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Franklin A. Long

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BROMAL AND CRICKARD'S REAGENT

by

Franklin A. Long

Presented in partial fulfillment of the  
requirement for the degree of  
Master of Arts.

State University of Montana

1932

Approved:

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BRONX AND DISTRICTS 12-10-1912

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Part I

THE PREPARATION OF BROMAL

## Part I

### The Preparation of Bromal

#### Historical

Tribromoacetaldehyde or bromal was first prepared by Löwig (1833) from ethyl alcohol and bromine vapor. It was natural that this method should be the first used since Liebig had successfully made chloral by chlorinating ethanol in 1832. Indeed this simultaneous halogenation and oxidation of alcohol is employed today on a large scale in the commercial manufacture of the much used chloral hydrate.

However the bromination of acetaldehyde itself would furnish a more direct approach to the problem and this was the method selected by Pinner (1875), who, following one used by Hagemann (1870), made bromal from paraldehyde and liquid bromine. Hagemann himself seems not to have actually obtained bromal but was more concerned with a general study of the bromination of acetaldehyde and the preparation of its dibrom derivative.

In all the chemical literature these two methods of preparation are the only ones listed and both were written up before 1875. As is frequently the case with early workers in organic chemistry yields were not mentioned, presumably because they were poor. Neither Löwig, Pinner, nor Schäffer, who improved

Löwig's method, state anything definite about the yield of bromal. Considering the interesting possibilities of bromal both from a chemical and a therapeutic standpoint as well as the close relation it bears to chloral, it is rather astonishing to note that in a period of almost 40 years, from 1833 to 1871, scarcely any mention of it is to be found in the literature.

Schäffer (1871) worked on Löwig's original preparation and innovated improvements of his own. According to him, one adds gaseous bromine in relatively small amounts to absolute alcohol. The resulting product is distilled. The fraction going over from  $165^{\circ}$  -  $180^{\circ}$  contains the bromal and this is separated by repeated crystallizations in the form of the hydrate from which the bromal may be recovered by heating. The addition of only small amounts of bromine vapor to the ethyl alcohol hindered the formation of ethyl bromide as much as possible, according to Schäffer. Schäffer confirms most of Löwig's data on bromal and bromalhydrate, only correcting the melting point of the latter. Schäffer also investigated the by-products formed in this reaction and found among others carbon tetrabromide and dibromacetic acid.

The method of brominating paraldehyde directly as first used by Hagemann in preparing dibromaldehyde was later employed by Pinner in preparing bromal. Hagemann and Pinner agree that the reaction is too violent when only bromine and the aldehyde are used, and decided that a diluent must be introduced.



Pinner found carbon disulfide and carbon tetrachloride unsatisfactory and finally used ethyl acetate. In the preparation of bromal Pinner used paraldehyde to which had been added more than double its weight of ethyl acetate. Into this bromine was dropped. The flask was provided with an outlet for the hydrogen bromide evolved and was cooled during the reaction. Pinner found the reaction went fairly easily until about two mols of bromine had been added to one mol of the aldehyde at which point it seemed to stop. However, he did secure some bromal, although he does not say how much. In all of his experiments Pinner found that large quantities of tarry by-products were formed by the reaction.

Others have worked on the bromination of paraldehyde and have greatly improved the method of making the dibromaldehyde, which Pinner found fairly easy to prepare. B. Nylo (1912) improved Pinner's method by using chloroform instead of ethyl acetate for a diluent, since the chloroform is not so easily or so fully brominated as the acetic ester. Nylo gives specific directions and finds that 33 g. of dibromacetaldehyde, from 22 g. paraldehyde and 160 g. bromine, is the maximum yield. He says nothing about bromal although he states he is making observations on the halogenation of the aldehydes.

Dworzak, (1926) following a method used by Freundler and Ledru (1905) in preparing monobromacetal, prepared the dibromaldehyde and then converted it into the dibromacetal by adding

absolute alcohol to the reaction mixture. This reduced the difficulties of the separation of the dibromaldehyde and enabled him to secure a 40 per cent yield. He found it very difficult to prepare the tribromacetal only succeeding in obtaining enough to identify. Hence he concluded that, although conversion into the acetal offers a good method of obtaining and separating the dibromacetaldehyde, it is not feasible with the tribromaldehyde.

As stated, these, the only two methods for preparing bromal, were written up before 1875, and since then almost nothing has been done to improve the methods for making this interesting and important compound. Chloral, its chlorine analog, is manufactured in great quantities but evidently iodal has never been prepared. At least no mention of it is to be found in the chemical literature. Evidently the difficulty of preparing bromal is intermediate between these two extremes.

## Discussion

The author desired to prepare bromal in fairly large quantities for use with Grignard's reagent and, searching for methods of preparation, found only those listed above. From the fact that nothing was said about yields except to state that complete bromination of either aldehyde or alcohol proceeds with difficulty, and from the fact that astonishingly little work has been done with bromal--a compound that should offer great possibilities to the research chemist--it follows that the preparation of bromal in quantity by any of the methods in the chemical literature is very difficult.

It is obvious that Schäffer's method, involving the introduction of bromine vapor into ethyl alcohol with distillation and repeated crystallizations of the bromalhydrate, represents a great deal of work. With, in addition, only a small yield, it is an unsatisfactory method. Yet it is the one listed in the Beilstein's Handbook and seems to have been the one used by most of the few who have worked with bromal. However, it was decided to use Pinner's method of brominating paraldehyde since the technical difficulties encountered in adding liquid bromine to paraldehyde are much less than in adding bromine vapor to absolute alcohol.

In the absence of specific directions in Pinner's article Mylo's directions were followed except, of course, using three

mols of bromine to one of paraldehyde. Also, carbon tetrachloride was used as a diluent instead of chloroform or ethyl acetate, since there is no chance of brominating it. The reaction proceeded just as Pinner had stated, with the exception that carbon tetrachloride was completely satisfactory as a diluent. After nearly two mols of bromine had been added to one of paraldehyde, almost no evidences of further reaction were seen and more bromine only colored up the reaction mixture. The tarry by-products found by Pinner were always found in these experiments.

For apparatus, a three-necked 500 cc. distilling flask was used. In the center hole a mercury-seal stirrer was inserted, in one of the other holes a dropping funnel for the bromine and into the other a glass tube leading over solutions of sodium hydroxide in two connected flasks to catch the hydrogen bromide evolved. For distillation, the product was transferred to an ordinary distilling flask. A filtering flask served as the receiver with the side tube connected to a flask of sodium hydroxide solution to prevent the escape of hydrogen bromide and bromine.

Pinner says nothing about the length of time required for the reaction, but only by leaving the reacting substances together for about a week with several hours stirring a day, could a decent yield be obtained. The best run (Protocol 1) using three mols of bromine to one of paraldehyde with 50 g. of carbon tetrachloride as a diluent, gave, by distillation, a 61 per cent yield of impure bromal which made, when purified, a 49 per cent

yield. If the time for the reaction were shortened, it only reduced the yield. (Protocols 3 and 4)

It was evident that no great quantity of bromal would be prepared by such a lengthy procedure so it was decided to search for catalyzers. As possibilities, it was decided to investigate the action of iron, antimony, iodine and phosphorus trichloride, all of which have been used as halogenation catalysts. As far as possible, the same experimental conditions were maintained with the runs extending over the same length of time and with approximately the same amount of stirring. Rather good indications as to the effect the possible catalyst was having on the speed of the reaction were found in two ways: first, by the change in color of the paraldehyde as the bromine was added; and second, by the temperature of the flask of sodium hydroxide solution which became heated in proportion to the amount of hydrogen bromide evolved.

One-half gram of each of the solid catalysts and 1 cc. of the phosphorus trichloride was added at the start of each respective experiment, and the reaction carefully followed. (Protocols 5-8) It was soon found that none of the original catalyzing agents would increase the yield, or accelerate the reaction. Antimony had seemingly no effect on the reaction except a possible slight negative one. Iodine also seemed to show a slight negative effect and in addition colored the final product. Iron acted as a strong negative catalyst, almost no bromal being produced when it was used. Phosphorus trichloride

seemed to show a slight catalytic action but not sufficient to help greatly. Observation also showed that none of these substances speeded up the reaction appreciably.

Since none of these catalysts were of use, it was next decided to try the influence of mass action. It seemed logical that complete bromination of the aldehyde would be more easily accomplished if the paraldehyde were dropped into excess bromine instead of dropping bromine into the paraldehyde. Accordingly, the bromine was placed into the flask and the paraldehyde dropped into it. When this was done and the run extended over the same length of time, the yield was increased somewhat, but when the time was cut down the yield also decreased just as before.

(Protocols 9 and 10) Next, in order to see what effect heat would have on the reaction, a reflux condenser was placed on the set-up. This was inserted in the neck of the flask that had been used for the hydrogen bromide tube and the latter was then attached to the upper end of the condenser. Then the reaction was allowed to proceed by its own heat while the paraldehyde was being slowly added, the temperature being regulated by the speed of dropping in the paraldehyde. After the aldehyde was all in the temperature of the flask was kept at  $60^{\circ}$ - $80^{\circ}$  by means of a burner flame. It was found this method materially cut the time necessary for the reaction and maintained or increased the yield of bromal. (Protocols 12 and 16) Also, in this method, a diluent is not necessary, the only precaution

being that the paraldehyde not be added too fast.

It was found that a period of four hours represented the minimum time necessary to obtain a good yield. The paraldehyde was all added during the first two hours and the reaction was allowed to proceed under its own heat. For the next two hours the mixture was heated to  $60^{\circ}$  -  $80^{\circ}$  and then the product was distilled and redistilled. In this way a 45 percent yield of pure bromal was obtained. (Protocols 18, 20, 23, 26 and 29)

Although by this method it was possible to secure in four hours a percentage yield as high as had been obtained in a week by any other way, additional work was done to increase this yield. Since the bromine represents by far the most expensive of the reacting substances, yields have been figured exclusively on it and proportions have also been varied with a view to the greatest yield per mol of bromine. The best proportions seem to be nearly equivalent amounts but with a slight excess of paraldehyde.

Since iron, iodine, and antimony had already given poor results as catalyzers, they were not further investigated. Phosphorus trichloride, which had acted positively in the earlier method was used again, but with no greater success than before. (Protocols 13 and 14) Aluminum acted as a negative catalyst. (Protocol 17) Sulfur, however, showed enough action warrant its use in the preparation of bromal. By the addition of  $1/2$  g. of sulfur to the bromine in the flask at the start

of the reaction, the yield can be increased from 5 - 10 per cent, although the time of the reaction is not shortened. (Protocols 18, 19, 20, 21, 25, 26, 29 and 30) But a sure yield of 55 per cent of pure bromal in a period of four hours represents a decided improvement over the original attempts.

The physical constants of bromal have been well established by Löwig, and confirmed by Schäffer, Linner, and others. Since the pure product agreed in boiling point, color, and odor with their specifications, only a determination of the per cent weight of the bromine by the Carius method was used to establish the purity of the bromal. Theoretically bromal should contain 85.40 per cent bromine by weight. Carius determinations on various samples of pure bromal prepared by the above methods range from 85.10 per cent to 85.39 per cent with 85.23 per cent as the average. Considering the errors inherent in the Carius method and the fact that bromal decomposes slightly on standing, this agreement is good.

In distilling the reaction mixtures the fraction from 155° to 175° has been taken as containing the major part of the bromal. Most of the bromal comes off from 164° - 166° at a barometric pressure of 67.5 cm. of mercury. The fraction from 50° to 155° weighs from 20 - 70 g. and, although varying with different runs, consists principally of excess bromine and mono and diacetaldehyde. There is sometimes a slight fraction



above  $175^{\circ}$  but usually it is so small that it has been disregarded. By saving the lower fractions, adding some more bromine to them and heating and stirring as with a regular run, substantial quantities of bromal have been secured. (Protocols 11 and 19) So in actuality the final yield of bromal is higher than the figures that have been given.

There is always a residue of tarry decomposition products left in the distilling flask, usually not over 10 grams, but these were not investigated.

In these experiments, an ordinary condenser with a 16-inch jacket was used as the reflux condenser. Since the dark-red color of the sodium hydroxide solution used to catch the hydrogen bromide shows that a fair amount of bromine is carried over, it is probable that a longer condenser, or a coiled reflux condenser would retain more of this bromine and thus increase the yield. It was also noticed that there was an increase in yield when the outlet tube was partially plugged. (Protocols 22 and 23), indicating that increase in pressure might help the yield. But because of the mercury seal stirrer that was being used it was not feasible to investigate this.

The following directions represent the final results of all the experiments:

A 500 cc. three-necked distilling flask is fitted with a mercury seal stirrer, a dropping funnel and a reflux condenser.

From the condenser a glass tube leads to two connected flasks containing sodium hydroxide solution to retain the hydrogen bromide. 1 1/2 mols of bromine and 1/2 g. of sulfur are placed in the flask and 23 g. of paraldehyde in the dropping funnel. The mixture is stirred constantly. The reaction is allowed to proceed with its own heat over a period of two hours while the paraldehyde is added. After this the mixture is heated for two hours more to a temperature of 60° - 80°. Then the product is distilled and the fraction from 155° - 175° (Bar. 68 cm.) containing the bromal, is redistilled. The pure bromal will be colored less if this redistillation is done under reduced pressure, but this is not necessary. The fraction from 50° - 155° is saved and several of these together treated as above with a small addition of bromine to make more bromal.

In conclusion it can be said that by dropping paraldehyde into bromine containing 1/2 g. of sulfur as a catalyst, using heat to carry on the reaction and a reflux condenser to return the vaporized bromine, it is possible to obtain a 50 per cent yield of pure bromal in four hours. In addition the lower fraction from the distillation may be rerun with a small addition of bromine to secure more bromal.

## Experimental

### Reagents

All of the reagents were dried before being used. The carbon tetrachloride was C.P. and was dried over calcium chloride. The paraldehyde was not labeled as to purity. It also was dried over calcium chloride. The bromine was dried under concentrated sulfuric acid and was the purified commercial product containing not over 1/2 per cent chlorine.

### Protocols

1. Monday. 25 g. paraldehyde and 50 g. carbon tetrachloride were placed in flask. 100 g. bromine was dropped in with cooling and 6 hours stirring. The color of the paraldehyde stayed light. On Tuesday after 30 g. more bromine had been dropped in, the flask became permanently colored. 30 g. more bromine was dropped in with a total of 5 hours stirring. Wednesday 140 g. bromine was added with 4 hours stirring. Thursday, the mixture was stirred 4 hours; Friday, 5 hours; Saturday, 4 hours; and Monday, 2 hours after which it was distilled. 108 g. crude bromal came over from 155° - 175°C. There was about 100 g. in the fore-run including the carbon tetrachloride, and a heavy tarry residue in the flask. The bro-

mal on redistillation gave 76 g. of the pure product boiling from  $161^{\circ}$  -  $169^{\circ}$  with most at  $164^{\circ}$  -  $166^{\circ}$ . This was a 49 per cent yield.

Analysis gave 85.18 per cent bromine; theoretical, 85.40 per cent.

2. Tuesday. Into the reaction flask were placed 23 g. paraldehyde and 40 g. carbon tetrachloride. Bromine was dropped in slowly, with cooling and 4 hours stirring, to the extent of 80 g. The reaction mixture stayed light colored. Wednesday, 70 g. bromine was added with stirring over a 5 hour period. The paraldehyde became permanently dark colored. Thursday, 90 g. bromine was added with 5 hours stirring. Friday the mixture was stirred 5 hours; Saturday, 4 hours, Sunday 2 hours; and Monday 4 hours. Tuesday, the mixture was distilled. From  $50^{\circ}$  -  $155^{\circ}$  bromine, carbon tetrachloride, and dibromacetaldehyde, with possibly some paraldehyde and monobromacetaldehyde came over. From  $155^{\circ}$  -  $175^{\circ}$ , bromal came over to the extent of 78 g., leaving behind a tarry residue of approximately 15 g. This fraction gave on redistillation 62 g. of pure bromal--a 44 per cent yield.

Analysis showed bromine to be 85.11 per cent.

3. Wednesday. 25 g. paraldehyde was placed in the flask along with 50 g. carbon tetrachloride. Bromine, to the extent of 100 g. was added Wednesday with constant stirring over a period of 4 hours. Thursday, 200 g. more bromine was added

with 6 hours stirring. Friday the mixture was stirred 4 hours and on Saturday, distilled. 64 g. crude bromal was obtained.

4. Friday. 50 g. paraldehyde and 50 g. carbon tetrachloride were placed in the flask. To this was added 170 g. bromine with constant stirring and some cooling over a period of 6 hours. The flask remained light-colored. Saturday morning 95 g. bromine was added which made the mixture permanently bromine-colored. Saturday evening the mixture was distilled and much dibromacetaldehyde was obtained but only 61 g. crude bromal.

5. Wednesday. 22 g. paraldehyde, 40 g. carbon tetrachloride and 1/2 g. pure iron powder were placed in the flask. Bromine was dropped in with stirring and cooling. The mixture became dark-colored from iron bromide almost immediately. 60 g. bromine was dropped in Wednesday with 4 hours stirring; Thursday, 80 g. more bromine with 4 hours stirring; Friday, 100 g. bromine with 5 hours stirring. Saturday, the reaction mixture was stirred 3 hours; Monday, 6 hours; and Tuesday, 7 hours. Wednesday the mixture was distilled but no bromal at all was secured. The temperature during the distillation never went above  $110^{\circ}$ , indicating that almost all of the paraldehyde was converted into monobromacetaldehyde.

6. Monday. Into the flask were placed 25 g. paraldehyde, 40 g. carbon tetrachloride and 1/2 g. powdered antimony. Bromine was added with cooling and stirring to the extent of 100 g.

over a period of 5 hours. Tuesday, 105 g. of bromine was added with 4 hours stirring. The mixture was now permanently bromine-colored showing that the antimony was not accelerating the reaction. Wednesday, the mixture was stirred 5 hours and 95 g. bromine added. Thursday it was stirred 4 hours; Friday, 4 hours; Saturday, 5 hours; and Monday, the product was distilled. 91 g. crude bromal were obtained which gave 68 g. pure bromal.

Analysis by Carius' method gave 85.22 per cent bromine in the pure bromal.

7. Monday. 25 g. paraldehyde, 40 g. carbon tetrachloride and 1/2 g. iodine were placed in the flask. The iodine immediately dissolved and characteristically colored the mixture. Into this mixture 110 g. bromine was dropped with 5 hours stirring and some cooling of the flask. Tuesday, 90 g. bromine was added with 4 hours stirring. It was evident from the amount of hydrogen bromide evolved that the iodine was not accelerating the reaction. Wednesday, 100 g. bromine was added and the mixture was stirred 3 hours; Friday, the mixture was stirred 4 hours; Saturday, 3 hours; and Monday, distilled. 81 g. crude bromal, highly colored by the iodine, was the yield.

8. Wednesday. 25 g. paraldehyde, 40 g. carbon tetrachloride and 1 cc. phosphorus trichloride were placed in the flask. 110 g. bromine was dropped in with cooling and 4 hours stirring. Thursday, 95 g. bromine was added with 4 hours stirring. The reaction was seemingly about stopped. Friday, the mixture was

stirred four hours and 95 g. bromine dropped in. Saturday, it was stirred 2 hours; Monday, 5 hours; Tuesday, 5 hours; and Wednesday, the mixture was distilled. 111 g. crude bromal was obtained.

9. Tuesday. 300 g. bromine and 50 g. carbon tetrachloride were placed in the flask, and 25 g. paraldehyde was placed in the dropping funnel. 15 g. paraldehyde was added Tuesday with cooling and 5 hours stirring. Wednesday, 10 g. paraldehyde was dropped in with 4 hours stirring and some cooling. Thursday the reaction-mixture was stirred 5 hours; Friday, 4 hours; Saturday, 3 hours; Monday, 5 hours; and Tuesday, the product was distilled. There was a fore-run of about 50 g., a fraction of 103 g. crude bromal from  $155^{\circ}$  -  $175^{\circ}$  and a medium-sized residue of tarry by-products. The crude bromal when redistilled gave 91 g. pure bromal which is a 52 per cent yield.

Analysis by Carius' method showed 85.17 per cent bromine in the pure product.

10. Wednesday. 300 g. bromine was placed in the flask without any diluent. The mixture was cooled and stirred for 4 hours, and 27 g. paraldehyde was added. Thursday, it was stirred 4 hours, and then distilled. 72 g. crude bromal was obtained.

11. Approximately 400 g. of fore-runs was placed in the flask and 200 g. bromine was added to this. The mixture was stirred 4 hours, allowed to stand 4 hours and then distilled.

300 g. crude bromal was obtained.

12. 300 g. bromine was placed in the flask. A reflux condenser was attached to the flask. 27 g. paraldehyde was dropped in over a period of 2 hours with constant stirring. Then the mixture was stirred and heated to  $60^{\circ}$  -  $80^{\circ}$  for 3 hours more. The mixture was allowed to stand for 5 hours and was then distilled. 112 g. crude bromal was obtained.

13. 300 g. bromine and 1 cc. phosphorus trichloride were placed in the flask. 27 g. paraldehyde was dropped in with cooling and 4 hours stirring. There was no reflux condenser in the setup and no heat was applied. The mixture was let stand for 5 hours and then distilled. 81 g. crude bromal was obtained.

14. 300 g. bromine and 1 cc. phosphorus trichloride were placed in the flask which was fitted with a reflux condenser. 27 g. paraldehyde was dropped in from 9 - 11 A.M. with no cooling but with constant stirring. The mixture was stirred and heated to  $60^{\circ}$  -  $80^{\circ}$  from 1 - 3 P.M. At 6 P.M. the mixture was distilled and 111 g. crude bromal was secured..

15. 1080 g. crude bromal was distilled and fraction from  $159^{\circ}$  -  $172^{\circ}$  containing 960 g. pure bromal was obtained.

Analysis gave 85.08 per cent bromine by weight in the final product.

Note: All the following runs have been done with a reflux condenser attached to the setup.



16. 300 g. bromine was placed in the flask. 27 g. paraldehyde was dropped in from 7 - 8:30 P.M. with constant stirring. Then the mixture was heated and stirred until 11:30 P.M., when it was distilled. 104 g. was secured in the fraction  $155^{\circ}$  -  $172^{\circ}$ .

17. 300 g. bromine and  $1/2$  g. aluminum shavings were placed in the flask. The aluminum was immediately converted to aluminum bromide with incandescence. Then 27 g. paraldehyde was added with constant stirring over a period of 2 hours. The mixture was stirred and heated to  $60^{\circ}$  -  $80^{\circ}$  for  $2\frac{1}{2}$  hours more. The hydrogen bromide was very slow in coming off. There was a large fore-run, only 79 g. crude bromal, and an average residue of resinous by-products.

18. 300 g. bromine and 1 g. flowers of sulfur were placed in the three-necked distilling flask. 28 g. paraldehyde was dropped in with stirring from 7:30 - 9:00 P.M. Then the mixture was stirred until 11:30 P.M. when it was distilled. 118 g. crude bromal was obtained.

19. Approximately 80 g. bromine was added to about 400 g. of fore-run in the flask. This mixture was run with heat and stirring for 4 hours. 260 g. crude bromal was obtained on distillation and there was a large fore-run which was saved to be rerun.

20. 300 g. bromine was placed in the reaction-flask. In  $1\frac{1}{2}$  hours and with constant stirring 28 g. paraldehyde was

dropped in. The mixture was heated to  $60^{\circ}$  -  $80^{\circ}$  and stirred for 2 1/2 hours more and then distilled. 100 g. crude bromal was secured.

21. 300 g. bromine and 1/2 g. sulfur were placed in the flask. 28 g. paraldehyde was added in 1 1/2 hours with constant stirring. The reaction-mixture was heated and stirred for 2 1/2 hours more and then distilled. 113 g. crude bromal was obtained.

22. 302 g. bromine and 1 g. sulfur were placed in the flask. The mixture was stirred constantly. 29 g. paraldehyde was dropped in over a period of 2 hours and then the mixture was heated to  $60^{\circ}$  -  $80^{\circ}$  for 2 hours more. On distillation 125 g. crude bromal was obtained. In this run the outlet tube for the hydrogen bromide was partially plugged and an increase in pressure seemed probable.

23. 300 g. bromine was placed in the flask. 29 g. paraldehyde was added in 2 hours and then heat was applied for 2 hours more. The mixture was stirred constantly. On distillation 110 g. crude bromal was secured. In this run, also, the outlet tube was partially plugged.

24. 1007 g. crude bromal was redistilled using a standardized thermometer and with the barometer at 67.57 cm. The fraction from  $160^{\circ}$  -  $171^{\circ}$  was taken as pure bromal with most of this coming over at  $164^{\circ}$  -  $166^{\circ}$ . 850 g. bromal was obtained.

Analysis on this bromal gave 85.31 per cent bromine.

Theoretical is 85.40 per cent bromine.

25. 300 g. bromine was placed in flask along with 1/2 g. sulfur. 29 g. of paraldehyde was added over a period of 2 hours with constant stirring. Then the mixture was heated and stirred for 2 hours more and distilled. 111 g. crude bromal was obtained. There was a rather large fore-run but only an average residue of tarry by-products left in the distilling flask.

26. 300 g. bromine was placed in the flask. To this 29 g. paraldehyde was added over a period of 2 hours with heating and stirring for 2 hours more. 103 g. crude bromal was obtained.

27. 810 g. crude bromal was redistilled. The fraction from  $160^{\circ}$  -  $171^{\circ}$  at a barometer pressure of 68.4 cm. was saved. 604 g. pure bromal was obtained approximately 450 g. of which came over from  $165^{\circ}$  -  $167^{\circ}$ . The fore and after-runs were saved and rerun along with fore-runs from other experiments.

28. 160 g. bromine was placed in the flask and to this 23 g. paraldehyde was added over a 2-hour period. The mixture was stirred constantly. It was heated for 2 hours more and distilled. On distillation 43 g. of dibromoacetaldehyde came over from  $133^{\circ}$  -  $150^{\circ}$ . On redistillation under reduced pressure this gave 35 g. of pure dibromaldehyde.

Analysis on the above gave 79.72 per cent bromine by weight. Theoretical is 79.18 per cent.

29. 240 g. bromine was placed in the flask and 23 g. paraldehyde was added to this with constant stirring over a period of 2 hours. Then the mixture was stirred and heated for 2 hours more. 86 g. of crude bromal was secured which gave 62 g. of pure bromal on redistillation.

Analysis showed 85.17 per cent of bromine.

30. 240 g. bromine and 1/2 g. sulfur were placed in the flask and 23 g. paraldehyde was dropped in with constant stirring over a period of 2 hours. Then the mixture was stirred and heated for 2 hours more. 93 g. crude bromal was secured which on redistillation gave 76 g. of pure bromal.

Analysis by the Carius method showed 85.24 per cent of bromine.

Several other runs were completed that have not been recorded here. Some of these were done purely to produce bromal. These confirm the ones listed above. All the pertinent experiments have been included in the above protocols.

All temperatures given in this article are uncorrected.

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\* The library of the University of Montana lacks these two volumes of the Annalen and other libraries consider them too valuable to lend. Hence it is impossible to give the titles of these two articles.

## Part II

BROMAL WITH GRIGNARD'S REAGENT

A Preliminary Study

## Part II

### Bromal with Grignard's Reagent

#### A Preliminary Study

#### Discussion

At the start of this work it was planned to study thoroughly the reaction of bromal on Grignard's reagent, but so much time was spent in finding a good method for preparing bromal that the original plan could not be completed. Because of this the results given in this section do not represent a completed project.

So much work has been done with Grignard's reagent, especially in producing secondary and tertiary alcohols, and the method of preparing the reagent itself is so well standardized that any historical discussion on these points is unnecessary. The particular reaction in question--between bromal and Grignard's reagent--has not been investigated previous to this study. Since the reaction of bromal might be expected to follow closely that of its analog, chloral, the methods used by J. W. Howard (1926) in preparing secondary alcohols from the latter have been used in these experiments.

To prepare the Grignard reagent, a liter three-necked distilling flask was used. To this a mercury-seal stirrer, a

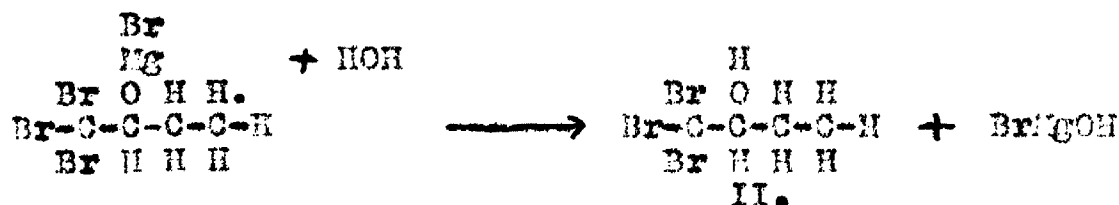
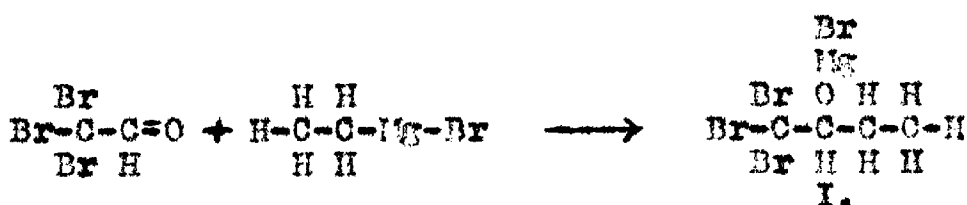
dropping funnel and a reflux condenser were fitted. Dry magnesium was placed in the flask and the mixture of the alkyl bromide and absolute ether was dropped on the magnesium. Ordinarily, after the reaction was completed, two or three grams of unused magnesium were left. In order to remove any possibility of this reacting with the bromal, the solution was quickly decanted into another three-necked flask before adding the bromal. (Protocols 1 and 2)

If the reaction of bromal and Grignard's reagent goes straightforward, a tribrom secondary alcohol would be the main product. In order to prepare the secondary alcohol represented

by the formula 
$$\begin{array}{c} \text{Br H H H} \\ | \\ \text{Br}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ | \\ \text{Br O H H} \\ | \\ \text{H} \end{array}$$
, magnesium ethyl bromide,

$$\begin{array}{c} \text{H H} \\ | | \\ \text{H}-\text{C}-\text{C}-\text{MgBr} \\ | | \\ \text{H H} \end{array}$$
, was used. The production of the alcohol would go

according to the following scheme:



Since only the preparation of the above alcohol was attempted, ethyl bromide was used in all our preparations of Grignard's



reagent.

To prepare the secondary alcohol, a mixture of bromal and absolute ether was dropped into the magnesium ethyl bromide. The reaction was very vigorous and took much cooling. About 45 minutes was needed to add all of the bromal. This mixture was heated for three hours and then hydrolyzed with water and a 30 per cent solution of sulfuric acid. The ether layer, which in all experiments appeared as a very dark brown solution, was separated and washed.

In the first attempt (Protocol 1) the ether was distilled off the final solution and the very dark, heavy solution which was left was steam distilled. After extraction with ether, the product from steam distillation was dried, the ether was distilled off, and the product distilled under reduced pressure. There was no constant boiling point in this distillation, except at the point where bromal boiled,  $64^{\circ}$ . The fraction from  $60^{\circ}$  -  $80^{\circ}$  was proven by analysis to be bromal. The next fraction from  $80^{\circ}$  -  $89^{\circ}$  showed a diminution in per cent of bromine but not sufficient to indicate it to be the secondary alcohol. But this fraction did show that something was in the product to cut down the per cent of bromine and it seemed logical that it was the secondary alcohol that was sought. From  $90^{\circ}$  -  $110^{\circ}$  the liquid that came over crystallized out in the condenser in the form of white, flaky crystals.

A determination of the bromine by the Carius method was used to establish the products. Pure bromal should contain 85.40 per cent bromine by weight. The secondary alcohol, 1 tri-brom 2 hydroxy butane, should contain 77.17 per cent bromine. The first fraction mentioned above, which the boiling point indicated to be bromal, gave 85.23 per cent bromine. The second fraction showed 82.71 per cent bromine, which made it seem logical that it was a mixture of bromal and the secondary alcohol. The crystals, after being dried, gave 85.14 per cent bromine. This did not check at all with the secondary alcohol, nor did the appearance and boiling point of the crystals check with bromal. Because of the small quantity formed it was probably a by-product.

One of the astonishing features of all these experiments was the small quantity of final product. The large amounts of black tarry residues left seemed to show that side reactions were extensive. In this first experiment, 140 g. of bromal gave on distillation, only 45 g. of total product, of which at least half was bromal. In order to cut down the amount of unchanged bromal, the proportions were altered on the third run from equivalent quantities of bromal and Grignard's reagent to an excess of the latter. (Protocol 3)

The second attempt was the same as the first, except that the steam distillation was omitted and the final ether solution

was dried, the ether distilled off, and then the residue was distilled under reduced pressure. The final fraction from  $55^{\circ}$  -  $70^{\circ}$  contained bromal as before. The next fraction from  $70^{\circ}$  -  $100^{\circ}$  showed a constant boiling point at  $94^{\circ}$  and gave 79.52 per cent bromine on analysis. No crystals were produced. Once again it seemed that the secondary alcohol was present but was contaminated with bromal.

The third run, which used the excess Grignard's, gave the same final products as the second. (Protocol 3) Unchanged bromal came over as before. In order to purify the product the upper fractions from the second and third runs were combined, washed with water to remove excess bromal, and fractionated under reduced pressure. (Protocol 4) From  $91^{\circ}$  -  $94^{\circ}$ , 5 cc. of a clear-yellow liquid came over which gave on analysis 81.00 per cent bromine. Above  $94^{\circ}$  crystals precipitated again in the condenser. A careful determination of per cent halogen and melting point showed them to be identical with the first crystals. When the liquid fraction was cooled, more of the crystalline substance was precipitated and the bromine content of the liquid free from crystals was 80.16 per cent. This added more evidence to the belief that the secondary alcohol, II, was present, but it still remained to separate it in pure form.

This proved to be very difficult. More experiments with careful fractionation of the runs and of combinations of frac-

tions seemed to reduce the per cent of bromine somewhat, but not down to where the product could be the secondary alcohol in pure form. (Protocols 5 - 9) The small amount of final product that was obtained in each experiment increased the difficulties of separation. It seemed that either the secondary alcohol was not present at all or it was mixed with a substance whose boiling point was close to its own. The latter view seemed the more probable since small amounts of the white crystals previously mentioned were found rather consistently.

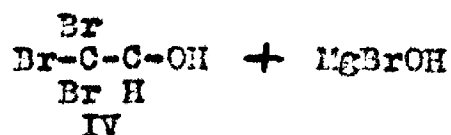
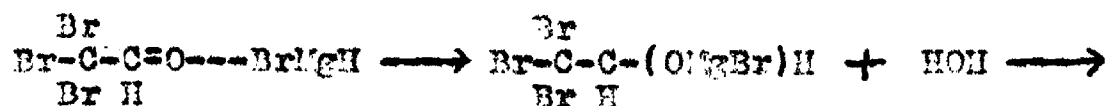
This white crystalline substance, appearing in small quantities from the upper fractions of several experiments, presented another problem. Being crystalline and showing a constant analysis and melting point it was logical to assume that it was a pure compound. Its content of bromine, 85.04, was close to that of bromal, 85.40. But it boiled under reduced pressure at least  $30^{\circ}$  above the bromal, and showed entirely different characteristics. It did not check with bromal hydrate, whose per cent bromine is 80.27. This latter was also eliminated because according to Schäffer, it would have decomposed under heat and given off water and bromal. The only probable compound that did check with it was tri-bromethyl alcohol, whose per cent bromine is 84.81. No mention of this compound was found so a check by melting point could not be made.

In order for tribromomethanol to be formed, the Grignard reagent would have to act as a reducing agent. This reducing action has been reported by Hess and Rheinbolt (1921), Hess and Mustrow (1924), Rheinbolt and Roleff (1924 and 1925), Blicke and Powers (1929), Comberg (1929), and others. The most thorough work seems to have been done by Hess, Rheinbolt, and Roleff, although all of their work was done on the reaction to produce tertiary alcohols. They found several evidences of reduction and, on the basis of these, postulated a new formula for the product of the Grignard reaction. According to them, reduction takes place as represented by these equations:

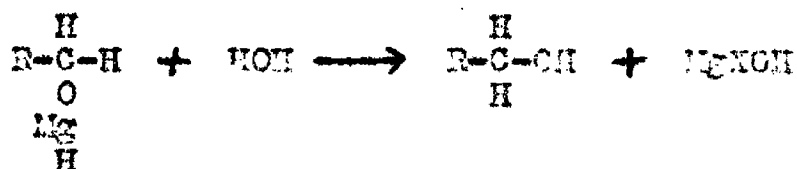
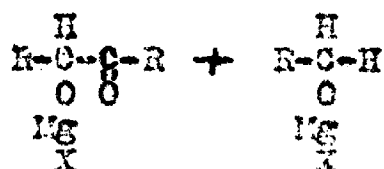
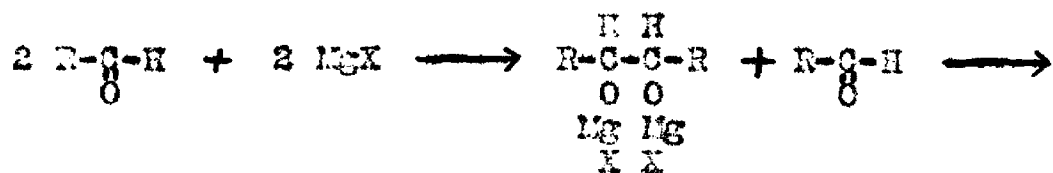


In the straightforward reaction a compound like III,  $R_2C=O \text{---} MgXH$ , would be formed instead of the usual  $R_2C(OMgX)_2$ .

To make tribromomethyl alcohol, IV, the reaction would be:



Comberg proposes a metastable  $MgX$  which causes a reaction of the type:



Either of these methods would explain satisfactorily the formation of the alcohol, IV. As has been stated, much heat is produced by the reaction of bromal and the Grignard reagent. Hess and Rheinbolt state that heat aids the reduction side reaction, thus making the formation of IV very plausible. The very small quantity of crystals which appeared also indicated that they represented a side reaction.

Because of the small quantity of crystals very little work could be done on them either for purification or identification. Finally all the crystals that had been obtained were heated with acetic anhydride to form a possible ester. (Protocol 13) After decomposing the acetic anhydride with water

about 1/4 cc. of heavy liquid remained. This was separated and a halogen determination made. This showed 74.53 per cent bromine. The acetic ester of IV should give 75.35 per cent. While this is not close enough agreement to prove conclusively the existence of the tribrom ethyl alcohol, nevertheless, considering the doubtful purity of the sample analysed, it makes its existence quite probable.

Since it had not been possible to purify the secondary alcohol which should be the main product, it was decided to reverse the order of mixing the reacting substances and add the Grignard reagent to the bromal. To do this the Grignard reagent was decanted quickly into a dropping funnel that was stoppered with a tube of calcium chloride and this funnel was fitted to a three-necked flask containing the bromal. The reaction went just as in the other method except that it seemed to be more vigorous. (Protocols 10 and 11) The final ether solution was washed and dried, the ether distilled away, and the product distilled under reduced pressure. No bromal appeared. In the two experiments the lower fractions from 75° - 85° and from 83° - 94°, respectively, were saved and analysed. Analysis on one showed 74.70 per cent bromine and on the other 75.41 per cent. This obviously did not check with any of the previous experiments, nor did it check with the secondary alcohol, II.

The upper fractions from the two experiments were combined and redistilled under reduced pressure. (Protocol 12) The first fraction came over from  $88^{\circ}$  -  $97^{\circ}$ , and consisted of about 6 cc. of a clear yellow liquid. The fraction of about 3 cc. from  $97^{\circ}$  -  $105^{\circ}$  was clear yellow also but darkened slightly on exposure. Analysis on the lower fraction gave 74.64 per cent bromine. This again did not check closely with any of the previous experiments but did check with the lower fractions from the same runs. The upper fraction showed on analysis 76.89 per cent bromine. This is a fair check for the secondary alcohol, II, which theoretically contains 77.17 per cent bromine.

To prove the existence of the secondary alcohol, an attempt was made to form its acetic ester. This was done as before by heating a sample with an excess of acetic anhydride for three hours. The excess anhydride was then decomposed by adding the mixture to water. The resulting product was separated and a halogen determination made. This process was carried out on a sample of material obtained in the experiment described in Protocol 9, and <sup>which</sup> contained 79.94 per cent bromine. Analysis showed 72.98 per cent bromine. (Protocol 14) The acetic ester of the secondary alcohol, II, should consist of 67.99 per cent bromine. This result again made it seem probable that the secondary alcohol was present but did not prove so definitely. If the sample that was used were a mixture of tri-



brom ethyl alcohol and the secondary alcohol, as was quite likely, a result corresponding to the one above--75 per cent--would be expected.

An attempt was next made to form the ester on the best sample obtained, the one showing 76.89 per cent bromine. This was done just as before by heating with acetic anhydride. (Protocol 15) A determination of the halogen in the supposed ester showed 69.35 per cent bromine. This is only a fair check to the 67.93 per cent that the ester theoretically contains. Hence final proof that 1 tribrom 2 hydroxy butane is formed by the reaction of bromal and the Grignard reagent was, disappointingly, not obtained. However, these results do make the existence of the compound most probable, and further efforts to obtain more of the substance and to isolate it in pure form will undoubtedly succeed.

Since the alcohol, II, was not definitely isolated, more research is needed to accomplish this, and also to establish its physical constants. In addition more work must be done on isolating the other products of the reaction not only when it is carried out ordinarily but when it is reversed.

In conclusion, it can be said that the reaction of bromal and the Grignard reagent was studied but not completely. The normal product from this reaction, 1 tribrom 2 hydroxy butane, was probably isolated but its properties were not

established. Strong evidence of the formation of a reduction product, tribromethyl alcohol, was secured but the existence of the compound was not definitely proved. It was found that the reaction of bromal with Grignard's reagent proceeds with much more difficulty than does the reaction of chloral. The final total yield was small and side reactions, as evinced both by the impurities contained in the final product and by the large amounts of tarry residues, were extensive. More work is needed to complete the study of this reaction.

## Experimental

### Reagents

All reagents, except the bromal, were dried carefully. The magnesium used was the ordinary magnesium shavings, washed with ether, oven-dried and kept in a dessicator. The ethyl bromide was J. T. Baker's purified. It was dried over calcium chloride. Absolute ether was prepared in the usual way by drying commercial purified ether over calcium chloride and distilling with phosphorus pentoxide. It was then kept dry over metallic sodium. The bromal used was what we have previously called pure bromal. It was kept in a tightly corked flask after being redistilled.

### Protocols

1. Tuesday. 12 g. magnesium was placed in a 1000 cc. three-necked distilling flask. 54 g. ethyl bromide and 100 cc. absolute ether were mixed and placed in the dropping funnel. The ethyl bromide and ether were dropped into the flask with cooling and some stirring. The reaction went vigorously until approximately  $3/4$  of the ethyl bromide had been added. After it was all in, the mixture was refluxed by heating with occasional stirring for 6 hours more and then

let stand over night.

Wednesday. The Grignard's reagent was quickly decanted into another three-necked flask and the unused magnesium weighing 2 g. was discarded. This flask was fitted as before and 140 g. bromal and 150 cc. ether were mixed and placed in the dropping funnel. This mixture was dropped into the Grignard's reagent very slowly over a period of 45 minutes with much cooling and stirring. The reaction was very vigorous. After all the bromal had been added, the mixture was refluxed for 2 1/2 hours with occasional stirring and then allowed to stand over night. The mixture separated into two parts, a dark-brown layer on the bottom and a clear light-yellow layer on top.

Thursday. 100 cc. water was added to the mixture with cooling and some stirring. The reaction was fairly vigorous at first and produced some heat. A dark-red precipitate was thrown down. 40 cc. of a 30 per cent solution of sulfuric acid was added to complete the hydrolysis. After this had been added with some stirring the mixture became clear with a heavy aqueous layer below and a dark-brown ether layer above. This ether layer was separated, washed twice with water, placed in a distilling flask and the excess ether and ethyl bromide distilled off. About 75 cc. of a heavy, dark liquid was left and this was steam distilled until about one liter of mixture had come over. A large tarry-residue was left in the distilling

flask. The aqueous mixture was extracted with ether and this ether solution was dried over calcium chloride.

Friday. The dry ether solution was placed in a Claissen distilling flask and the ether distilled off. A dark liquid of about 20 cc. was left. This was distilled under reduced pressure with the manometer reading 1 cm. The distillate was fractionated. The first fraction taken was from  $60^{\circ}$  -  $79^{\circ}$  and consisted of about 7 cc. of a clear yellow liquid. The second fraction of about 5 cc. was also clear yellow and boiled from  $80^{\circ}$  -  $89^{\circ}$ . From  $90^{\circ}$  -  $110^{\circ}$  a small amount of liquid came over but was trapped by the formation of white crystals in the condenser. These crystals were removed and dried on unglazed porcelain. A slight tarry residue remained in the distilling flask.

The first fraction showed 85.23 per cent bromine on analysis by the Carius method, and since pure bromal boils at  $64^{\circ}$  under a reduced pressure of 1 cm. this was taken to be bromal. The second fraction showed by a Carius analysis, 82.71 per cent bromine. The crystals showed 85.14 per cent bromine, and melted at  $74^{\circ}$  -  $76^{\circ}$ .

2. Tuesday. 12 g. of magnesium was placed in the flask and a mixture of 54 g. ethyl bromide and 100 cc. absolute ether was dropped in with cooling and stirring. The reaction proceeded as before. After the ethyl bromide had been added the mixture was refluxed with heat for 6 hours and then allowed to

stand over night.

Wednesday. The Grignard's reagent was quickly decanted as before and a mixture of 140 g. bromal and 150 cc. of absolute ether was added over a period of 45 minutes with cooling and stirring. This mixture was heated for 5 hours more and allowed to stand.

Thursday. 100 cc. of water was added to the ether solution with cooling and stirring and then the hydrolysis was completed with 40 cc. of a 30 per cent sulfuric acid. The ether layer was separated, washed with water, then with a weak solution of sodium carbonate, next with weak sodium bisulfite solution--an attempt to remove the bromal--and finally with water again. After this, the ether solution was put in a flask with anhydrous calcium chloride and allowed to stand.

Friday. The ether solution was filtered into a Claissen distilling flask and the ether distilled off. Then the dark liquid of about 20 cc. that remained was distilled under reduced pressure with the manometer at .9 cm. The first few drops from 45° - 55° were discarded. From 55° - 70° about 5 cc. came over, most of it at 64° - 65°. This fraction was a clear yellow liquid. The next fraction was from 70° - 100° and consisted of about 4 cc. of a light yellow liquid. No crystals appeared. The thermometer climbed rapidly from 70° to 93° and then held fairly constant at 94°. A heavy tarry residue was left in the distilling flask.

Analysis showed the first fraction to be bromal as its boiling point would indicate. The other fraction from  $70^{\circ}$  -  $100^{\circ}$  showed 79.52 per cent bromine.

3. The complete run was just as in protocol 2 except that the amounts of ethyl bromide and magnesium were increased proportionately to 67 1/2 g. and 15 g. respectively, while the amount of bromal was cut to 105 g. This was done to decrease the unused bromal. The final ether solution was washed only with water.

On distillation, 5 cc. came over from  $55^{\circ}$  -  $70^{\circ}$ , manometer at .8 cm. This was discarded as being unchanged bromal. From  $70^{\circ}$  -  $90^{\circ}$ , 2 cc. came over. From  $90^{\circ}$  -  $103^{\circ}$ , 4 cc. came over as a clear yellow liquid which soon darkened. A tarry residue was left in the distilling flask.

4. The upper fractions from runs 2 and 3 were combined, washed with water to take out any bromal, extracted with ether and dried over calcium chloride. The ether was distilled off and the remaining liquid distilled under reduced pressure. The thermometer climbed quickly to  $90^{\circ}$ . From  $91^{\circ}$  -  $94^{\circ}$  about 5 cc. of clear yellow liquid was obtained. Then crystallization started in the condenser and white crystals, identical with those in run 1, appeared. These were washed out with ether, the ether was evaporated away and then the crystals were dried on unglazed porcelain. On cooling to  $0^{\circ}$ , crystals ap-

peared in the liquid fraction but on standing at room temperature these crystals went back into solution.

A Carius determination on the liquid containing the dissolved crystals showed it to contain 81.00 per cent bromine. The crystals themselves contained 85.06 per cent bromine. They melted at  $76^{\circ}$  which showed them to be identical with the crystals previously obtained.

The liquid fraction was cooled to  $0^{\circ}$  c. and the white crystals precipitated again. The liquid was decanted and a Carius determination on this liquid gave 80.18 per cent bromine.

5. This run was identical with 3 in all respects except that on final distillation there was very little bromal in evidence. No crystals were produced.

6. This run was identical with 5 in every way.

7. The fractions from  $85^{\circ}$  -  $105^{\circ}$  from runs 5 and 6 which were darkened by decomposition products were redistilled under reduced pressure. The resulting product came over from  $84^{\circ}$  -  $100^{\circ}$  and seemed to consist of two layers, both clear yellow.

8. The lower fractions from runs 3, 5, and 6 were combined and distilled and the fraction from  $84^{\circ}$  -  $94^{\circ}$  saved. This consisted of about 4 cc. of a clear yellow product. On analysis it showed 80.54 per cent bromine.

9. The product from runs 7 and 8 and the liquid decanted



from the crystals in run 4 were combined and redistilled under reduced pressure. From  $75^{\circ}$  -  $90^{\circ}$  5 cc. of a clear yellow liquid came over which precipitated white crystals in the receiver and in the condenser. The excess liquid was decanted from these crystals and the crystals dried on unglazed porcelain.

An analysis of the first liquid fraction showed 79.94 per cent bromine.

10. A solution of Grignard's reagent was made in exactly the same way as in run 3. This was quickly decanted into a dropping funnel which was corked with a stopper to which was attached a calcium chloride tube containing anhydrous calcium chloride. This Grignard's reagent was then dropped slowly, with cooling and stirring, into a solution of 105 g. bromal in 150 cc. of absolute ether. This latter solution was contained in a three-necked flask fitted with a reflux condenser and stirrer as before. The reaction was vigorous and approximately 40 minutes was taken to add the Grignard's reagent. After this the mixture was heated 3 hours more and then allowed to stand. 100 cc. of water and 40 cc. of 30 per cent sulfuric acid were added and the ether solution was separated, washed and dried just as in previous experiments.

On distillation under reduced pressure, fractions from  $75^{\circ}$  -  $85^{\circ}$  and from  $85^{\circ}$  -  $100^{\circ}$  consisting of 4 and 5 cc. respectively were saved. The lower fraction contained a slight quan-

tity of water probably from a small amount of hydrated calcium chloride which was in the distilling flask. To remove this water the liquid was extracted with ether and then the ether evaporated off by heating.

Analysis of the first fraction showed 74.70 per cent bromine. Evidently the heat applied produced some decomposition.

11. This run was conducted exactly the same as 10. But on adding the Grignard's to the bromal the reaction was much more vigorous. Over an hour was taken to complete the addition. The subsequent hydrolysis also seemed to be more vigorous. The ether solution was treated as before, except that in the final washing sodium chloride was added to the water to make a more effective separation.

On redistillation under reduced pressure, no bromal appeared. 3 cc. came over from  $83^{\circ}$  -  $94^{\circ}$  and once again it was contaminated with water. 5 cc. of a dark solution came over from  $94^{\circ}$  -  $105^{\circ}$ . No crystals were in evidence.

The fraction from  $88^{\circ}$  -  $94^{\circ}$  was dried with calcium chloride as well as it could be. Because of the small amount it was not feasible to extract it with ether and then dry it. Analysis showed 75.41 per cent bromine.

12. The upper fractions from runs 10 and 11 were combined, extracted with ether and dried. The ether was distilled off and the remaining liquid was distilled under reduced pressure.

From  $88^{\circ}$  -  $97^{\circ}$  6 cc. of a clear yellow liquid came over. 3 cc. of a clear yellow liquid came over from  $97^{\circ}$  -  $105^{\circ}$  but this later darkened slightly. No crystals were produced. A slight tarry residue remained in the distilling flask.

An analysis of the lower fraction showed 74.65 per cent bromine. The upper fraction gave 76.89 per cent.

13. All of the crystals that had been secured amounting to about  $1/2$  g. were placed in 10 cc. of acetic anhydride and kept at a temperature of  $125^{\circ}$  -  $135^{\circ}$  for 3 hours. Then the mixture was poured into 75 cc. of water and the acetic anhydride thus decomposed. About  $1/2$  cc. of a heavy yellow liquid settled out. This was washed well by decantation and then separated. Because of the small amount it was not dried but the separation was done carefully with a clean, dry separatory funnel.

Analysis showed 74.53 per cent bromine in the sample.

14. 2 cc. of the lower fraction from run 9 was treated just as in run 13. After decomposing the acetic anhydride about 2 cc. of a brown heavy liquid was left. This was separated as before.

Analysis showed 72.98 per cent bromine in the sample.

15. The upper fraction from run 12 was treated with acetic anhydride just as in protocol 13. 2 cc. of a heavy, brown liquid remained after decomposing the acetic anhydride. This

was separated and a Carius determination made.

Analysis showed 69.55 per cent bromine. Theoretical for the acetic ester of 1 tribrom 2 hydroxy butane is 67.99 per cent.

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