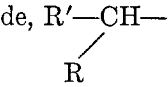
[CONTRIBUTION NO. 1486 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Synthesis of (−)-6-*exo*,7-*endo*-Dihydroxy-3-tropanone; An Optically Active Product from a Robinson-Mannich Condensation[1]

ROBERT STERN[2] AND HARRY H. WASSERMAN

Received April 27, 1959

Oxidation of 3,4-monoacetone-D-mannitol (I) by means of lead tetraacetate, followed by acid hydrolysis and treatment of the resulting L-tartardialdehyde solution with acetone dicarboxylic acid and methylamine hydrochloride, resulted in the formation of (−)-6-*exo*, 7-*endo*-dihydroxy-3-tropanone (IVa).

We wish to report the synthesis of (−)-6-*exo*, 7-*endo*-dihydroxy-3-tropanone[3,4] ("levorotatory teloidinone"), using D-mannitol as starting material, and involving L-tartardialdehyde[6] as an intermediary product. Our results, along with other recent work in this field,[7] show that a Mannich-type reaction involving an enolizable optically active aldehyde,  $\underset{\mathrm{R}}{\mathrm{R'{-}CH{-}CHO}}$, can lead to an optically active condensation product.

Partial hydrolysis of triacetone-D-mannitol,[8] obtained from D-mannitol and acetone, yielded 3,4-monoacetone-D-mannitol,[9] I, m.p. 86–88°, $[\alpha]_{\mathrm{D}}^{20.0}$ +23.0. The oxidation of I with pure lead tetraacetate according to the procedure of Fischer and Appel afforded acetone-L-tartardialdehyde[10] (acetone-D-α,α'-dihydroxysuccindialdehyde), II, an intermediate which was not isolated. Hydrolysis of the crude reaction product with 0.1N sulfuric acid, to

---

(1) Presented at the 131st Meeting of the American Chemical Society in Miami, Fla., April 8, 1957.

(2) Present address: Dept. of Chemistry, Connecticut College, New London, Conn.

(3) We are using the *exo-endo* designations in describing derivatives of tropane (N-methyl-8-aza-[1, 2, 3]-bicyclooctane) in accordance with the usage of K. Alder and H. A. Dortmann, *Ber.* **86**, 1545 (1953). An alternate nomenclature used for tropane derivatives has been adapted from steroids by G. Fodor and K. Nador, *J. Chem. Soc.*, 722 (1953).

(4) The absolute configuration of this optically active compound is identical to that of L(−)-tartaric acid.[5] It can be called R(−)-6,7-dihydroxy-3-tropanone, according to a general stereochemical nomenclature recently proposed by R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia*, **12**, 81 (1956).

(5) (a) K. Freudenberg, "Stereochemie", Franz Deuticke, Leipzig and Wien, 1933, p. 668; (b) C. D. Nenitzescu, *J. Chem. Educ.*, **34**, 147 (1957).

(6) An alternative designation of this compound is D-α,α'-dihydroxysuccindialdehyde.

(7) Since we first reported our results [see footnote (1)] E. Hardegger and H. Furter, *Helv. Chim. Acta*, **40**, 872 (1957), have published the account of an independent synthesis of S(+)-6,7-dihydroxy-3-tropanone from D(+)-tartaric dialdehyde. Their condensation product is the dextrorotatory enantiomer of the one we have prepared. Furthermore, K. Zeile and A. Heusner, *Ber.*, **90**, 1869 (1957), have recently published an independent synthesis of (−)-alloteloidinone, a product which appears to be identical with our material.

(8) E. Fischer, *Ber.*, **28**, 1167 (1895).

(9) L. F. Wiggins, *J. Chem. Soc.*, 13 (1946).

(10) H. O. L. Fischer and H. Appel, *Helv. Chim. Acta*, **17**, 1574 (1934).