[CONTRIBUTION FROM THE PHYSICAL CHEMICAL LABORATORY, NORTHWESTERN UNIVERSITY]

FURTHER STUDIES IN LUMINESCENT GRIGNARD COMPOUNDS

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Owing to the fact that work on the Grignard compounds is usually conducted in a lighted laboratory, one peculiar property of these compounds has escaped general observation, namely, their property of giving off light upon oxidation. This luminescence has been noted with regard to certain of the reagents specifically and the literature contains references to such isolated cases, but the widespread occurrence of the phenomenon has not been commented upon.

In their observation of this fact the authors have made more than 90 Grignard compounds and in all cases where a reaction was assured and a Grignard compound formed, the luminescence resulted upon oxidation, except in the case of methyl and ethyl halides or halides with a radical of low molecular weight.

Of the 90 compounds investigated, all gave light except 21. Of this number, 11 were chlorides with which we were not sure a reaction had taken place and 9 contained radicals of low molecular weight. With the chloro compounds we were not sure of a reaction in every case when we had a radical heavier than a propyl group, but in every case where a reaction was certain luminescence appeared upon oxidation except in the case of the light radicals. In some cases where the solution itself gave no luminescence the solid precipitated was quite luminescent. This was true with heavy organic radicals that gave insoluble Grignard compounds. Diphenyl ether, for example, produced a solid with *p*-dibromobenzene which was notably luminescent.

According to Dufford,[1] luminescence appears in no case unless the magnesium is attached to an unsaturated carbon, but the present writers had no difficulty in securing light from the Grignard compounds formed from lauryl bromide, propyl bromide, butyl bromide, bromocyclohexane and trimethylene bromide. It is true that the aromatic compounds, as a rule, seem to give more light than the aliphatic compounds but there can be no generalization that only those with unsaturated carbon give light. The Grignard compounds formed from these saturated compounds were luminescent in many different ethers during oxidation and gave off light continuously even when the heat of the reaction was not sufficient to ignite the ether; and the light from some of these was comparable to the light from phenylmagnesium bromide.

In order to detect the luminescence of some of the aliphatic compounds

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[1] Dufford, Calvert and Nightingale, THIS JOURNAL, **45**, 2068 (1923).

it was necessary to remain in a dark room for a considerable time until the eyes became sensitive to the faint light. In other cases the light was more readily visible. Dufford[1] states that the dichlorobenzene compounds give dim light. We found that the light from them is quite bright when any considerable concentration of the Grignard compound is secured. We found it necessary to make these substances in sealed Pyrex tubes in order to get the maximum luminescence. *p*-Chlorophenylmagnesium chloride, made in this way, was one of the substances which yielded a spectrogram.

It has been interesting to determine just how general such luminescence might be and to extend this observation, a number of rather rare Grignard compounds were made. Dufford[1] has published a list of the light-giving compounds of Moeller,[2] stating that four are wrongly included—namely, propylmagnesium bromide, *iso*-amyl magnesium bromide, benzyl magnesium bromide and ethylmagnesium bromide. Confirming Moeller, however, we found light from all but the last of these. Moeller states that he gets no reaction with propyl chloride, symmetrical tribromobenzene and chlorobenzene, whereas we have made Grignard compounds with these substances and found that they also give light.

All observations on each substance were made visually by three different observers, the observations noted separately and later compared. This procedure resulted in the following list of substances producing Grignard

TABLE I

SUBSTANCES GIVING LUMINESCENT GRIGNARD COMPOUNDS

VERY BRIGHT

p-Butyl-*p*-bromodiphenyl
p-Bromobenzyl chloride

BRIGHT

p-Chlorophenetole
o-Bromobenzyl chloride
m-Bromo-anisole
1-Bromo-2,5-diethylbenzene
p-Bromo-anisole
o-Iodo-anisole
p-Chlorobenzyl chloride
o-Chlorobenzyl chloride
m-Iodo-anisole

FAINT

1-Iodo-2,4-dimethyl-benzene
1-Bromo-2,5-dimethoxy-benzene
m-Bromo-iodobenzene
o-Bromo-diethylaniline
o-Bromo-iodobenzene
p-Chloro-anisole
sym.-Tribromobenzene
Trimethylene bromide
o-Iodo-chlorobenzene
Benzyl chloride
Propyl chloride
iso-Amyl bromide

VERY FAINT

1-Iodo-2,5-dimethylbenzene
p-Iodo-anisole
n-Propyl bromide
n-Butyl bromide
n-Lauryl bromide
Bromocyclohexane
m-Iodo-chlorobenzene

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[2] Moeller, *Arch. Pharm. Chem.*, **21**, 449 (1914).

compounds (Table I) that give light, additional to those already listed by Moeller and Dufford. The order of intensity of light is noted as very bright, bright, faint, very faint.

Weight of Radical

Moeller[2] concludes that the brightness of the luminescence is in proportion to the molecular weight of the halogen derivative. This is certainly the case so long as a definite series is considered, without change in the chemical nature of the group or—in the case of aromatic compounds—in the position. The increase in the luminescence with molecular weight can be shown with the series C_6H_5MgBr, *p*-$CH_3C_6H_4MgBr$, *p*-$C_2H_5C_6H_4MgBr$ and *p*-$C_4H_9C_6H_4MgBr$; also *p*-$C_6H_5C_6H_4MgBr$ and *p*, *p'*-$C_4H_9C_6H_4$-C_6H_4MgBr, written in the order of increasing brightness.

If the position is *para*, the luminescence increases decidedly for such groups as CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9 and C_6H_5, as is further proved by the fact that the Grignard compound from *p*-bromo-diethylaniline gives more light than that from *p*-bromo-dimethylaniline and the Grignard compound from 1-bromo-3,6-diethylbenzene than the corresponding dimethyl compound. The same relation holds with the aliphatic compounds, that is, methyl and ethyl give little if any light, while the light increases with propyl, butyl, *iso*-amyl and lauryl bromide.

When the loading group is a halogen this increasing molecular-weight relationship does not seem to hold, as was noted by Dufford, but compounds as vastly different as *p*-ethylphenylmagnesium bromide and *p*-diethylamino-phenylmagnesium bromide cannot be compared, since luminescence is influenced by three factors—mass, chemical nature of group and position. In order to test the effect of any one of these the others must be kept constant.

Effect of Halide Radical

In general it may be stated that the RMgBr compounds give the most light and that the RMgI compounds are poor light-givers; although they are readily formed. The Grignard compounds of the following substances, for example, produce little luminescence: iodobenzene, *p*-di-iodobenzene, *p*-iodotoluene, 1-iodo-2,4-dimethylbenzene, *p*-iodoanisole, 1-iodo-2,5-dimethylbenzene, *m*-iodo-chlorobenzene and *o*-iodo-chlorobenzene. The RMgCl compounds are difficult to make and as a rule are slightly dimmer than the bromo compounds.

Effect of Position

To determine the effect of position on the intensity of the light given off on oxidation, a test was made of the halogenated toluenes prepared in ethyl ether, *n*-butyl ether and anisole. The compounds were mixed in molecular proportions, although we do not know that the solutions investigated contained molecular proportions of the Grignard compounds.

The order of decreasing intensity was found to be *para*, *ortho*, *meta*. Substances with the radical in the *para* position are much brighter than those with radicals in the *ortho* or *meta*, with little difference between the last two. All the very bright compounds we have investigated were *para* compounds, such as *p*-bromophenylmagnesium bromide, *p*-chlorophenylmagnesium bromide, *p*-chlorophenylmagnesium chloride and the Grignard compounds formed from *p*-butyl-*p*-bromodiphenyl, *p*-bromodiphenyl and *p*,*p'*-dibromodiphenyl. β-Bromonaphthalene (which may be regarded as a benzene with both the *para* and *meta* positions loaded) also gave a bright compound.

The only other compounds of which we consider it possible to secure spectrograms are *o*-dibromobenzene and *o*-chlorobromobenzene which indicate the *ortho* position to be second in order of brightness. The same order was secured in testing the dihalide benzenes. In all of this work as well as with the monohalide benzene we found, as previously stated, the halide order of decreasing intensity to be RMgBr, RMgCl, RMgI.

When the phenyl group is unsubstituted the light is dim, as with phenylmagnesium halide. A substituent in the phenyl group increases the luminescence. Two substituents invariably decrease the luminescence; thus *sym.*-tribromobenzene and the halogenated xylenes invariably give less light than when there is only one substituent. When there are two organic radicals in the phenyl group, there are evidently a number of possibilities. The radicals may be in the 2,3, 2,4, 2,5, 2,6, 3,4, or 3,5 positions in respect to the magnesium. We should expect that of these the 3,4 would be the brightest, for β-bromonaphthalene is brighter than α-bromonaphthalene. The present study and Dufford's observation bear out this theory since, of the xylene compounds, 1-bromo-3,4-dimethylbenzene gives the brightest Grignard compound.

The next position as to brightness should be the 2,4- and 1-bromo-2,4-dimethylbenzene is found to be so placed. The light from this compound has about the same intensity as does that from 2-bromocymene, a 2,5 compound which should be expected to appear less bright. However, here the heavier *iso*propyl radical increases the brightness, as previously stated. Next in order of light-giving power of the series should be 1-bromo-3,5-dimethylbenzene, a 3,5 compound, and it is found in this order. There should be very little difference between 1-bromo-2,6-dimethylbenzene and 1-bromo-2,3-dimethylbenzene, compounds which we have not investigated. The same relationship holds for the iodine compounds, as far as we have studied them.

Effect of Different Solvents

In order to discover the effect different solvents might have on the luminescence of Grignard compounds, 14 different ethers, benzene and dimethylaniline were used as solvents. In this work the solutions were again made up in molecular proportions.

Lifschitz and Kalberer[3] state that luminescence is due to instability of the etherates of the aromatic magnesium halides. If this is true, the luminescence might be expected to vary with the ether used. All the solutions give light of slightly varying intensity. This variation, when different solvents were used for the same substance, seemed to depend on (1) the viscosity of the medium and (2) the solubility of the Grignard compound in the solvent used. (Anisole and phenetole were particularly good solvents for these compounds.)

According to Bischoff[4] phenetole is a negative catalyst, yet it can be used as a solvent and the reaction is quite vigorous. Many of the compounds prepared required special catalysis or had to be heated in sealed tubes for hours. The catalysts used were chiefly butyl bromide and iodine,

TABLE II

SOLVENTS IN THE ORDER OF LIGHT-GIVING POWER

FOR α-BROMONAPHTHALENE		FOR *o*-BROMO-ANISOLE	
1	*n*-Butyl ether	1	*n*-Butyl ether
2	*iso*-Amyl ether	2	*iso*-Amyl ether
3	Ethyl ether	3	*iso*Propyl ether
4	Resorcinol-dimethyl ether	4	Dimethylaniline
5	*n*-Amyl ether	5	Ethyl ether
6	α-Naphthyl-ethyl ether	6	Phenyl ether
7	*iso*Propyl ether	7	Resorcinol-dimethyl ether
8	α-Naphthyl-methyl ether	8	*n*-Propyl ether
9	*n*-Propyl ether	9	Anisole
10	Benzyl-ethyl ether		

FOR *p*-BROMOTOLUENE		FOR *o*-IODOTOLUENE	
1	Anisole	1	Anisole
2	Ethyl ether	2	Ethyl ether
3	*n*-Butyl ether	3	*n*-Butyl ether
4	Resorcinol-dimethyl ether	4	*iso*-Amyl ether
5	*iso*-Amyl ether	5	Resorcinol-dimethyl ether
6	*iso*Propyl ether	6	*iso*Propyl ether
7	*n*-Propyl ether	7	*n*-Propyl ether

FOR 2-BROMOCYMENE			
1	Phenetole	9	Diphenyl ether
2	Anisole	10	*n*-Propyl ether
3	β-Naphthyl-ethyl ether	11	Benzyl-ethyl ether
4	Butyl ether	12	*iso*-Amyl ether
5	Ethyl ether	13	β-Naphthyl-methyl ether
6	Resorcinol-dimethyl ether	14	α-Naphthyl-ethyl ether
7	α-Naphthyl-*iso*-amyl ether	15	Dimethylaniline
8	β-Naphthyl-*iso*-amyl ether	16	*iso*Propyl ether

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[3] Lifschitz and Kalberer, *Z. physik. Chem.*, **102**, 393 (1922).

[4] Bischoff, *Ber.*, **38**, 2078 (1905).

the butyl bromide having special value as a catalyst in the formation of complex Grignard compounds.

In Table II is a list of the various solvents used for a particular Grignard compound, in order of their light-giving power. Thus, alpha-bromonapthalene gave most light in butyl ether and least in benzyl ethyl ether.

The luminescence of these compounds in different ethers did not appear to be affected by the chemical nature of the solvent but by the nature of the substance being oxidized and the rate of oxidation. The solvent influences the intensity of the light only as it affects the concentration of the Grignard compound and the speed with which it can be oxidized. There does appear to be a maximum concentration beyond which the intensity of light diminishes but this is due to the increased viscosity slowing down oxidation. The light from a given solution was found to affect a plate just half as much as a similar amount of solution of one-half the concentration. In short, the light is due to the oxidation of the molecules and is independent of the solvent.

Spectra of Chemiluminescence

With the advice and assistance of the Eastman Kodak Company, the authors have been able to make a number of photographs of the spectra of luminescent Grignard compounds. Dufford, Nightingale and Calvert[5] have recently published the spectra of three of these substances. Work on the compounds was begun in the hope that a comparison of the different spectra might enable us to measure the shift of the spectra for different homologs and also the shift as the molecular weight of the radical was increased.

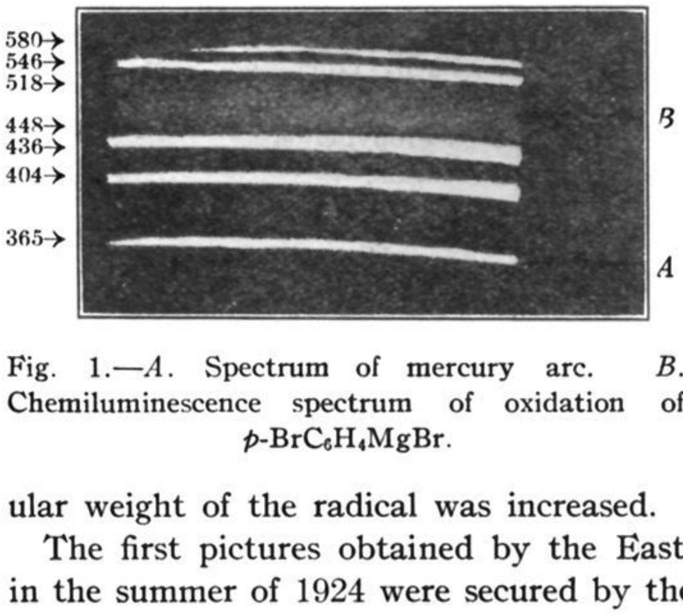

Fig. 1.—*A*. Spectrum of mercury arc. *B*. Chemiluminescence spectrum of oxidation of *p*-BrC_6H_4MgBr.

The first pictures obtained by the Eastman Kodak Company for us in the summer of 1924 were secured by the use of a special spectroscope designed to give a relatively low dispersion, employing lenses of f/2.5 aperture ratio. The spectrograms of *p*-bromophenylmagnesium bromide obtained with this instrument (Figs. 1 and 2) bring out the rather startling fact that the spectra occur at the same position. The luminescence in the case of both substances was found to lie in a band 448$\mu\mu$ to 518$\mu\mu$ and no evidence of any radiation outside this band was detected.

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[5] Dufford, Nightingale and Calvert, This Journal, **47**, 95 (1925); *J. Opt. Soc. Am.*, **9**, 405 (1924).

The intensity of the luminescence was found to be much greater in the case of the *p*-chloro compound than in the case of the *p*-bromo compound and the radiation in both cases fell off more rapidly on the long wave-length side than on the short wave-length side of the band, the maximum being at approximately 475$\mu\mu$.

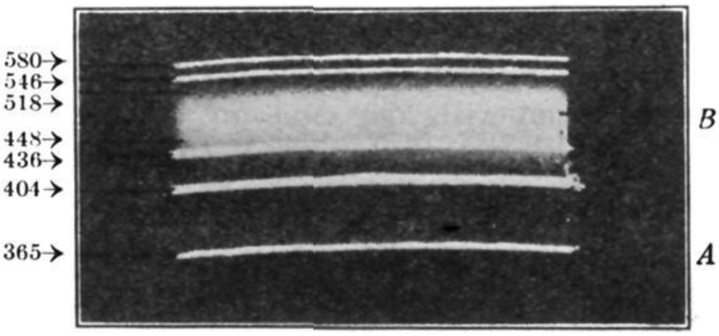

Fig. 2.—*A*. Spectrum of mercury arc. *B*. Chemiluminescence spectrum of oxidation of *p*-ClC_6H_4MgBr.

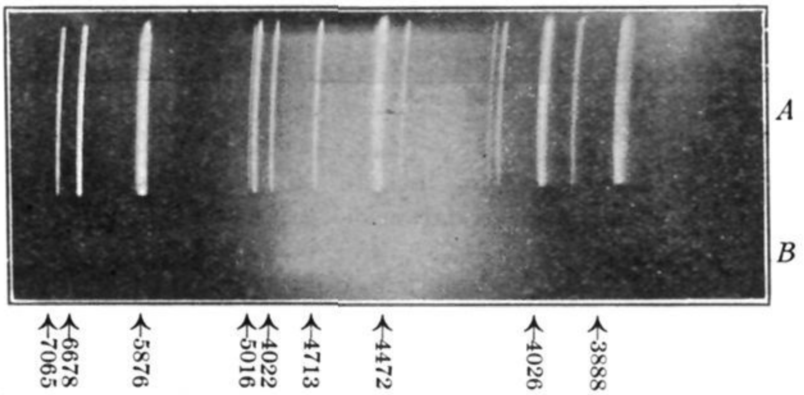

Fig. 3.—*A*. Spectrum of helium. *B*. Chemiluminescence spectrum of oxidation of *p*-ClC_5H_4MgBr.

Hoping to secure more dispersion and find a structure in the band, we used a spectroscope having an aperture ratio f/4, designed for this par-

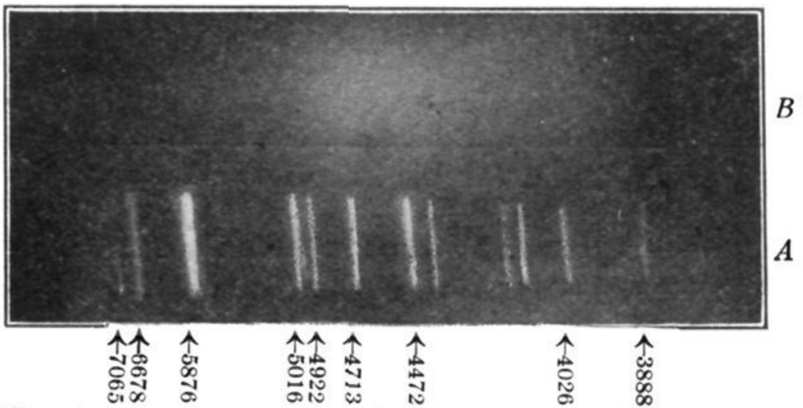

Fig. 4.—*A*. Spectrum of helium. *B*. Chemiluminescence spectrum of oxidation of *p*-BrC_6H_4MgBr.

ticular use. Figs. 3 and 4 show the spectra of the same substances taken with the new instrument. Though these spectra are distributed more, we find them occupying still the same position but in this case their limits are not so well defined and, owing to the longer exposure, the bands are wider. Dufford,[1] who has taken spectrograms of these two substances, comments on the fact that with long exposure the bands are wider but he does not note the fact that they occupy the same position when a different halogen is introduced.

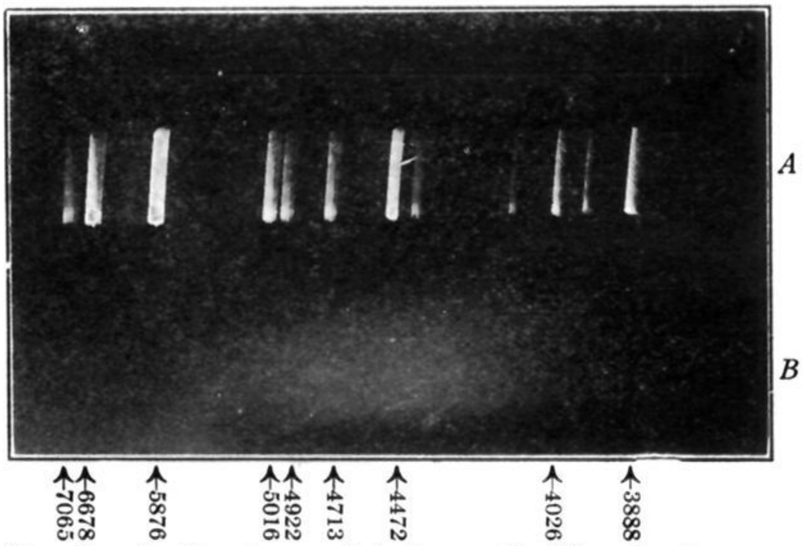

Fig. 5.—*A*. Spectrum of helium. *B*. Chemiluminescence spectrum of oxidation of *p*-ClC_6H_4MgCl.

Figs. 5 and 6 show the spectra of *p*-chlorophenylmagnesium chloride and α-naphthylmagnesium bromide, substances whose spectra have not before been photographed. The spectrogram of *p*-tolylmagnesium bromide was also obtained but is too dim for reproduction here. Again band spectra appear, but no structure. An interesting fact in this connection is that visual observation shows that the compounds differ in the color of light they give out. The character of this light changes as the oxida-

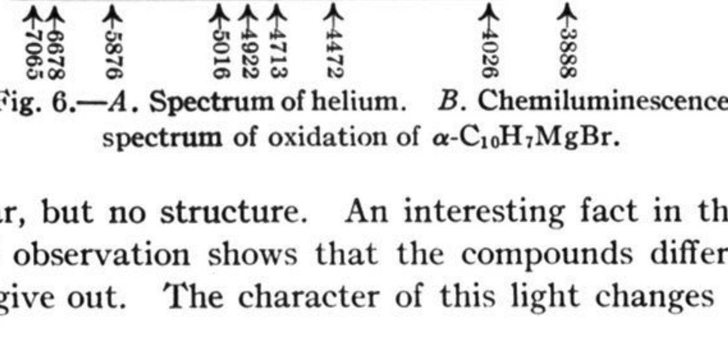

Fig. 6.—*A*. Spectrum of helium. *B*. Chemiluminescence spectrum of oxidation of α-$C_{10}H_7MgBr$.

tion proceeds, that is, the light shifts toward the red end of the spectrum. This visual shift might be explained on the ground that, since the compounds are fluorescent, the fluorescent spectra begin to appear as soon as some material has been oxidized; this would change the nature of the spectra and the final photograph would be a composite containing both the chemiluminescent and the fluorescent spectra.

McVicker, Marsh and Stewart[6] have shown that compounds containing a $C_6H_5C\equiv$ group give a Tesla luminescent spectrum in the region $382\mu\mu$ to $497\mu\mu$ and the light seems to occupy the same position independent of the group in the nucleus.

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Summary

1. The property of Grignard compounds of giving off light on oxidation is more general than has been noted, prevailing with aliphatic as well as with aromatic compounds. The only Grignard compounds that do not give this light are those in which the magnesium is attached to a radical of low molecular weight.

2. Twenty new light-giving Grignard compounds have been prepared.

3. The effect of different solvents has been investigated and the luminescence found in all solvents in which the compounds can be prepared.

4. The *para* position ranks first as to light-giving power, with the *ortho* and *meta* much inferior.

5. More work has been done to confirm the statement that luminescence increases with the weight of the radical when position and chemical nature remain constant.

6. Three new compounds have been photographed, *p*-ClC_6H_4MgCl, α-$C_{10}H_7MgBr$ and *p*-$CH_3C_6H_4MgBr$.

7. A new method is suggested for the preparation of different Grignard compounds by the use of sealed tubes.

Evanston, Illinois

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[6] McVicker, Marsh and Stewart, *J. Chem. Soc.*, **123**, 2147 (1923).