mercaptan and that the reaction was complete in about twenty-four hours.

Ethyl Disulfide.—Since no method of analysis is known for disulfides, it was necessary to weigh a sample of ethyl disulfide for each experiment. This was done by introducing the disulfide from a dropping pipet with a long capillary into a weighed, thin-walled glass weighing ampoule. The ampoule was iced, sealed, dried and reweighed, after which it was dropped into a 250-cc. glass-stoppered flask containing a known excess amount of bromine in carbon tetrachloride and 100 cc. of water. The subsequent treatment was the same as with the mercaptan.

In these experiments it was found that the bromine used was almost always about 1% high. Blank experiments showed that this error was due to loss of bromine during the manipulations, probably chiefly during the introduction of the ampoule containing the ethyl disulfide. Table I gives two typical experiments.

Table I

Expt.	R_2S_2, g.	Eq. Br_2 per mole R_2S_2	Correction	Eq. Br_2 per mole R_2S_2 corr.
1	0.0776	10.11	0.15	9.96
2	.1324	10.14	.14	10.00

In view of the above data it seems safe to conclude that these measurements are good to about 1.5% in spite of the relatively high volatility of every substance involved, and that the main reactions are probably those suggested in equations 1 and 2.

Oxidation of Ethyl Mercaptan by Dry Bromine.—The amount of bromine used by ethyl mercaptan in the absence of water was measured by mixing dilute carbon tetrachloride solutions of a known amount of ethyl mercaptan with a known excessive amount of bromine. After various times, the solutions were shaken with aqueous solutions of potassium iodide and the resulting iodine titrated with sodium thiosulfate solution.

The amount of hydrogen ion produced in the reaction was measured in a similar fashion by using excess ethyl mercaptan. The carbon tetrachloride solutions were extracted and washed with water and the extract titrated with standard sodium hydroxide solution.

The results of a series of experiments in which the mercaptan concentration varied from 0.003 to 0.03 *M* showed that 1.00 ± 0.01 equivalents of bromine were used per mole of mercaptan; those of a second series in which the bromine concentration varied from 0.003 to 0.025 *M* indicated that 1.00 ± 0.03 moles of hydrogen ion were liberated per equivalent of bromine used.

These experiments also showed that the reaction was complete within forty-five seconds after mixing, and that no further reaction took place.

Identification of Ethyl Sulfonic Acid.—The oxidation reactions were allowed to go to completion in reaction mixtures containing 12 g. of the sulfur compound and 100 g. of bromine. The water layer was separated, concentrated by evaporation, neutralized with sodium hydroxide and evaporated to dryness. After drying at 120° for three hours, the sodium ethyl sulfonate was extracted by use of hot 95% ethyl alcohol. The sodium salt was then converted to the corresponding acid chloride by the method of Marvel, Helfrick and Belsley.[4] The acid chlorides obtained boiled at 177° which compares with a boiling point of 177.5° given by Carius.[5]

Summary

1. Ethyl mercaptan and ethyl disulfide are oxidized to ethylsulfonic acid by bromine water, the oxidation requiring 3 and 5 moles of bromine per mole of the sulfur compound, respectively.

2. Ethyl mercaptan is very rapidly oxidized to ethyl disulfide by dry bromine.

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[4] Marvel, Helfrick, and Belsley, This Journal, 51, 1272 (1929).

[5] Carius, *J. prakt. Chem.*, [2] 2, 264 (1870).

Davis, Calif. Received December 11, 1936

[Contribution from the Division of Chemistry, College of Agriculture, University of California]

The Rate of Oxidation of Ethyl Disulfide by Bromine

By H. A. Young and M. B. Young

In the preceding paper,[1] it has been shown that bromine oxidizes ethyl disulfide to ethylsulfonic acid in the presence of water, and that under proper conditions five moles of bromine are used for each mole of disulfide oxidized. While performing the experiments described in the above paper, it was noted that immediately upon the addition of ethyl disulfide to a carbon tetrachloride solution of bromine, the color of the latter changed perceptibly, becoming lighter and a more pronounced yellow. Also when excess disulfide was added to bromine, distributed between water and carbon tetrachloride, the bromine was almost completely removed from the water layer.[2] These observations suggest the rapid formation of an addition compound between bromine and ethyl disulfide. That the formation of the addition compound is reversible is shown by the fact that a known amount of bromine which has been treated for several hours

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[1] H. A. Young, This Journal, 59, 811 (1937).

[2] A similar effect is noticed with iodine. Excess ethyl disulfide in carbon tetrachloride will remove enough iodine from a water layer to prevent the formation of a blue color in the presence of starch, as first noted by Sampey and Reid, *ibid.*, 54, 3405 (1932).

with ethyl disulfide in carbon tetrachloride solution (water absent) shows no loss in oxidizing power. The purpose of the present work is to investigate the addition compound by measuring the rate of disappearance of bromine during the oxidation of ethyl disulfide in the two-phase system consisting of bromine and disulfide dissolved in carbon tetrachloride as one phase and bromine in water as the second. Since the final products of the reaction are found in the water layer, the reaction steps involving water presumably take place either across the boundary of the carbon tetrachloride or in the carbon tetrachloride itself with subsequent diffusion. The authors undertook the investigation realizing the difficulties involved in the interpretation of rate measurements in such a heterogeneous system, as pointed out by Bell,[3] yet they believe the simplicity of the obtained initial rates is significant.

Experimental Part

The desired amount of ethyl disulfide for each experiment was weighed in a weighing ampoule, and the ampoule was broken in 100 cc. of carbon tetrachloride which was at the reaction temperature and which was contained in a 300-cc. glass-stoppered flask. A bromine solution for each experiment was prepared and analyzed iodimetrically after being brought to the reaction temperature.

An experiment was carried out as follows: 100 cc. of water at 25° and 50 cc. of bromine solution were introduced, respectively, into a 300-cc. glass-stoppered conical flask. Fifteen cc. of the disulfide solution was pipetted into the flask and the mixture was then placed in a shaker in a thermostat at 25.0 ± 0.1°. Zero time was taken when half the disulfide had run into the flask. In each experiment five such mixtures were prepared. At various intervals, the flasks were removed from the thermostat, 2 g. of solid potassium iodide was added and the liberated iodine titrated with sodium thiosulfate solution.

Experimental Results

The bromine concentrations for the carbon tetrachloride layer were calculated on the assumption that all of the bromine was in the carbon tetrachloride. This point will be referred to later. These bromine concentrations were plotted as abscissas against time in minutes as ordinates, and values of $-d(Br_2)/dt$ obtained by taking slopes of the tangents. After preliminary work indicated that the values of $-dBr_2/dt$ taken at zero time were reproducible to within 5% a series of fourteen experiments was made. There were occasional inexplicable erratic points which obviously lay off the bromine–time curves. In only one experiment was there more than one such point, and in that case the experiment was discarded. Table I contains the complete data for three representative experiments; Fig. 1 is the bromine–time plot for the same experiments.

Table I

Representative Experimental Data

	Expt. 1 R_2S_2 = 0.0133		Expt. 2 R_2S_2 = 0.00542		Expt. 5 R_2S_2 = 0.0252	
	Concentrations					
Time, min.	Br_2	Corr. Br_2	Br_2	Corr. Br_2	Time, min.	Br_2 concn.
0	0.0785	0.0739	0.0775	0.0730	0	0.0158
60	.0642	.0598	.0713	.0670	20	.0123
120	.0533	.0492	.0670	.0627	52	.00870
180	.0467	.0427	.0632	.0588	80	.00788
240	.0411	.0374	.0611	.0568	110	.00586
300	.0371	.0336	.0597	.0555	155	.00453

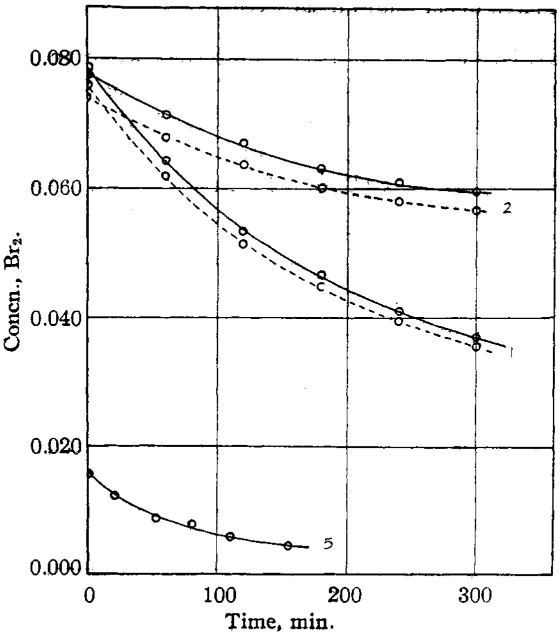

Fig. 1.—Plot of bromine concentration against time in minutes for Expts. 1, 2 and 5.

Table II contains a summary of the thirteen experiments. The initial concentrations of the reactants are given in columns two and three and the initial values of $-dBr_2/dt$ in column 4.

Discussion of Results

From the initial slopes in Expts. 1, 2 and 3, it is seen that when the concentration of bromine is high and that of disulfide low, the initial rate is independent of bromine concentration and may be expressed by the equation $-dBr_2/dt = k_1 (R_2S_2)$. The values given in column 5 of Table II indicate that k_1 has an average value of 0.020. Examination of the initial rates obtained in

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(3) Bell, *J. Phys. Chem.*, **32**, 882 (1928).

TABLE II

SUMMARY OF EXPERIMENTS

Expt.	R_2S_2, initial	Br_2, initial	$-\frac{d(Br_2)}{dt}$ initial	$-\frac{d(Br_2)}{dt}\Big/R_2S_2$	$-\frac{d(Br_2)}{dt}\Big/R_2S_2$ corr.	$-\frac{d(Br_2)}{dt}\Big/Br_2$	$R_2S_2(Br_2)_2$
1	0.0133	0.0785	0.000259	0.019	0.019		0.0133
2	.00542	.0775	.000115	.021	.020		.00542
3	.00493	.0328	.000101	.020	.020		.00493
4	.0302	.0188	.000213			0.011	.00940
5	.0252	.0158	.000180			.011	.00790
6	.0548	.0187	.000201			.011	.00935
7	.0526	.0416	.000415			.010	.0208
8	.0275	.0437	.000500			.011	.0218
9	.0279	.0507	.000523			.010	.0253
10	.0245	.0402	.000490			.012	.0201
11	.0254	.0401	.000514			.013	.0200
12[a]	.0272	.0182	.000464			.025	
13[b]	.0154	.0854	.000279	.018			

[a] Expt. 12, original $H^+ = 0.10\ M$. [b] Expt. 13, shaker reduced to one-fourth usual speed.

Expts. 4, 5, 6 and 7 indicates that when the disulfide concentration is high and the bromine low, the initial rate is independent of the disulfide concentration, and may be expressed by $-dBr_2/dt = k_2(Br_2)$. From column 7, Table II, k_2 has an average value of 0.011.

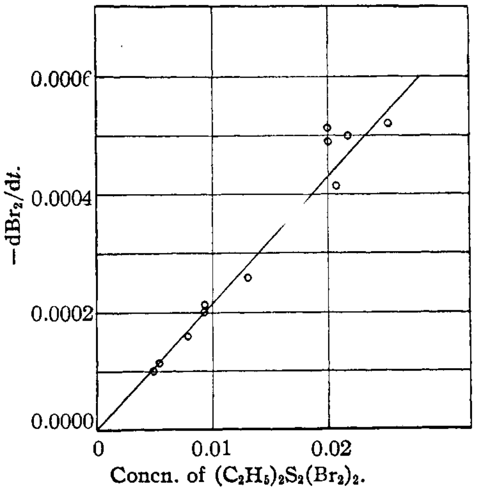

Fig. 2.—Initial rates of disappearance of bromine plotted against calculated concentration of intermediate.

The simplest explanation for the results of Expts. 1 to 7 is that the initial rate of using bromine is proportional to the concentration of a compound which is in equilibrium with one molecule of disulfide and two molecules of bromine, as represented by the equation

$$R_2S_2 + 2Br_2 \rightleftarrows R_2S_2(Br_2)_2$$

From the results of Expts. 8, 9, 10, 11 as shown in column 7 of Table II, it appears that within the limits of experimental error the formation of the addition compound is complete.

The original assumption that all the bromine is found in the carbon tetrachloride may now be seen to produce no appreciable error in the experiments in which the disulfide is in excess, for in this case all but the minute equilibrium quantity of the bromine is in the form of addition compound which is insoluble in water. With bromine in excess, however, an appreciable amount of it is in the water layer. Using 27 as the distribution ratio of bromine between carbon tetrachloride and water and assuming the concentration of the intermediate to be that of the disulfide, corrected values of bromine concentrations in the carbon tetrachloride layer were obtained and plotted against time as before for Expts. 1, 2 and 3. The corrected data for Expts. 1 and 2 are given in Table I, and the corrected plots are shown by broken curves in Fig. 1. In only Expt. 2, where the value of k_1 dropped from 0.021 to 0.020, was the corrected initial value of k_1 significantly different from the uncorrected value.

Concentrations of the addition compound, taken as one-half the bromine concentration when the disulfide is in excess and as the disulfide concentration when the bromine is in excess are listed in column 8 of Table II. These concentrations are plotted against the corresponding initial values of $-d(Br_2)/dt$ in Fig. 2. The points lie very close to a straight line of slope 0.021, so that within the limits of experimental error the initial rates are given by the expression $-d(Br_2)/dt = 0.021[R_2S_2(Br_2)_2]$. The two points which lie farthest from the line represent Expts. 10 and 11, in which the uncertainties in the slopes are probably greater than in any other of the experiments.

The rate measurements do not distinguish between intermediates of the types $R_2S_2(Br_2)_2$ and $RSBr_2$, although the existing independent evidence appears to favor the breaking of the sulfur–sulfur linkage by bromine. Zincke and Farr[4] have prepared mono-*o*-nitrophenyl sulfur bromide from the corresponding disulfide by treatment with bromine. Hunter and Sorenson[5] in their discussion of the mechanism of the reduction of sulfonyl bromides by phosphorus tribromide assumed an equilibrium of

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[4] Zincke and Farr, *Ann.*, **391**, 67 (1912).

[5] Hunter and Sorenson, THIS JOURNAL, **54**, 3668 (1932).

the form RSSR + $Br_2 \rightleftarrows$ 2RSBr. They were able to demonstrate that *o*-nitrophenyl sulfur bromide gave small amounts of *o*-nitrophenyl disulfide upon standing, but were unable to prepare the sulfur bromide from the disulfide and bromine. Zincke and Frohneburg[6] have studied the oxidation of dithiohydroquinone and thiocresol by chlorine and bromine in the presence of water and have postulated the first step to be the formation of a disulfide, followed by an intermediate of the type $RSBr_3$.

It seems probable, therefore, that the oxidation of ethyl disulfide by bromine in the presence of water takes place in steps, the first of which is a rapid reversible one of the type $2Br_2$ + RSSR $\rightleftarrows$ $2RSBr_2$. The second and rate determining step is probably the hydrolysis of the product of the first reaction, *i. e.*, $RSBr_2 + H_2O = RSO + 2HBr$. In view of the recent work of Johnson and Sprague[7] who isolated ethyl sulfonyl bromide from aqueous solutions when S-ethylisothiourea hydrogen bromide was oxidized by bromine at temperatures below 5°, and the work of Zincke and Frohneburg,[6] who showed that the ultimate oxidation product of both dithiohydroquinone and thiocresol by bromine in the presence of water was a sulfonyl bromide, it seems probable that another of the intermediate products in the system under consideration is ethyl sulfonyl bromide.

Effect of Hydrogen Ion and Rate of Shaking

The presence of hydrogen ion materially increases the initial rate as is indicated by Expt. 12. In this experiment the initial hydrogen ion concentration was 0.10 *N* and the value of k_2 obtained was 0.025 as contrasted with 0.011, the average value in the other experiments. The accelerating effect of hydrogen ion was not unexpected in view of the results of some measurements on the rate of oxidation of ethyl mercaptan by excess bromine in the presence of water. As shown in the preceding paper, the first step in the oxidation of the mercaptan is the rapid formation of ethyl disulfide with the liberation of hydrobromic acid, so that except for the presence of hydrogen ion the mercaptan experiments would be identical with those involving disulfide. The initial rates in the mercaptan experiments were found to be determined by the mercaptan concentrations, but were anomalously high. The effect of hydrogen ion upon the initial rate is being investigated further.

The effect of the rate of shaking upon the reaction rate is shown by Expt. 13 in which the speed of the shaker was reduced to one-fourth its usual value. The initial rate yielded a value of k_1 equal to 0.018, which is not far from the average value of 0.020. However, in the latter stages of this experiment the reaction rate was much slower than usual. This suggests that toward the end of the reaction the rate determining step is one of diffusion. If such is the case, the rate of using bromine in all of the experiments except number 13 might finally approach the same first order rate law. To test this hypothesis, values of $-dBr_2/dt$ at various times were plotted against calculated concentrations of the intermediate $[R_2S_2(Br_2)_2]$ (Fig. 3). The curves in that plot appear to approach a straight line of slope 0.014.

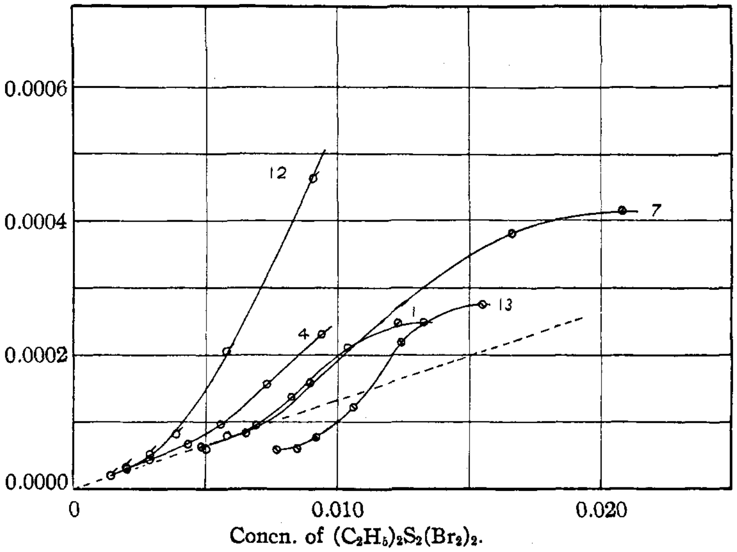

Fig. 3.—Rates of disappearance of bromine plotted against calculated concentration of intermediate.

Summary

1. The rate of the reaction between carbon tetrachloride solutions of bromine and ethyl disulfide in the presence of water has been measured at 25°.

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[6] Zincke and Frohneburg, *Ber.*, **42**, 2721 (1909); **43**, 1348 (1916).

[7] Johnson and Sprague, THIS JOURNAL, **58**, 1348 (1936).

2. The initial rates have been shown to be represented by the equation $-dBr_2/dt = k \times [R_2S_2(Br_2)_2]$ where k is a function of the rate of shaking.

3. The first steps in the oxidation of ethyl disulfide by bromine in the presence of water are suggested as

$$R_2S_2 + 2Br_2 \rightleftarrows 2RSBr_2, \text{ and} \tag{1}$$

$$RSBr_2 + H_2O = RSO + 2H^+ + 2Br^- \tag{2}$$

DAVIS, CALIF. RECEIVED DECEMBER 11, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WHEATON COLLEGE]

Raman Spectra. II. Monomethoxy Derivatives of Ethyl Benzoate

BY DOROTHY D THOMPSON

The Raman spectra of several derivatives of benzoyl chloride were determined[1] in an attempt to find a relationship between this property and the rates of esterification of the acid chlorides, and these spectra were compared with those of the corresponding ethyl esters.[2] Since, however, the spectra of the methoxy derivatives of ethyl benzoate had not been determined, it was thought advisable to prepare them and study their Raman spectra.

Experimental

Apparatus.—The same Hilger E-439 glass spectrograph,[3] system of filters, light source, Raman tube and photograph plates were employed as were described in a previous paper.[1] The frequencies of the lines were determined as before except that the deviation curves were made from the difference from linear dispersion in terms of wave numbers instead of wave lengths. The accuracy is about the same as before (±1 for the strong, sharp lines, but a greater error up to ±4 cm.$^{-1}$ for very weak diffuse lines).

Purification of Compounds.—The esters were prepared from the corresponding acid chloride and absolute alcohol or by the action of absolute alcohol saturated with hydrogen chloride on the corresponding acid (*o*-methoxybenzoic acid prepared by methylation of salicylic acid with dimethyl sulfate; *p*-methoxybenzoic acid was Eastman White Label). The esters were washed rapidly with ice-cold sodium carbonate and several times with cold water, then dried over calcium chloride. They were distilled *in vacuo* from an ordinary Claisen flask several times or until the index of refraction of the major portion remained constant. One distillation through a modified Vigreux[4] column showed that the boiling point range was in every case not greater than 0.2°. The densities were determined in the usual way with a pycnometer having a capacity of 5 ml. The average deviations of three to five independent determinations never exceeded one part in twenty thousand. The calculations were made in the usual way correcting for the buoyancy of air and for the expansion of glass. The indices of refraction were measured with an Abbé refractometer and the molecular refractions calculated from the equation of Lorenz and Lorentz.

Data

Explanation of Tables.—The values of the Raman spectra have been summarized in the usual way. The value for the Raman shift is followed by a number in parentheses indicating the relative intensity (estimated)—the large numbers indicating greater intensity, the letter "b" for broad and "d" for diffuse. This is followed by letters indicating the mercury exciting lines as follows: a = 24,705 cm.$^{-1}$, b = 24,516 cm.$^{-1}$, c = 23,039 cm.$^{-1}$, d = 22,995 cm.$^{-1}$ and e = 22,938 cm.$^{-1}$. Each compound was photographed four times—twice with "Greenish Nultra" filter only, with long and short exposure times, once with "Greenish Nultra" + quinine sulfate, and once with "Red-Purple Ultra" glass + sodium nitrite. Each Raman line occurred on at least two plates unless indicated with a *.

Ethyl *o*-Methoxybenzoate.—Boiling point 104.4–104.5° at 2 mm.; n^{20}_D 1.5224; d^{20}_4 1.1124; d^{25}_4 1.1077; R_M calcd. 48.40, obsd. 49.42.

$\Delta\nu$ = 80(0)(a, +b, c, e); 115(00)(a, e); 230(00)(a, e); 276(0)(a, e); 305(00)(a, e); 333(4)(a, b, c, e); 395(00)(a, e); 434(0)(a, d, e); 459(00)(a, e); 523(0)(a, e); 563±5-(1b)(a, e); 582(2)(a, b, d, e); 657(2)(a, b, ±e); 780±10-(4band)(a, d, e); 854(2)(a, e); 877(1)(a, e); 1020(0b)(a, e); 1049(6)(a, b, c, e); 1166(4)(a, b, d, e); 1251(8b)(a, b, d, e); 1302(2d)(a, b, e); 1354(00)(a, e); 1448(0)(a, c, e); 1491(0)(a, e); 1600(6)(a, c, d, e); 1721(2d)(b, d, e); 2929(1)(a); 3077(2)(a).

Ethyl *m*-Methoxybenzoate.—Boiling point 97.6–97.8° at 1 mm.; n^{20}_D 1.5161; d^{20}_4 1.0993; d^{25}_4 1.0949; R_M, calcd. 48.40, obsd. 49.50.

$\Delta\nu$ = 94(00)(a, +b); 107(00)(a); 128(00)(a, e); 192(0)(e); 223(00)(a, e); 252(00)(a, e); 263(0)(e); 301(0)(a, e); 330(2)(a, e); 390(00)(a, e); 416(00)(a, e); 452(2)(a, b, e); 482(0)(e); 550(00)(a, e); 572(2d)(a, e); 588(0)(a); 667(3)(a, e); 765(2)(a, e); 804(2b)(a, e); 863(2d)(a, e); 996(10)(a, b, c, d, e); 1038(00)(a, e); 1102-(0b)(a, e); 1172(1)(a, b, e); 1235(00)(a, e); 1281(10b)(a,

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[1] Thompson and Norris, THIS JOURNAL, 58, 1953 (1936).

[2] Kohlrausch and Pongratz, *Monatsh.*, 63, 427 (1933–1934); Kohlrausch and Stockmair, *ibid.*, 66, 323 (1935).

[3] The author wishes to express appreciation to the Research Laboratory of Organic Chemistry of the Massachusetts Institute of Technology for the use of this apparatus and to the Physics Department for the use of their Hilger comparator.

[4] Thanks are due to Mount Holyoke College Chemical Laboratory for this column.

* Occurred on one plate only.