acids show slightly greater acidity than the others.

The fact that the ionization constants were found to vary consistently with concentration led to an investigation of the ionization constants at equimolar concentrations. As indicated by the data in Table II the constants found agree closely, the magnitude showing that all five are weak acids with iminodiacetic the weakest. Closer investigation, as revealed by a study of Fig. 2, indicates, however, that the *manner* in which the apparent dissociation constants vary with changes in concentration is characteristically different in the case of each individual acid. For example, although the apparent dissociation constants decrease with increasing dilutions in the case of I and III, they increase under these conditions in the case of IV and V, while II seems to represent a superposition of these tendencies. In the case of the dilution curves the phenomena measured are admittedly complex since there are unknown chemical factors dependent on dilution; IV shows an abnormal behavior which may be indicative of decomposition. However, it is of interest and possibly of significance that I and III, which alone contain phenyl groups in the α-position, are similar in the above respect, while I and IV resemble each other and II is intermediate, a grouping which also suggests itself not only from their probable chemical constitution but from a comparison of the upper parts of their respective titration curves.

Summary

The electrometric titration curves of iminodiacetic acid and of four of its phenylated derivatives have been determined and have been found to be in close agreement, all showing the greatest change of P_H at the point corresponding to the addition of one equivalent of base. A comparison of these curves shows that while the introduction of a phenyl group in the β-position is of minor importance, a phenyl group in the α-position corresponds to a relatively greater acidity of the mono-potassium salts and a distinct break in the curve at the second end-point. The dissociation constants as calculated agree closely and indicate that all five substances are weak acids. A comparison of their dilution curves shows characteristic variations for each acid.

SOUTH HADLEY, MASS. RECEIVED JULY 17, 1933

[CONTRIBUTION FROM BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Reactions of 2-Halogen Ethers. I. The Action of Magnesium on Alkyl 2-Bromoethyl Ethers

BY RALPH C. TALLMAN

It has been known for some time that 2-halogen ethers when treated with metals give products other than those which might normally be anticipated. Grignard[1] using magnesium and later Wohl and Berthold[2] using sodium, found that 2-bromoethyl phenyl ether yielded as products, ethylene and phenol. In more recent years, Boord[3] and his co-workers have treated certain alkyl substituted 2-bromoethyl ethers with zinc dust for the preparation of various unsaturated hydrocarbons. Up to the present time, however, this reaction has not been studied using the simple alkyl 2-halogenethyl ethers with a view toward determining more accurately the course of the reaction and, if possible, explaining its mechanism in greater detail.

In the present paper are reported the results obtained by treating ethers of the type $R-O-CH_2-CH_2-Br$ with magnesium in the presence of anhydrous ethyl ether. The compounds investigated were those in which R is methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl and *n*-amyl. The behavior of these compounds toward magnesium is comparable with that of similar substances reported by previous workers, the products in the present cases being ethylene and the alkoxy magnesium bromide. In addition to these main products of the reaction, a quantity of material corresponding to the general formula $R-O-CH_2-CH_2-CH_2-CH_2-O-R$ was found to be present due to the action of part of the bromo ether in the Wurtz reaction.

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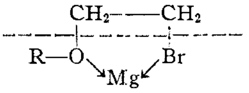
(1) Grignard, *Compt. rend.*, **38**, 1048 (1904).

(2) Wohl and Berthold, *Ber.*, **43**, 2177 (1910).

(3) Boord and collaborators, THIS JOURNAL, (a) **52**, 651, 3396 (1930); (b) **53**, 1505, 2427 (1931); (c) **54**, 751 (1932); (d) **55**, 3293, 4930 (1933).

The reactions all proceeded smoothly. The molecular weight of the R group seemed to have little effect except that those containing more carbon atoms were a bit sluggish at the start, and gave larger quantities of product due to the Wurtz reaction at the expense of the other products, (see Table III, experimental part). The effect of branching the chain of carbon atoms in the R group seemed to be negligible also, the branched chain compounds giving, in general, results comparable with their straight chain isomers.

No completely satisfactory mechanism for the reaction has been offered. It seems possible that the decomposition could be explained by assuming an intermediate compound of the chelate type. Two such structures (I) and (II) may be formulated on consideration of the factors involved in this reaction



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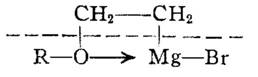

II

There is evidence causing one to believe that (II) is the preferable intermediate. First, it involves a four-membered ring which should be more unstable than the five-membered ring in (I) and therefore more susceptible to decomposition. Second, it is known[4] that ordinary Grignard reagents may be prepared from γ- and δ-halogen ethers. These should however be unstable also if (I) is the correct structure.

An attempt was made to secure definite experimental evidence of even the transitory existence of a Grignard reagent. Qualitative tests[5] for the presence of Grignard reagent were made during the reaction and after the completion, but were consistently negative. It was hoped that the Grignard reagent might be captured as a derivative before decomposition took place.[6] Accordingly, the usual experimental procedure was followed (see experimental part) using ethyl 2-bromoethyl ether in an atmosphere of carbon dioxide. No evidence of the expected β-ethoxypropionic acid was obtained. This result, however, may merely mean that decomposition of (II) in the usual way is a much more rapid reaction than that between the Grignard reagent and carbon dioxide.

Further study of this type of compound is now in progress in this Laboratory.

Experimental Part

The alkyl 2-bromoethyl ethers used in this work were prepared from the corresponding alkyl 2-hydroxyethyl ethers sometimes known commercially as "cellosolves." Of the compounds of this type used, the methyl, ethyl and *n*-butyl 2-hydroxyethyl ethers were obtained from the Carbide and Carbon Chemical Co., and the others prepared by the method of Cretcher and Pittenger[7] from the sodium derivative of the proper alcohol and ethylene oxide. The properties of these compounds are summarized in Table I.

TABLE I

PHYSICAL PROPERTIES OF ALKYL 2-HYDROXYETHYL ETHERS[8]

Alkyl group	B. p., °C.	Press., mm.	d_4^{20}	n_D^{20}	MR$_D$ (calcd.)	MR$_D$ (obs.)
Methyl	122.5–123.0	736	0.9605	1.40150	19.22	19.25
Ethyl	134.0–134.6	736	.9286	1.40737	23.84	23.88
n-Propyl	149.9–150.5	736	.9112	1.41328	28.45	28.47
Isopropyl	141.3–141.7	736	.9030	1.40954	28.45	28.50
n-Butyl	169.9–170.4	746	.9012	1.41904	33.07	33.06
Isobutyl	159.0–159.5	746	.8900	1.41428	33.07	33.14
sec-Butyl	158.4–159.0	746	.8966	1.41606	33.07	33.03
n-Amyl	85.5–86.5	23	.8927	1.42233	37.69	37.60

The 2-bromoethyl ethers were prepared from the various 2-hydroxy compounds by the method of Palomaa and Kenetti.[9] This method consists of treating the alkyl 2-hydroxyethyl ethers with phosphorus tribromide in the presence of pyridine. The alkyl 2-bromoethyl ethers thus formed are colorless liquids when pure and if carefully distilled do not turn yellow on standing in a dark bottle. The lower members, particularly methyl 2-bromoethyl ether, have an odor like that of chloroform, while the higher homologs have a pleasant spicy odor. Physical constants of these compounds appear in Table II.

TABLE II

PHYSICAL PROPERTIES OF ALKYL 2-BROMOETHYL ETHERS[10]

Alkyl group	B. p., °C.	Press., mm.	d_4^{20}	n_D^{20}	MR$_D$ (calcd.)	MR$_D$ (obs.)
Methyl[10a]	111.0–111.4	746	1.4788	1.45165	25.46	25.51
Ethyl[10b]	127.3–127.7	743	1.3573	1.44474	30.08	30.02
n-Propyl[10a]	146.9–147.3	743	1.2795	1.44153	34.69	34.80
Isopropyl	139.9–140.2	743	1.2609	1.43922	34.69	34.61
n-Butyl[9]	67.0–67.5	25	1.2149	1.44254	39.32	39.46
Isobutyl	56.5–57.0	21	1.1945	1.43352	39.32	39.42
sec-Butyl	47.0–47.5	15	1.2216	1.44384	39.32	39.35
n-Amyl	75.0–76.0	14	1.1719	1.44574	43.93	43.98

Reactions of Alkyl 2-Bromoethyl Ethers with Magnesium.—Since the procedure followed was identical in all cases, a detailed description of only one will be given. A 1-liter three-necked round-bottomed Pyrex flask was equipped with an efficient reflux condenser, a stirring device with a mercury seal, and a dropping funnel. Connected with the top of the condenser by a rubber stopper was a bent glass tube which led to three Friedrichs gas wash bottles connected in series. By means of a T-tube inserted between the condenser and the gas wash bottles, a

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(4) (a) Hamonet, *Bull. soc. chim.*, [3] **33**, 527 (1905); (b) Palomaa and Jansson, *Ber.*, **64**, 1606 (1931).

(5) Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

(6) Gilman and Harris, *ibid.*, **49**, 1826 (1927).

(7) Cretcher and Pittenger, *ibid.*, **46**, 1503 (1924).

(8) For comparison see reference 7 for all compounds except secondary butyl 2-hydroxyethyl ether.

(9) Palomaa and Kenetti, *Ber.*, **64**, 797 (1931).

(10) (a) Karvonen, *Acad. Sci. Fennicae*, **3A**, 1–103; *C. A.*, **14**, 2175 (1920); (b) Henry, *J. Chem. Soc.*, 1163 (1885).

rubber tube was connected to the top of the dropping funnel to maintain equality of pressure in the system during the reaction.

In the reaction flask were placed 5 g. (0.2 mole) of magnesium turnings covered with 100 cc. of anhydrous ethyl ether. In the dropping funnel were placed 27 g. (0.2 mole) of ethyl 2-bromoethyl ether diluted with an equal volume of anhydrous ethyl ether. In the first gas wash bottle was 35 g. (0.21 mole) of bromine dissolved in 150–200 cc. of carbon tetrachloride. Half of this quantity or 17 g. of bromine in carbon tetrachloride was placed in each of the two remaining gas wash bottles.

To start the reaction, a few cubic centimeters of the solution of bromo ether in ethyl ether were allowed to drop into the reaction flask from the dropping funnel. A reaction took place immediately or after slight warming[11] similar to that observed in the formation of an ordinary Grignard reagent. Gases at once started passing through the wash bottles. These consisted mostly of air at first, and finally ethylene. After the reaction had been in progress for a short time, all the gas evolved was absorbed in the first wash bottle, which became slightly warm. The rate of evolution of the gases was governed by the rate at which the bromo ether was added to the mixture. When all the bromo ether had been added, the mixture was heated on a steam-cup for an hour.

TABLE III

YIELDS OF PRODUCTS FROM ALKYL 2-BROMOETHYL ETHERS

Alkyl group	Yield, % Ethylene	Yield, % Alcohol	High boiling fraction
Methyl	33.0	..	17.9[12]
Ethyl	50.1	46.3	18.0
n-Propyl	49.7	47.0	22.5
Isopropyl	47.0	36.7	17.2
n-Butyl	40.0	41.2	24.8
Isobutyl	37.7	36.8	28.7
sec-Butyl	35.9	34.0	29.9
n-Amyl	30.2	28.5	30.4

Separation and Identification of Reaction Products.—The flask was allowed to cool after refluxing, and the gas wash bottles were disconnected. The solution of bromine in carbon tetrachloride from the first two wash bottles which then contained some ethylene bromide was washed with a saturated solution of sodium bisulfite, with water, and dried over calcium chloride. The ethylene bromide was separated from the carbon tetrachloride by fractional distillation, and identified by its boiling point and index of refraction. The yields of ethylene bromide represent directly all the ethylene evolved, and vary with the bromo ether used.

The material remaining in the reaction flask consisted of a dark gray lower layer and a clear, colorless upper layer. It was treated with an excess of cold dilute sulfuric acid, and the whole mixture transferred to an apparatus for continuous extraction and extracted with ether for about forty-eight hours.[13] The ether extract was dried over anhydrous magnesium sulfate and fractionally distilled. After the ether had been removed, the residue contained the alcohol corresponding to the alkyl group in the original bromo ether and some of the dialkyl ether of butanediol-1,4 from the Wurtz reaction. From a consideration of the mechanism, it will be seen that the alcohols should be obtained in the same percentage yields as the ethylene. This was found to be approximately true (Table III). It is also believed that the Wurtz reaction in this case is entirely independent of the formation of the suggested chelate rings. Since products from the Wurtz reaction accompany nearly all ordinary Grignard reactions, there seems to be no reason for assuming anything different in this case. The alcohols were carefully purified and identified by means of their 3,5-dinitrobenzoates.

Identification of Butanediol-1,4 Dialkyl Ethers.—The high-boiling material from the ether extract after the alcohol was removed was found to be the dialkyl ether of butanediol-1,4 in an almost pure state. It was distilled under reduced pressure, the density and index of refraction taken, and analyzed for carbon and hydrogen by combustion on the semi-micro scale. These compounds are colorless liquids having rather pleasant although not especially strong odors. Their physical properties and the results of their analyses are shown in Table IV.

TABLE IV

PHYSICAL PROPERTIES OF BUTANEDIOL-1,4 DIALKYL ETHERS

Alkyl group	B. p., °C.	Press., mm.	d_4^{20}	n_D^{20}	MR_D (calcd.)	MR_D (obs.)	Hydrogen, % Calcd.	Hydrogen, % Found	Carbon, % Calcd.	Carbon, % Found
Ethyl[14]	59–60	18	0.8455	1.40610	42.43	42.43	12.41	12.34	65.69	65.13
n-Propyl	94–95	20	.8409	1.41368	51.66	51.68	12.73	12.80	68.90	68.69
Isopropyl	77–78	18	.8310	1.40954	51.66	51.82	12.73	12.81	68.90	68.70
n-Butyl	117–118	16	.8392	1.42064	60.90	60.90	12.96	13.08	71.22	71.06
Isobutyl	107–108	19	.8269	1.41398	60.90	60.93	12.96	13.19	71.22	70.92
sec-Butyl	102–103	16	.8238	1.41370	60.90	60.92	12.96	13.26	71.22	70.96
n-Amyl	134–135	12	.8402	1.42682	70.13	70.25	13.13	13.33	72.97	72.65

Summary

The reactions of eight alkyl 2-bromoethyl ethers on magnesium have been studied and have been found in each case to yield ethylene, the alcohol corresponding to the alkyl group of the

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(11) In the cases of *n*-butyl and *n*-amyl 2-bromoethyl ether, a small crystal of iodine was added to induce the reaction.

(12) The "high boiling material" in the case of the methyl 2-bromoethyl ether was not the dimethyl ether of butanediol-1,4 in analogy with the other substances, but recovered methyl 2-bromoethyl ether.

(13) For the higher molecular weight alcohols which are relatively insoluble in water, a shorter extraction period is sufficient. Methyl alcohol, on the other hand, could not be obtained from the ether extract even on long extraction. Its presence was established qualitatively.

(14) Gauthier, *Ann. chim.*, [8] **16**, 351 (1909).

bromo ether and a small amount of the dialkyl ether of butanediol-1,4.

A mechanism for this reaction has been offered based on the intermediate formation of chelate rings.

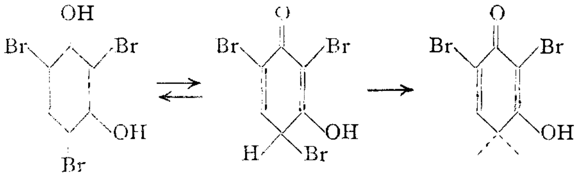
ITHACA, N. Y. RECEIVED JULY 17, 1933

[CONTRIBUTION NO. 97 FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, RESEARCH LABORATORY OF ORGANIC CHEMISTRY]

The Pseudo-Quinoid Character of Tribromoresorcinol[1]

BY TENNEY L. DAVIS AND VALENTINE F. HARRINGTON

Tribromoresorcinol is definitely an oxidizing agent. Although it lacks the common quinoid character of being colored, it liberates iodine from hydriodic acid or from potassium iodide in alcohol solution in a manner which is characteristic of quinones. It oxidizes stannous chloride and sodium sulfite. It does not contain "positive bromine," for a solution of the substance in alkali does not brominate toluene sulfone amide. These facts, and others mentioned later, may be explained by supposing that tribromoresorcinol tautomerizes, as indicated below, to form a pseudo-quinone which breaks down into hydrogen bromide and a quinyl radical.



The first part of this hypothesis contains no novelty, for it is generally agreed that phenols exhibit this kind of tautomerism. The second part of the hypothesis is suggested by the fact that tribromoresorcinol, when warmed in aqueous solution or when heated above its melting point, gives off hydrogen bromide, and is confirmed by the circumstance that dark-colored amorphous polynuclear compounds are formed under these conditions, evidently by the combination of the quinyl radicals. We have not found any evidence which indicates that the breaking down is reversible and do not regard the quinyl as a "free" radical, but we have secured products which correspond both to the combination of the quinyl radicals with one another and to their reaction with a number of reagents.

The combination of two of the quinyl radicals would yield dibromoresoquinone or 3,3′,5,5′-tetrabromo-2,2′-dihydroxy-*p*-xenoquinone. An earlier paper[2] of this series has reported that the oxidation of tribromoresorcinol in benzene solution with aqueous chromic acid yields the products which would be expected from the action of bromine on dibromoresoquinone, a result which appears to be explained better by the present hypothesis than by that of the earlier paper.

Pyridine or alkali, in aqueous solution and in moderate amount, by removing hydrogen bromide from tribromoresorcinol, produces dark-colored amorphous polynuclear compounds; but dry pyridine in benzene, or aqueous alkali in large excess, by forming salts of the substance in its phenol form, reverse the equilibrium and suppress quinonization and the formation of the quinyl radical. The dark-colored substances correspond to the removal of two bromine atoms from each molecule of tribromoresorcinol. Whether the second bromine is removed by the hydrolysis of a bromine *ortho* to a quinone oxygen, or is lost by the spontaneous splitting out of hydrobromic acid following a second tautomeric change, we have not yet been able to determine.

Mild reduction of tribromoresorcinol with sodium sulfite or stannous chloride successively removes the bromine atoms *para* to the hydroxyl groups, and ceases with the production of 2-bromoresorcinol—a result which can be explained, without recourse to the quinyl radical, by supposing that the effect of the reducing agent is to add hydrogen to the conjugate system of the pseudo-quinone to form a compound which spontaneously loses hydrogen bromide, that this new compound in its turn quinonizes, etc. The intermediate reduction product, 2,6-dibromoresorcinol, has been isolated. Since tribromoresorcinol tends to lose hydrogen bromide any-

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(1) A summary of a portion of the Doctor's Dissertation of Valentine F. Harrington, Massachusetts Institute of Technology, June, 1931.

(2) Davis and Hill, THIS JOURNAL, **51**, 493 (1929); compare also Davis and Walker, *ibid.*, **52**, 358 (1930).