

The trialkylsilyl fluorides were very stable and did not respond to the action of sodium in liquid ammonia and therefore could not be analyzed by the sodium-liquid ammonia⁴ method.

The fluorine was qualitatively determined in each compound by oxidation with chromic acid in sulfuric acid solution to silicon tetrafluoride which was passed into aniline⁵ to form a solid addition compound.

TABLE I

PROPERTIES AND ANALYSES OF TRIALKYLSILICYL FLUORIDES

Trialkyl- silyl fluorides	B. p., °C. (745 mm.)	n_{25}^D	d_{25}^4	Yield, %	Carbon, %	
					Calcd.	Found
Ethyl ²	109	1.3900	0.8354	45.0	53.66	52.50
Propyl	175	1.4107	.8339	62.0	61.28	60.93
Butyl	224	1.4250	.8372	70.1	65.97	65.96
Amyl	267	1.4305	.8389	57.6	69.10	69.10

(4) Vaughn and Nieuwland, *Ind. Eng. Chem., Anal. Ed.*, **3**, 274 (1931).

(5) Comey and Jackson, *Am. Chem. J.*, **10**, 166 (1888).

The compounds were analyzed quantitatively for carbon by a modified Chalmer's⁶ method which is a wet combustion method. The results of this analysis are given in Table I.

Summary

A study was made of the reaction between silicon tetrafluoride and ethyl, propyl, butyl and amylmagnesium halides.

Three new trialkylsilyl fluorides were prepared.

The fluorine atom in trialkylsilyl fluorides is very inactive, much less reactive than the corresponding bromide or chlorides.

The reaction between alkylmagnesium halides and silicon tetrafluoride is completed in less than one hour.

(6) Chalmer, *Ind. Eng. Chem., Anal. Ed.*, **4**, 1 (1932).

NOTRE DAME, INDIANA

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[CONTRIBUTION FROM KENT AND GEORGE HERBERT JONES CHEMICAL LABORATORIES, UNIVERSITY OF CHICAGO]

Lactones in Liquid Ammonia

BY J. W. E. GLATTFELD AND DUNCAN MACMILLAN¹

In an earlier article² the authors described the preparation of aldonic and saccharinic acid amides in liquid ammonia. In the procedure employed

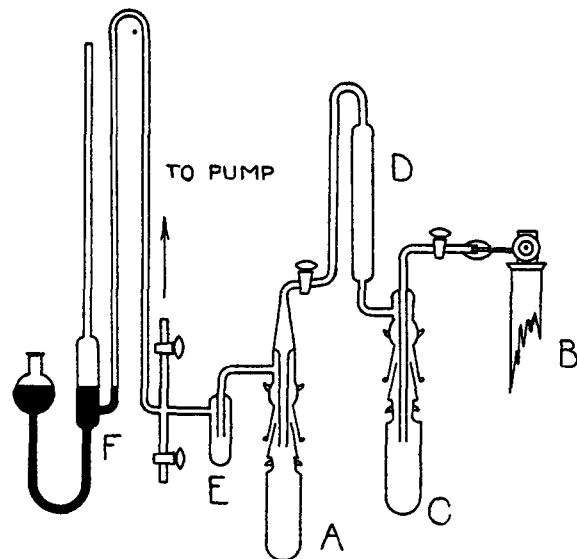


Fig. 1.

it was found that the lactones of sugar acids were readily ammonolyzed and gave quantitative

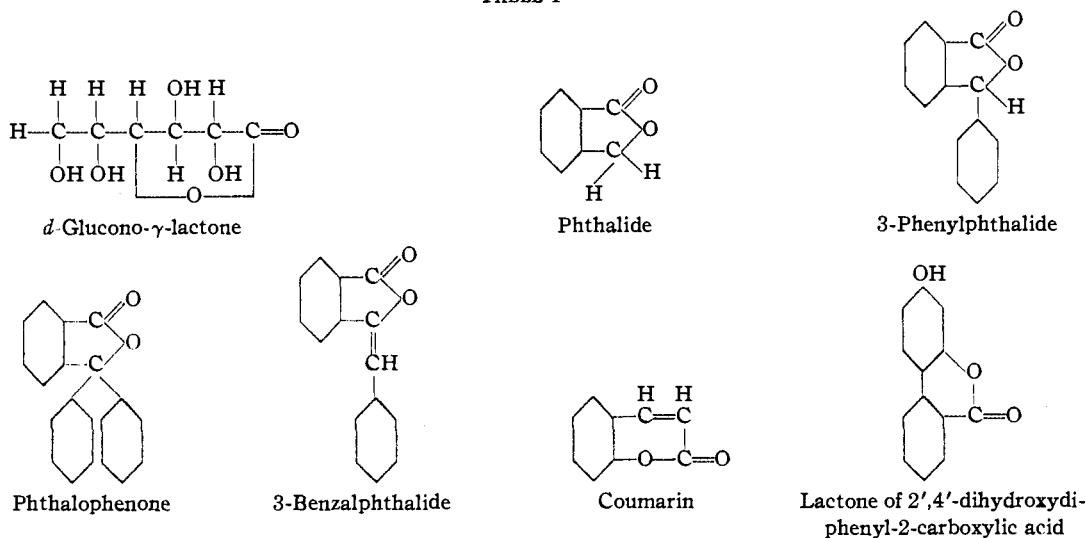
yields of the amides. Experiments with lactones of the other types indicated that not all lactones show this property. This suggested that further study might contribute to an understanding of the lactone bond. It seemed desirable that the work be done on a quantitative basis, and under anhydrous conditions. For this purpose a system capable of evacuation was constructed, as shown in the figure.

Since the same procedure was used in all cases, a general description may be given. A quantity of the material to be studied was placed in a weighed tube (A), the open end of which was the inner cone of a ground-glass joint; the joint was greased and the tube placed in the line. The system was evacuated to a pressure of 10^{-4} mm. with a mercury vapor pump. The tube was then detached, the joint cleaned with ether, and the tube weighed, after which it was again placed in the line and evacuated. Ammonia was then condensed from a small tank (B) into a tube (C) which contained sodium metal, over which the ammonia was allowed to stand until the blue color became permanent. The ammonia was then distilled through a column (D) packed with glass wool, into the reaction tube (A). The purpose of the glass wool was to remove small amounts of

(1) The material in this article will be used by Duncan Macmillan as a part of his dissertation for the degree of Doctor of Philosophy in the University of Chicago.

(2) Glattfeld and Macmillan, *THIS JOURNAL*, **56**, 2481 (1934).

TABLE I



Substance	Initial wt., g.	Final wt., g.	Calcd. for lactone + 1 NH ₃
<i>d</i> -Glucono- γ -lactone	0.8878	0.9723	0.9726
Phthalide	.0408	.0402	
3-Phenylphthalide	.1010	.1006	
Phthalophenone	.2655	.2642	
3-Benzalphthalide	.3337	.3582	.3593
Coumarin	.0428	.0425	
Lactone of 2',4'-dihydroxydiphenyl-2-carboxylic acid	.0456	.0461	

sodium or sodium amide which might have been carried over, a complication which has occurred in other work in these laboratories.

In general, if the material dissolved readily the ammonia was removed soon after solution was complete. This was done by condensing it in the trap (E). If the material did not dissolve readily the mixture was allowed to stand for several hours. The vacuum pump was applied as soon as the ammonia had been distilled into the trap (E), except in some of the experiments with the phthaleins, in which it was necessary to know the weight of the material very soon after treatment with ammonia. In the latter case the ammonia was allowed to boil out of the trap through the blow-off tube (F). Pumping was continued until the system had returned to its initial pressure, after which the tube was detached, cleaned and weighed. In all experiments save those with the phthaleins, the original pressure and a constant weight were reached in a few hours; in the phthalein experiments constant weight was not reached until many weeks had passed. In Table I are shown the results of the experiments on a number of lactones.

It will be seen from the data that, as was stated in the earlier article, *d*-glucono- γ -lactone is com-

pletely ammonolyzed, but that, of the other lactones investigated, only one, benzal phthalide, is ammonolyzed. The product obtained in the last case melted at 164–165°, and was, therefore, the amide of desoxybenzoin carbonic acid, C₆H₄(CONH₂)(COCH₂C₆H₅), prepared originally by Gabriel³ formed presumably by the opening of the lactone ring and not by the absorption of ammonia at the ethylene linkage of benzal phthalide.

Because acid lactones are regarded as intramolecular esters the behavior in ammonia of some simple esters was studied. Due to the volatility of the esters the vacuum technique did not lend itself to the work, and the experiments were carried out in a reaction tube of the type described by Fernelius and Johnson.⁴ The results are of a qualitative nature. Esters ammonolyzed by liquid ammonia at its boiling point are methyl, ethyl, propyl and butyl lactates, ethyl mandelate and ethyl phenyl acetate. Esters not ammonolyzed under the same conditions as above are butyl acetate, ethyl benzoate, methyl salicylate and glycerol monoacetate. It is interesting to note that, while the lactones studied have been

(3) Gabriel, *Ber.*, **18**, 2434 (1885).

(4) Fernelius and Johnson, *J. Chem. Ed.*, **6**, 445 (1929).

TABLE II

Substance	Wt. before soln., g.	Wt., g., after		Subst. +	Calcd. for G.
Phenolphthalein I	0.1062	1 hour	0.1113	1 NH ₃	0.1119
Phenolphthalein II	.4615	3 hours	.4886	1 NH ₃	.4862
Phenolphthalein III	.2173	1 week	.2206	1 NH ₃	.2289
Phenolphthalein IV	.2711	1 month	.2726		
		1.5 months	.2722		
		4 months	.2717	1 NH ₃	.2856
Phenolphthalein V	.1436 +	5 weeks	.1446		
NH ₄ NO ₃	.7598				
Fluorescein I	.1930	20 hours	.2103	1 NH ₃	.2092
Fluorescein II	.2199	1 month	.2315		
		4 months	.2300	1 NH ₃	.2883
Maleinfluorescein	.2094	1 hour	.2432	3 NH ₃	.2474
		1 month	.2312		
		3 months	.2282	1 NH ₃	.2221

either quantitatively ammonolyzed or not ammonolyzed at all, the reaction is often incomplete in the case of the esters. For example, the lactates were ammonolyzed to the extent of 30-50%. The combined data of the present and preceding articles indicate that oxygen atoms bound to carbon atoms within the ring weaken the lactone bond.

Since phenolphthalein and fluorescein are lactones related to phthalide, their behavior in liquid ammonia was also studied. The results of the experiments were entirely different from those of the other lactones investigated. In general it may be said that phenolphthalein and fluorescein add ammonia, but the data indicate that definite, stable compounds are not formed. A gradual loss of the added ammonia continues for several weeks before constant weight is reached. To demonstrate that this property of gradual loss of ammonia is not shared by ammonia derivatives of similar compounds, ammonium benzoate and the amide of desoxybenzoin carbonic acid were kept in evacuated tubes in the line for periods comparable with those required for complete loss of ammonia by the phthaleins. A sample of ammonium benzoate of which the initial weight was 0.4899 g. weighed 0.4903 g. after five weeks. A sample of the amide of desoxybenzoin carbonic acid of which the original weight was 0.1848 g., weighed 0.1840 g. after four weeks.

The case of phenolphthalein is more clear cut than either of the others, and it may be worth while to describe its behavior in some detail. Phenolphthalein dissolves in liquid ammonia giving an intensely purple solution, the color of which shows no tendency to fade. When the

ammonia is removed a red residue is obtained. As pumping is continued, the color fades to a bright pink which seems permanent. Prolonged evacuation finally brings the compound very close to the original weight of phenolphthalein. This final residue has a very strong tendency to absorb moisture from the air, a property which dry phenolphthalein does not have. While a quantitative analysis of the residue for carbon and hydrogen was made difficult by this property, analysis for nitrogen showed that none was present. The exact nature of the pink compound is not known. Heating discharges the color, and the compound melts at the melting point of phenolphthalein.

Gibbs⁵ treated phenolphthalein with methylamine under conditions similar to those described in this work, and obtained a white compound to which he gave the formula C₆H₇C₂O₂(C₆H₄ONH₃-CH₃)₂. Dehn⁶ prepared a colorless ammonium salt by treatment of phenolphthalein with aqueous ammonia. The pink material obtained in the present research is apparently not analogous to either of these substances, but seems to be, rather, another form of phenolphthalein which is deposited in an ammoniated condition.

The authors wish to thank Dr. W. C. Johnson and Dr. A. E. Sidwell, Jr., of these Laboratories for technical assistance and advice.

Summary

The authors have continued their studies of the ammonolysis in liquid ammonia of the lactone bond. The lactones studied were either completely ammonolyzed or not ammonolyzed at all.

(5) Gibbs, *THIS JOURNAL*, **28**, 1405 (1906).

(6) Dehn, *ibid.*, **54**, 2947 (1932).

All those which were not ammonolyzed had no hydroxyl group attached to a carbon atom in the lactone ring. Phenolphthalein is temporarily am-

monolyzed but the product formed loses its ammonia completely on prolonged evacuation.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS]

The Measurement of "Bound" Water by the Freezing Method

BY S. S. KISTLER

The Concept "Bound" Water.—Hydrophilic colloids either in solution or as gels generally reduce the thermodynamic activity of the water abnormally, as judged from the basis of the laws of dilute solutions. The abnormality of their behavior, particularly with varying concentration, resembles under certain circumstances what would be anticipated were part of the water so held by the colloid that it no longer can behave as solvent. This analogy has led to the loose concept of "bound" water.

Although there is no generally accepted definition for "bound" water, numerous investigators have considered it profitable to measure it, tacitly adopting as their definition, that quantity of water which, under the particular experimental conditions, behaves as though it has no solvent power or has been removed from the field of action. It is, therefore, not surprising that the results obtained by different investigators on the same material, gelatin for example,¹ vary widely, although considerable wonder has been expressed in the literature.

In view of this unsatisfactory condition, Briggs² excellent paper laying a foundation for the intelligent comparison and correlation of several of the experimental methods is of great value. He demonstrated that the freezing point and vapor pressure methods of Newton and Gortner³ and of Hill⁴ respectively are capable of precise treatment, though the problem of the physical significance of the numerical values obtained yet remains to be clarified.

It is beyond the scope of this paper to discuss in detail the numerous methods used for the measurement of "bound" water or to attempt to correlate their results. Rather it is its purpose

to focus attention upon one method that has gained considerable favor, and to offer a possible explanation for the failure of the method to yield values consistent with thermodynamics.

Not all Water in Hydrophilic Colloids Freezes.—Rubner⁵ observed that when a solution of a hydrophilic colloid is frozen, not all of the water freezes. A fraction remains uncrystallized even at very low temperatures. The quantity of water remaining unfrozen was assumed to be "bound" by the colloid.

Now from thermodynamics it is evident that if a colloid in water reduces the activity of the water, the freezing point of the solution will be reduced to the point where the activity of the water in solution is equal to that of pure ice at the same temperature. As freezing takes place, the colloidal solution will be concentrated and its freezing point will drop. If the activity *vs.* water content of the solution is known, one should be able to predict the amount of water remaining unfrozen at any desired temperature. Either the vapor pressures or freezing points (temperatures at which a minute quantity of ice is in equilibrium with the solutions) serve to give the activities.

Thoenes,⁶ using a calorimetric method, found that from 0.9–1.8 g. water per gram of colloid in blood and muscle failed to freeze at -20° . A study by Hill of the aqueous vapor tension over these materials showed, however, that at this temperature little if any water should have remained unfrozen.

Briggs calculated from his vapor pressure measurements on gelatin solutions that at -20° each gram of gelatin should be accompanied by 0.33 g. of unfrozen water. Moran⁷ froze disks of gelatin gel very slowly so that all of the ice formed on the surface and found that for each

(1) D. M. Greenberg and M. M. Greenberg, *J. Gen. Physiol.*, **16**, 559 (1933), give a table comparing the results of measurements on gelatin using different methods.

(2) David R. Briggs, *J. Phys. Chem.*, **36**, 367 (1932).

(3) R. Newton and R. A. Gortner, *Bot. Gas.*, **74**, 442 (1922).

(4) A. V. Hill, *Proc. Roy. Soc. (London)*, **106A**, 477 (1930).

(5) M. Rubner, *Abhand. pruss. Akad. Wiss.*, **1**, 1 (1922).

(6) F. Thoenes, *Biochem. Z.*, **157**, 174 (1925).

(7) T. Moran, *Proc. Roy. Soc. (London)*, **A112**, 30 (1926).